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by

I-CHING CHIU

A dissertation submitted to the Graduate
Faculty in Chemistry in partial fulfillment of the
requirements for the degree of Doctor of Philosophy,
The City University of New York

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Klaus Grohmann
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ABSTRACT

THE SYNTHESIS OF 1,3-DITHIA-4,6-CYCLOHEPTADIENE, 1,4-DITHIA-2,5-CYCLOHEPTADIENE, THEIR DERIVATIVES AND INVESTIGATION OF THEIR POTENTIALLY TEN π-ELECTRON HETEROAROMATIC ANIONS

by

I-Ching Chiu

Adviser: Professor Klaus Grohmann

In Part One, 1,3-dithia-4,6-cycloheptadiene 43 has been synthesized from the reaction of 1,3-dithia-5-cycloheptene 46 with N-chlorosuccinimide, followed by elimination of HX. It shows a characteristic fragmentation under electron impact lossing m/e 46, $CH_2=S$ to give a mass spectrum resembling that of thiophene. The anion of 43, generated from 43 with n-butyllithium in THF, has been fully characterized through its reactions with D_2O, trimethylsilyl chloride, benzophenone and methyl iodide, to give the expected products 53a-d.

The reactions of its fulvene derivatives 58a-b with organometallic compounds did not show the same behavior as the fulvenes of

cycloheptadiene. The organometallic compound absorbed the proton α to sulfur to form compounds 64a-b, instead of addition to the polar exocyclic double bond, tend to form a stable anion ring possessing a group of 10π electrons.

From the ^{1}H and ^{13}C nmr spectra, it is difficult to estimate the magnitude of the "aromatic" deshielding effect in the 1,3-dithia-4,6-cycloheptadienyl anion 52. However, the ^{1}H nmr spectrum of anion 52 indicates extensive electron delocalization.

Competitive base catalyzed deuterium exchange experiments show that 1,3-dithia-4,6-cycloheptadiene is much more acidic than 1,3-dithiacycloheptane 70 and bis-(vinylmercapto)methane 67. A qualitative determination of the equilibrium acidities confirms this. The chosen model compounds exclude differences caused by different polarizabilities. It is therefore concluded that the increased acidity of the 1,3-dithia-4,6-cycloheptadiene is caused by the additional stability (aromaticity) of the corresponding anion, 1,3-dithia-4,6-cycloheptadienyl anion 52. The conclusion is also supported by the H/D exchange experiments of 2-methyl-1,3-dithia-4,6-cycloheptadiene 53d with 67 or 70. The substituent effect by methyl group does not considerably affect the acidity of the compound itself.

The results suggest that 1,3-dithia-4,6-cycloheptadienyl anion 52 can be considered a heteroaromatic 10π-system, although the degree of aromaticity seems to be small.

In Part Two, 1,4-dithia-2,5-cycloheptadiene 44 has been synthesized by two independent routes: by a Pummerer reaction on 1,4-dithia-2-cycloheptene 102, and by the elimination of HX from the benzenesulfonate of 1,4-dithia-2-cyclohepten-6-ol.

The reaction of 44 with n-butyllithium in THF did not give the expected potentially aromatic 10 π-anion 25. Instead, vinylic metallation of 44 formed 3-lithio-1,4-dithia-2,5-cycloheptadiene 116, which has been trapped with various electrophiles giving the expected products, (115 a-d). Anion 116 was stable at -40° C but underwent ring opening at -15° C to the acetylene anion 124, which was trapped by trimethylsilyl chloride to give 112, or trapped by methyl iodide to give 114. The ring reclosure occurred when the acetylenic trimethylsilane 112 was treated with KOH.

The similar behavior toward lithiation in THF was observed in the cases of 1,4-dithia-2-cycloheptene 102 and 1,4-dithiacyclohexadiene 132. However, allyl anion 144 could be afforded when reaction 1,4-dithia-5-cycloheptene 142 with n-butyllithium in THF, and the formation of this anion has been verified by its characteristic behavior toward alkyl halides.

Treatment of 3-methyl-1,4-dithia-2,5-cycloheptadiene 115b with n-butyllithium in THF, followed by quenching with methyl iodide gave a dimethyl derivative of 1,4-dithia-2,5-cycloheptadiene. Its

^{1}H nmr spectrum is in agreement with 3,5-dimethyl-1,4-dithia-2,5-cycloheptadiene <u>150</u> or 2,5-dimethyl-1,4-dithia-2,5-cycloheptadiene <u>151</u>, and its mass spectrum is unable to distinguish between them as well.

Tha abnormal behavior of 1,4-dithia-2,5-cycloheptadiene towards lithiation suggests that 1,4-dithia-2,5-cycloheptadienyl anion <u>25</u> is not characterized by a special stabilization, therefore it is unlike a heteroaromatic 10π-system. However, no clear conclusion concerning the aromatic character of <u>25</u> can be made at this moment.

ACKNOWLEDGEMENTS

The author is ever indebted to Professor Klaus Grohmann for his warm friendship, understanding, and guidance throughout his graduate studies. It was a pleasure and a privilege to work under his direction. He also wishes to thank Dr. W. Berkowitz and Dr. R. Odum for serving on his Special Committee.

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TABLE OF CONTENTS

PART TWO

INTRODUCTION

In 1931, E. Huckel[1] noted that if electron pairs are filled into energy-level pattern A or B (see Figure I), a closed-shell structure (all electrons paired) will result only when the total number of pairs is odd (4n + 2) (A in Fig. I); if the number of pairs is even (4n) (B in Fig. I), the last pair will be the only occupants of a doubly degenerate level, and each electron will occupy one orbital with spins parallel. Because open shell molecules are ordinarily highly reactive (diradical-like), the 4n electron rings should be chemically unstable. The planar monocyclic conjugated systems having a closed shell of 4n + 2 (where n = 0, 1, 2, ...) π-electrons are predicted to experience an energetically beneficial electron delocalization effect, and have been defined as aromatic systems.

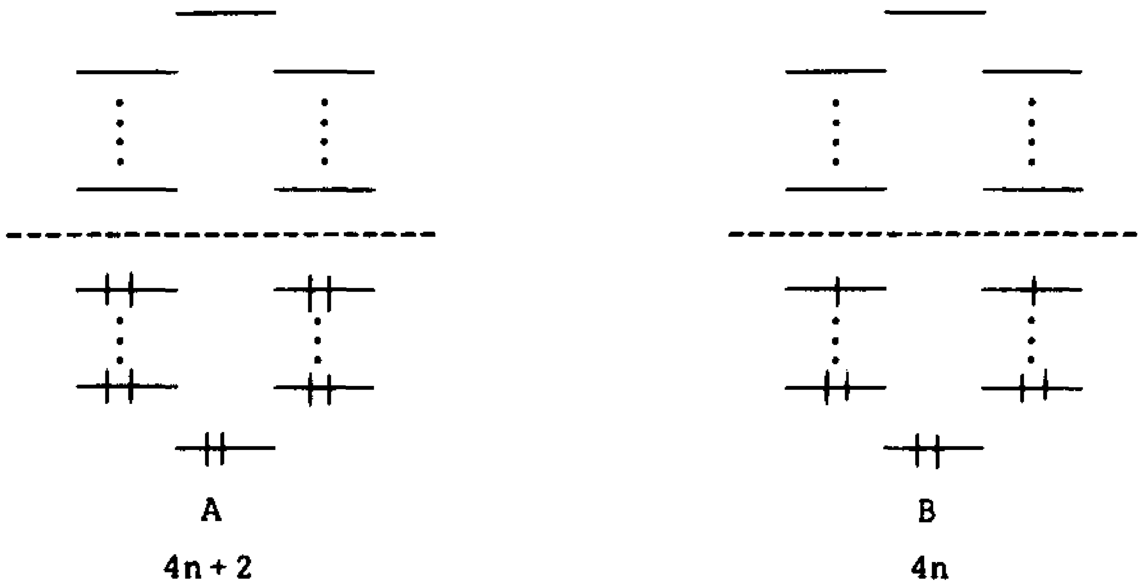
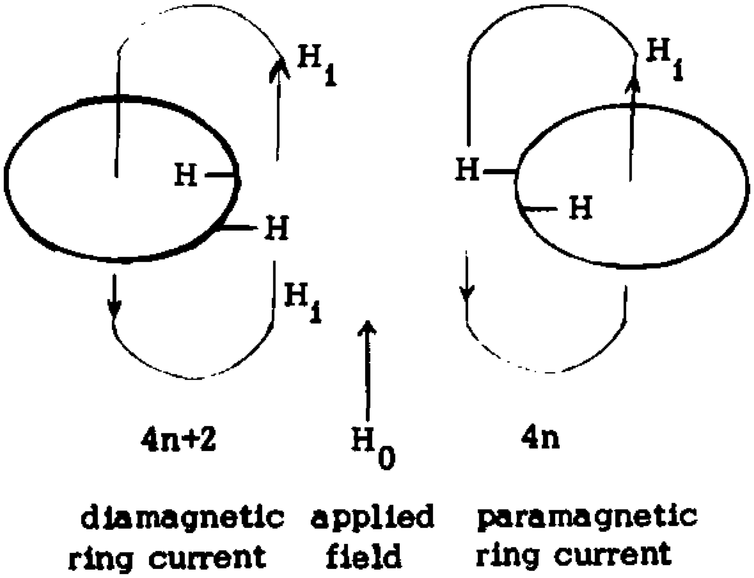


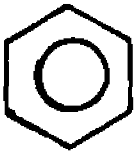
FIGURE I

Aromatic systems (4n + 2 π-electrons in a closed shell) are characterized by a measurable degree of π-electron delocalization. A consequence of this π-electron delocalization is the ability of the molecule to sustain a diamagnetic ring-current in an applied magnetic field, which causes deshielding for protons outside the plane of the ring and strong shielding for protons within or above the ring. Antiaromatic systems (4n π-electrons) exhibit the reverse effect (as shown in Figure II). This has been demonstrated in the case of the carbocyclic conjugated polyenes, called annulenes, the higher homologs of

Figure II



Isoelectronic with benzene are the cyclopentadienyl anion $\underline{1}$ and the cycloheptatrienyl cation $\underline{2}$, two classical aromatic ions. The observed shieldings for the protons in these ions are caused by two effects, the charge and the diamagnetic ring-current. A positive charge causes a general downfield shift, while a negative charge causes a general upfield shift.



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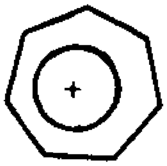

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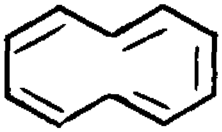

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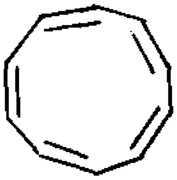

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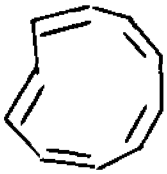

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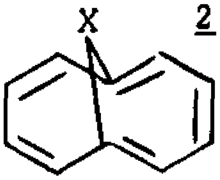
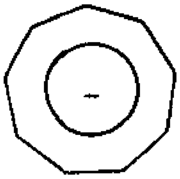


4

X = CH_2
X = O
X = NH

The next higher member of the Huckel-family is cyclodecapentaene (3a[3], 3b[4] and 3c[4]) which contains ten π-electrons. The neutral cyclodecapentaenes (3a-c) do not seem to exhibit any aromatic properties. Probably the system is not planar. However, the bridged derivatives 4[5,6] have been synthesized and shown to be aromatic. Isoelectronic with cyclodecapentaene is the cyclononatetraene anion 5[4a,7] the cyclooctatetraene dianion 6[8,9] and the cycloundecapentaene cation 7. The anions have been shown to be aromatic, showing a definite diamagnetic ring-current. Most likely, the skeletal strain could be relived by a distortion from planarity, or the negative charge electrostatically induces a planar geometry of the carbon skeleton, therefore allowing electron delocalization.



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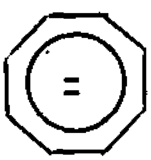

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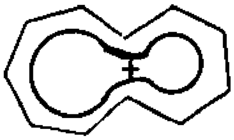

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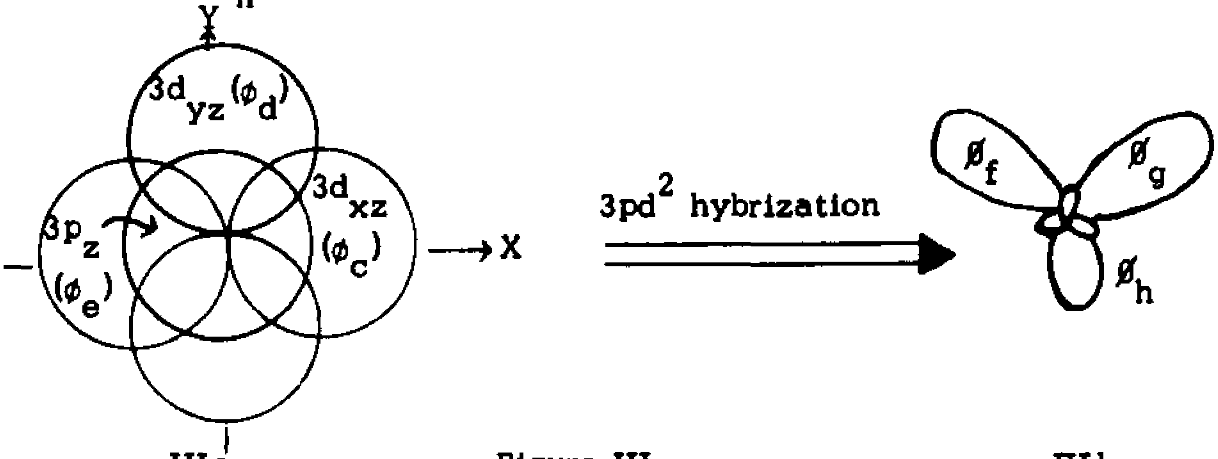
Once the predictive value of Huckel theory was recognized, application of the 4n + 2 rule was naturally extended to heterocyclic systems as well. Thus, the long-known stability of the π-excessive heterocycles 8 were reasonably traced to their being iso-π-electronic with benzene.

8

X = 0
X = S
X = NH

In 1949, Longeut-Higgins,[10] his starting point being the analogy between thiophene and benzene, studied the properties of sulfur atom orbitals resulting from hybrization of 3p and 3d orbitals and formulated them in term of the MO theory. He set the $2p_z$ atomic orbitals of carbon atoms adjacent to the sulfur atom as ϕ_a and ϕ_b, and the $3p_z$, $3d_{yz}$, $3d_{xz}$ orbitals of the sulfur atom are designated ϕ_c, ϕ_d and ϕ_e, respectively (see Figure IIIa). By linear combination of the ϕ_c, ϕ_d and ϕ_e orbitals, hybrid $3pd^2$ orbitals ϕ_f, ϕ_g and ϕ_h are introduced. Their shape are apparent from Figure IIIb, where the ϕ_h does not interact with other atomic orbitals.



IIIa Figure III IIIb

For the sake of numerical calculations within the H.M.O. framework, the ϕ_f and ϕ_g orbitals may simply be replaced by carbon $2p_z$ orbitals. Consequently, the resonance energies, bond orders, bond lengths and dipole moments of thiophene were calculated with satisfactory results.

From the comparison of the atomic orbitals of thiophene and benzene (see Figure IV and V), one can easily realize that there is a very close similarity both in energy and forms of molecular orbitals between =CH - (S) - CH= and =CH - (CH=CH) - CH= . Thus the divalent sulfur can be considered electronically equivalent to the carbon carbon double bond and can participate in π-electron delocalization.

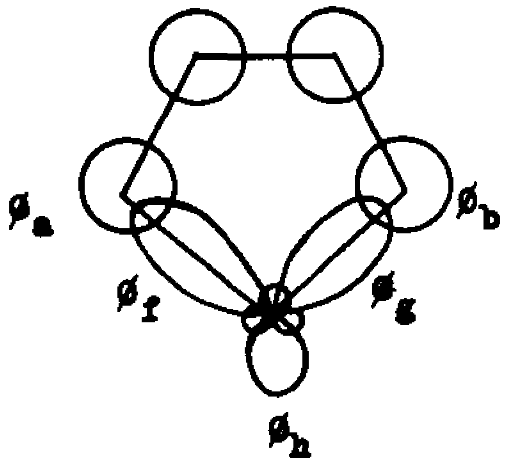


Figure IV

Model of atomic orbitals in thiophene

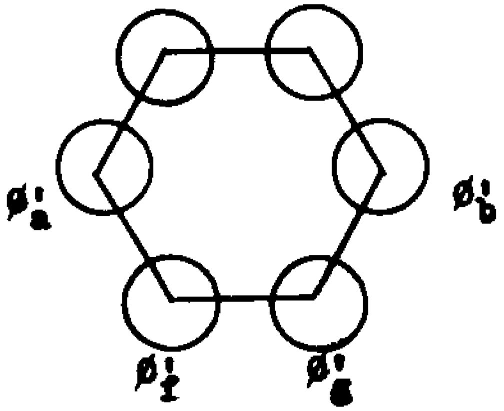
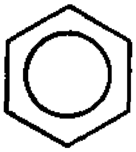
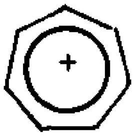


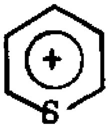
Figure V

Model of atomic orbitals in benzene

Formal replacement of a double bond in a given aromatic system by divalent sulfur should result in the formation of an isoelectronic heteroaromatic system. This is clearly demonstrated in the similarity between benzene and thiophene. From the cycloheptatrienyl cation one would obtain the thiapyrylium cation 9,[11] 1,2-dithiolium cation 10,[12] and 1,3-dithiolium cation 11.[13]







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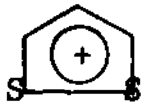

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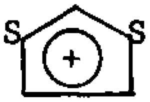

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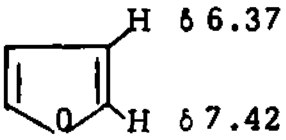
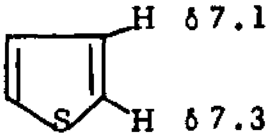
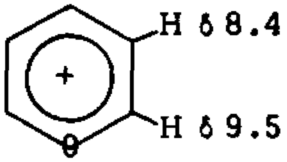
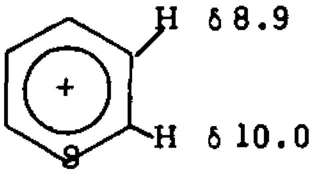
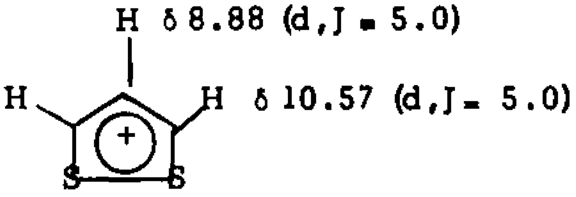
These first representatives of the heteroaromatic cations have been investigated in great detail (their chemical shifts of protons are shown on the diagrams) and are considered to be aromatic.

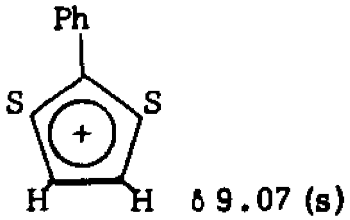












The validity of Huckels rule for the 10 π-heterocycles is much less well documented. So far only the 1H-azonin appears to be the representative of a monocyclic neutral aromatic 10-π system.[14] Calculation by N. Allinger[15] and R. Breslow[16] (see Figure VI) predict a definite aromaticity for the 10 π-heterocycles.

However, Allinger and Youngdale[15] have prepared a series of the dibenzo-fused analogs (12a-e) of this type using nitrogen and found that the UV spectra in all were rather similar, suggesting a lack of delocalization in the ten π-electron system. The sulfur analog 12e, however, is a slightly weaker base than the carbon analog 12a (pKa's 2.81 and 3.10), which implies a small degree of aromatic character in the former. Indeed, an nmr study showed that the hydrazo protons of 12e were somewhat deshielded with respect

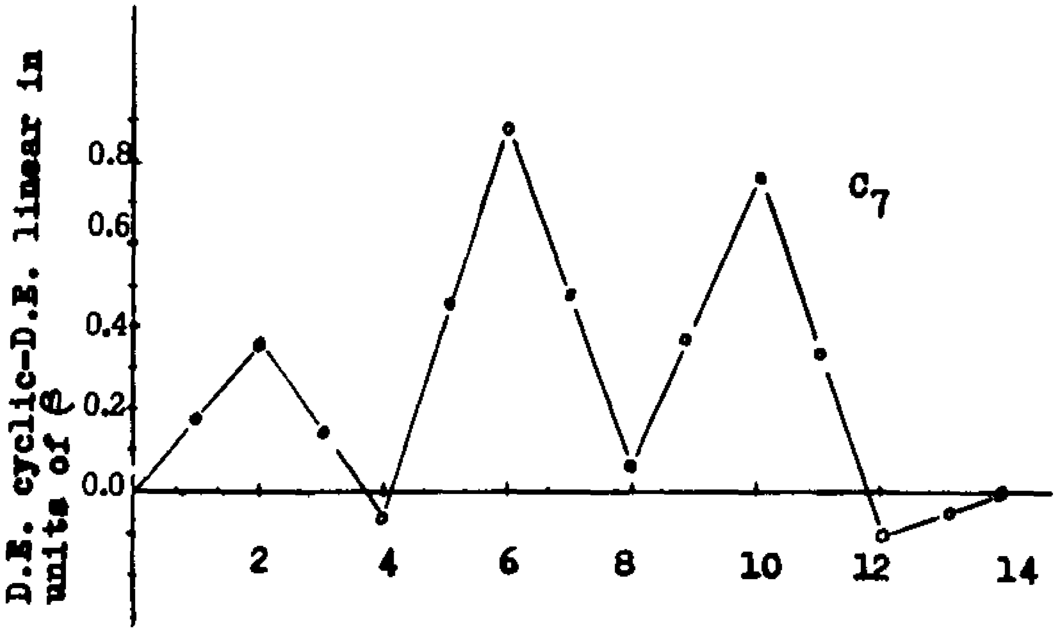
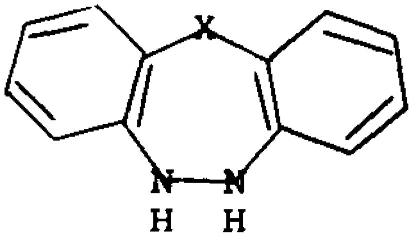


FIGURE VI: Difference in π electron delocalization energies (from a Huckel calculation) between cyclic and linear simple conjugated systems as a function of the number of π-electrons.

to those in 12a. The authors concluded that while 12a-d are non-aromatic, 12e may have some aromatic character.



12 a X = CH_2

b X = NH

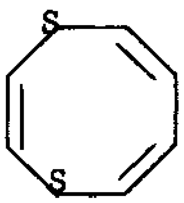
c X = NCH_3

d X = O

e X = S

From the results of MO calculation, Balaban and Simon[17] predicted that the resonance energy of the planar conformation of 1,4-dithiocin 13 be sufficient to overcome the strain energy involved in achieving planarity. However, recently B.A. Hess and L.J. Schaad[18] calculated a resonance energy of -0.005β for 13 and predicted that this molecule is not aromatic.

In 1967, Schroth and co-workers[19] prepared compounds 15 and 16, the first derivatives of 1,4-dithiocin 13 and 1,4-dioxocin 14. Later on, Coffen[20] studied 17 and Fowler[21] studied the nitrogen analog, dimethylbenzdiazocin 18. The chemical shifts of proton are shown on the diagrams and the values do not seem to indicate the presence of appreciable ring current in these compounds. The UV spectra show a lack of conjugation, indicating that the molecules exist in tub-shaped conformations.



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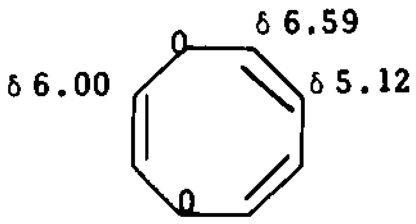

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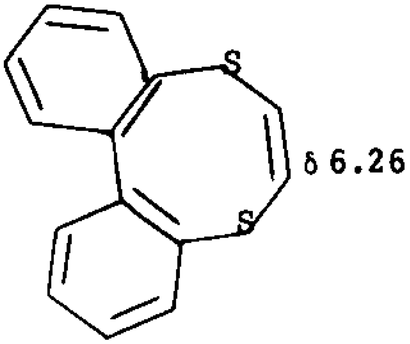

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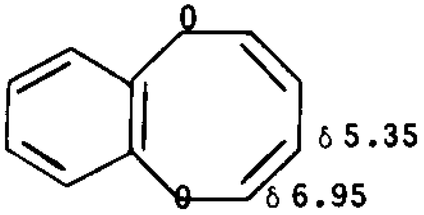

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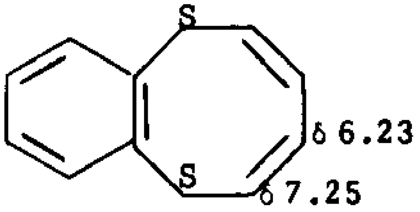

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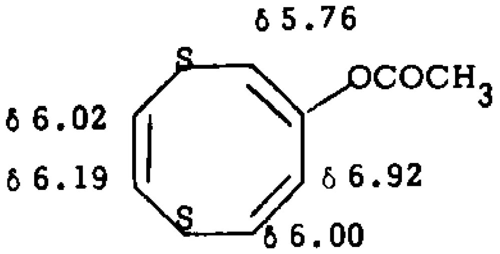

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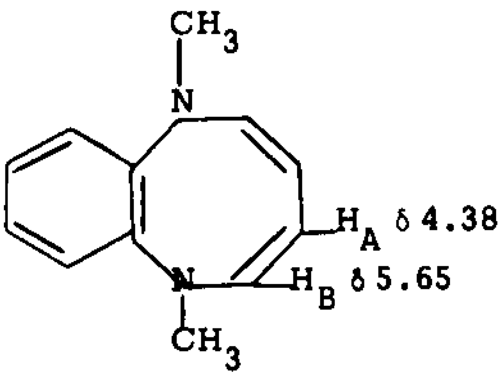

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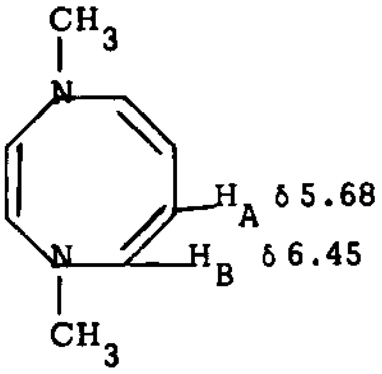
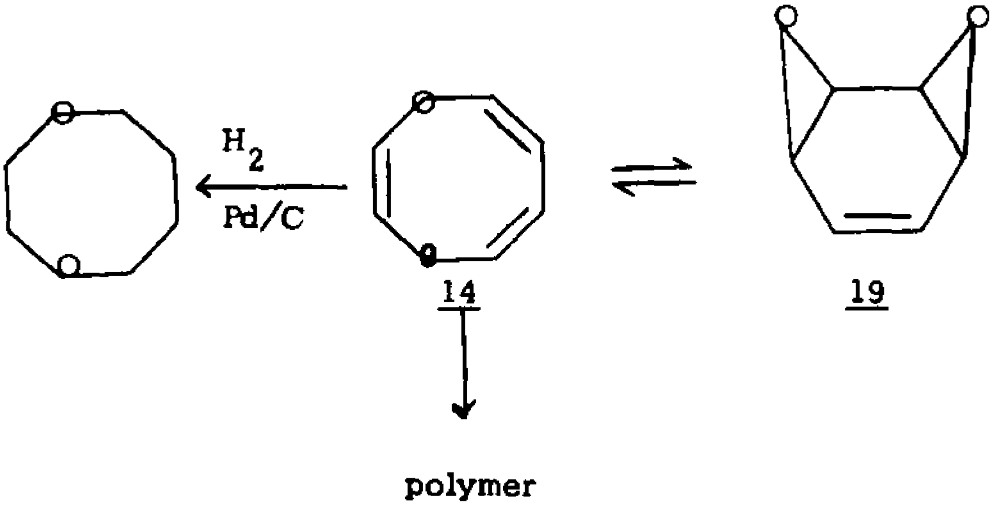


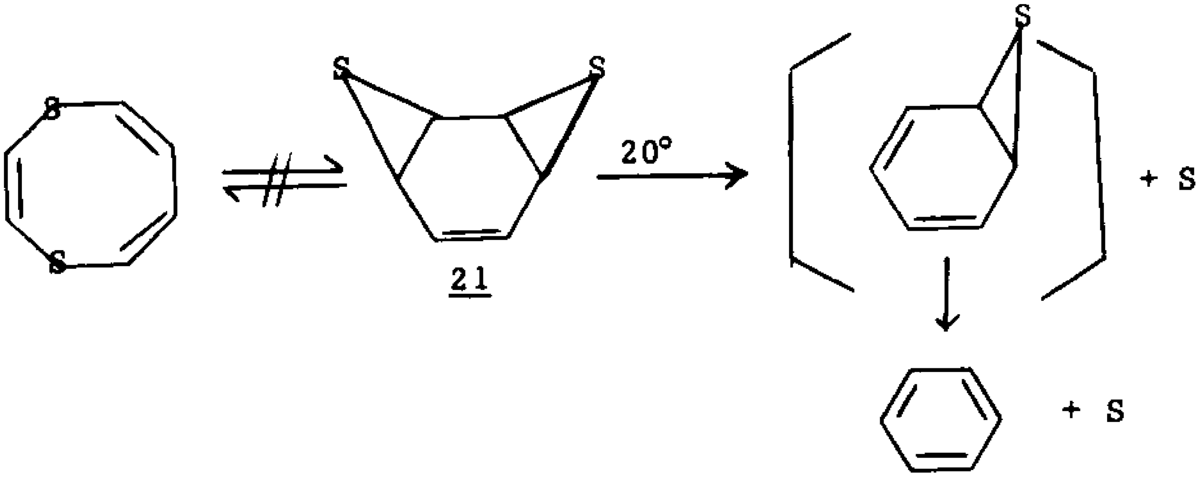
22

In 1972, 1,4-dioxocin 14 was first synthesized by E. Vogel,[22] and was unambiguously shown to be an olefinic compound by its spectra (^{1}H nmr spectrum shown on the diagram) and by its chemical behavior: it polymerized rapidly, could be hydrogenated to give the corresponding saturated compound in 95% yield, and formed valence isomer, syn-benzene dioxide 19, at 60° C.

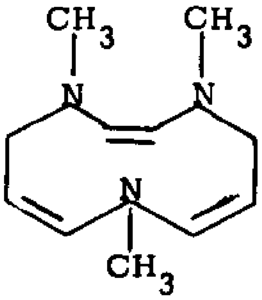


So far only 1,4-dithiocin-6-yl acetate 20, having the structural element of a fully conjugated 1,4-dithiocin, has been synthesized.[23] Its spectroscopic properties (^{1}H nmr spectrum shown on the diagram) do not appear to indicate an aromatic character, although the nmr spectrum is not so clearly olefinic in character as that of 1,4-dioxocin. Furthermore, an X-ray structure of this molecule indicates a nonplanar structure with a C-S-C angle of about 90°.[24]

E. Vogel has attempted to synthesize 1,4-dithiocin by the conversion of its valence isomer, syn-benzenebisepisulfide 21,[25] but 21 decomposed at 20° C with a half-time about 30 minutes, giving benzene and sulfur as final products. In view of the thermal instability of 21, the authors concluded it unlikely that 1,4-dithiocin will prove to have aromatic character.



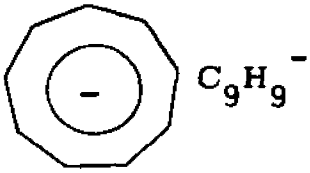
On the other hand, recently D. Humkler and coworkers[26] have studied the 1,4-dimethyldiazocin 22 and its relatives. Judging from the ^{1}H nmr and ^{13}C nmr spectrum, the δ value of H_A and H_B in 22 are shifted downfield about 1.3 and 0.8 ppm relative to dimethylbenzpdiazocin 18, and the ^{13}C-signals of the ring carbon atoms in 22 show substantial diamagnetic shift with respect to those of the ring carbon atoms in 22a



22a

Compound 22, in contrast to 1,4-dioxocin and 1,4-dithiocin exhibits effective cyclic 10 π-electron delocalization induced diamagnetic ring current and therefore could be considered as a 10 π-aromatic system.

The systems derived from the cyclononatetraenide anion are the seven-membered ring 1,2-dithiepinide 23, 1,3-dithiepinide 24 and 1,4-dithiepinide 25, and the eight-membered ring thiacyclononatetraenyl anion 26 and azacyclononatetraenyl anion 27.



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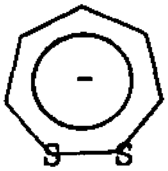
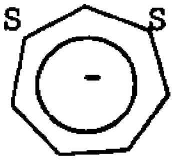
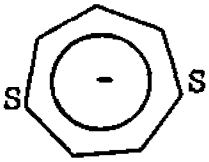


23



24



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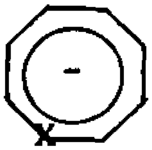
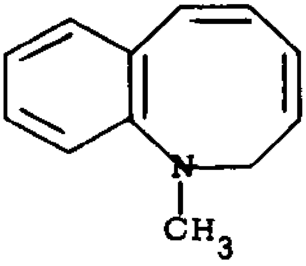


26 X = S

27 X = NH



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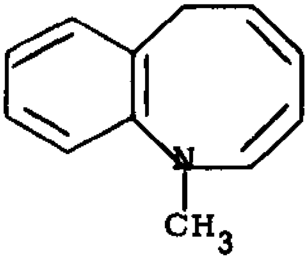

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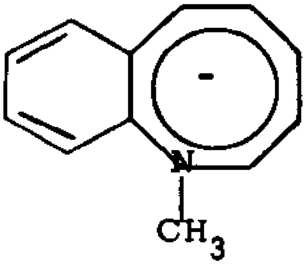

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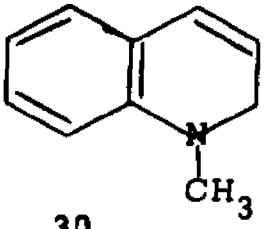

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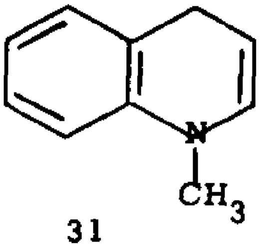


31

Coates and Johnson[27] have examined the kinetic acidities of the dihydrobenzazocines 28 and 29, the derivative of 27, and compared them with the acidities of 30 and 31. They reported that 28 and 29 showed only a moderate enhancement and concluded that the anion 32 could only exhibit a small degree of aromatic character.

In 1965, R. Zahradnik and C. Parkanyi[28] adapted the MO-LCAO method (assuming sulfur d-orbitals participate in conjugation) and set empirical parameters given in the form as below:

$$\alpha_S = \alpha_C + \delta_X \beta \quad ; \quad \beta_{xy} = \rho_{xy} \beta$$

and the following values were used in the calculation:

$$\delta_S = 0.00 \qquad \rho_{CS} = 0.6 \qquad \rho_{SS} = 0.5$$

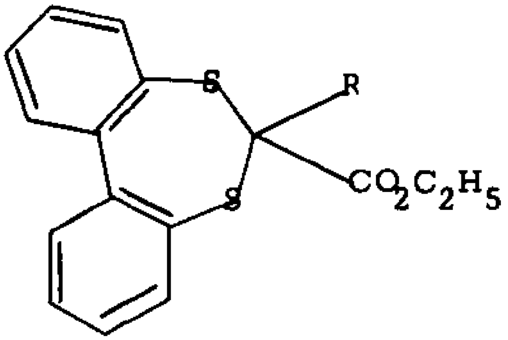
where α is the carbon Coulomb integral and β is the resonance integral of carbon bond. The results are outlined in table I (all units in β).

	ω	HOMO		LUMO		E
	π-electron energy	k_2	k_1	k_{-1}	k_{-2}	Transition energy
5	11.5176	0.3473	0.3474	-1.0000	-1.0000	1.3473
23	10.1412	0.5905	0.5905	-0.8957	-0.9167	0.9895
24	9.6770	0.4668	0.1188	-0.6921	-1.0000	0.8109
25	9.7915	0.5765	0.0864	-0.8114	-0.9627	0.8978

TABLE I: MO-LCAO Calculation for 1,2-, 1,3- and 1,4-Dithiepinide Ions.

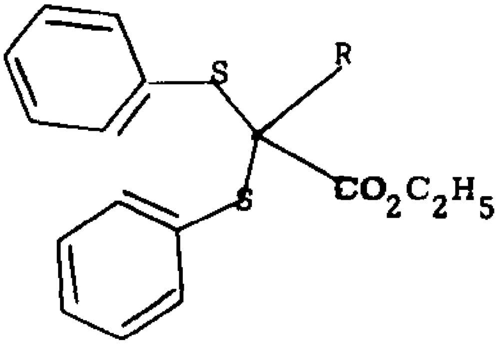
Due to low values of the specific delocalization energy and the high energies of the highest occupied π-MO's, according to the authors, all these compounds will be quite unstable and difficult to prepare.

In 1965, Breslow and Mohacsi[16] investigated the kinetic and thermodynamic acidity of 2-carboethoxydibenzo (d,f) (1,3)-dithiepin 33 and the corresponding ring-opened compound 34.



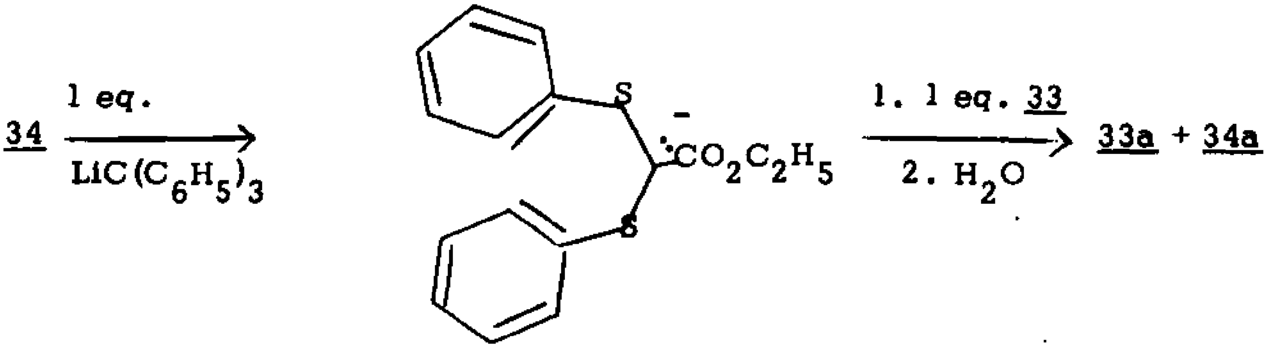
33 R = D

33a R = H



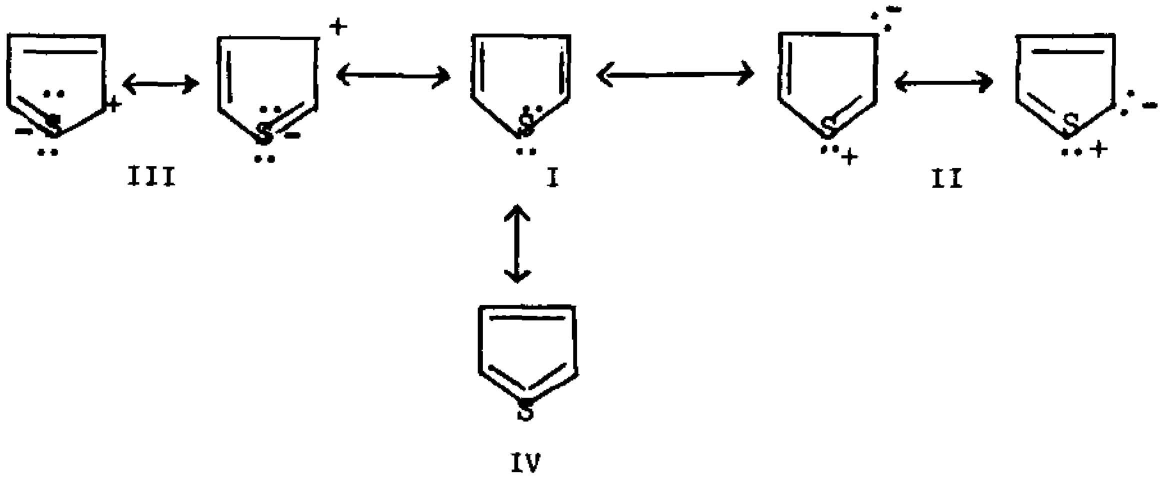
34 R = D

34a R = H

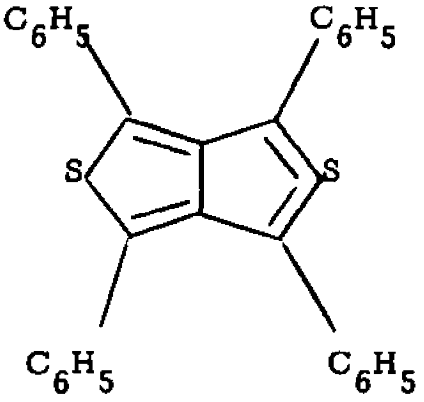


Based upon nmr analysis, the ratio in the equilibration mixture was (34a : 33a=) 5 : 1 in favor of the open-chain compound. The same result was obtained when the reaction was carried out with the reverse order of addition of the esters. These results did not indicate any detectable additional stability. The authors concluded that no aromaticity associated with the cyclic 10 π-electron system could be observed. However, as stated,[16] this does not preclude aromatic character in the parent ion 24.

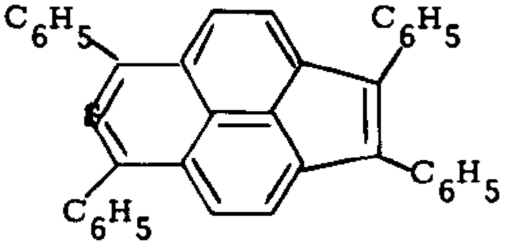
Sulfur can act both as π-electron acceptor and as π-electron donor. The involvement of its 3d orbitals was first discussed by Schomaker and Pauling[29] who adopted a V-B approach to the question of whether or not 3d orbitals of sulfur may be used for bonding in thiophene. From a consideration of bond length, resonance energies and dipole moments these authors concluded that all the following types of structure were important in thiophene.



The relative weights assigned to the different types of structure were type I, 70%; type II, 20%; type III and IV, 10%. Of these structures those of type III and IV must involve the sulfur d orbitals, because in such structures the sulfur atom has a decet of electron in its valence shell. The positive evidence for through-conjugation by way of sulfur stems from the synthesis of stable sulfur heterocycles of the type 35 [30] and 36 [31] in which sulfur may be viewed as quadricovalent in a delocalized system.



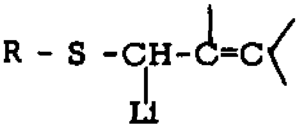
35



36

The electron-donating through-conjugation at sulfur is well documented by the established aromatic character of the thiapyrylium cation and the two dithiolium cations, 10 and 11, while the electron accepting through-conjugation has a marked stabilizing effect on adjacent carbanions. It is generally assumed that the stabilization of these anions results from overlap of the "anion orbital" with d shells of the sulfur. For instance, the central C atom in the anion of 37 may be

sp^2-hybridized and p-d overlap then occurs; in 38 the C^- atom could be sp-hybridized (p-d overlap) or sp^2-hybridized (sp^2-d overlap) while in the anion of 39, the anionic C atom cannot be forced into coplanarity with the neighboring sulfur atoms so that sp^3-d overlap should occur.[32]



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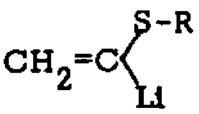

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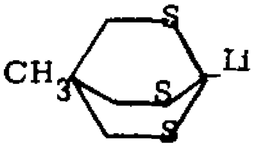
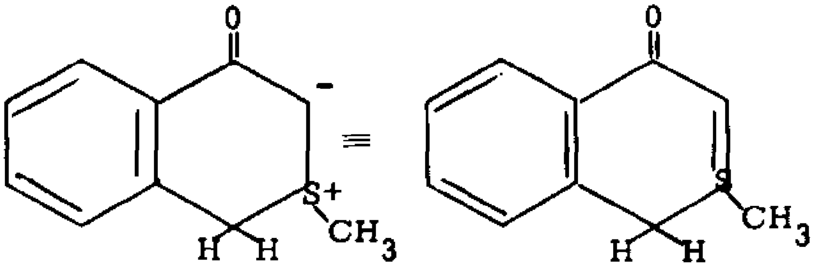
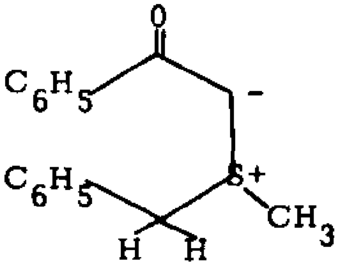


39

However, this concept of (p→d) bonding was questioned in the case of thianaphthalene ylid 40.[33]



40



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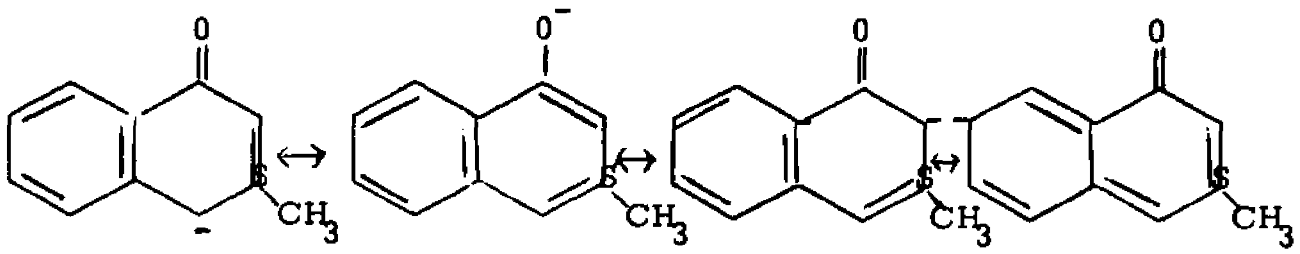
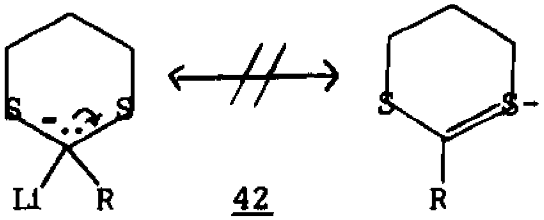


Scheme I

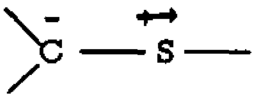
It is anticipated that the acidity of the benzylic proton should be enhanced if the vacant 3d orbitals of sulfur accept the electron from the filled 2p of the adjacent carbon and then delocalized through the ring. However, as a matter of fact the H/D exchange rates between 40 and the open-chain analogs 41 (which lacks electron delocalization) were not remarkably different. .herefore, the extent of delocalization implied in Scheme I is questionable.

In more recent times, Streitwieser has studied the acidities of dithianes in cyclohexylamine[34] and pointed out the substituent effects imply a highly localized carbanion with no significant role to be assigned to sulfur delocalized structure like 42. The authors suggest instead that the principal mechanism of stabilization of carbanions by adjacent sulfur is by polarization. The effect of induced dipole of polarizable sulfur electrons may be symbolized by 43.



42

R	pKa
H	31.1
CH_3	37.1
C_6H_5	28.2



43

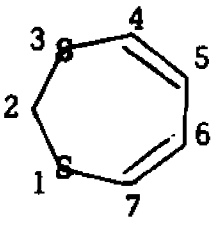
It is expected that the investigation of the dithiepin anions 23 - 25 will provide experimental evidence for or against the electron-accepting through conjugation in cyclic sulfur compounds and also provide insight into the validity of previously theoretical predictions. Therefore, we have synthesized 2H-1,3-dithiepin (1,3-dithia-4,6-cycloheptadiene) and 5H-1,4-dithiepin (1,4-dithia-2,5-cycloheptadiene) and have examined the aromaticity of their respective anions.

PART ONE

1,3-DITHIA-4,6-CYCLOHEPTADIENE

DISCUSSION AND RESULTS

The nomenclature for the heterocycles described in this work follows the Chemical Abstracts system.[35] For example, compounds 43 and 44 are named as 1,3-dithia-4,6-cycloheptadiene and 1,4-dithia-2,5-cycloheptadiene, respectively. It should be noted that the alternative so-called Hantzsch-Widman system,[35] is also used by some authors, thus compounds 43 and 44 are also named 2H-1,3-dithiepin and 5H-1,4-dithiepin, respectively.



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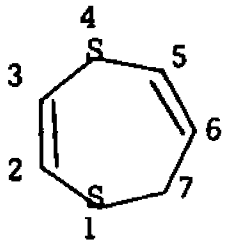
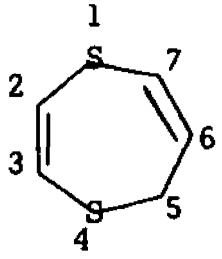


44

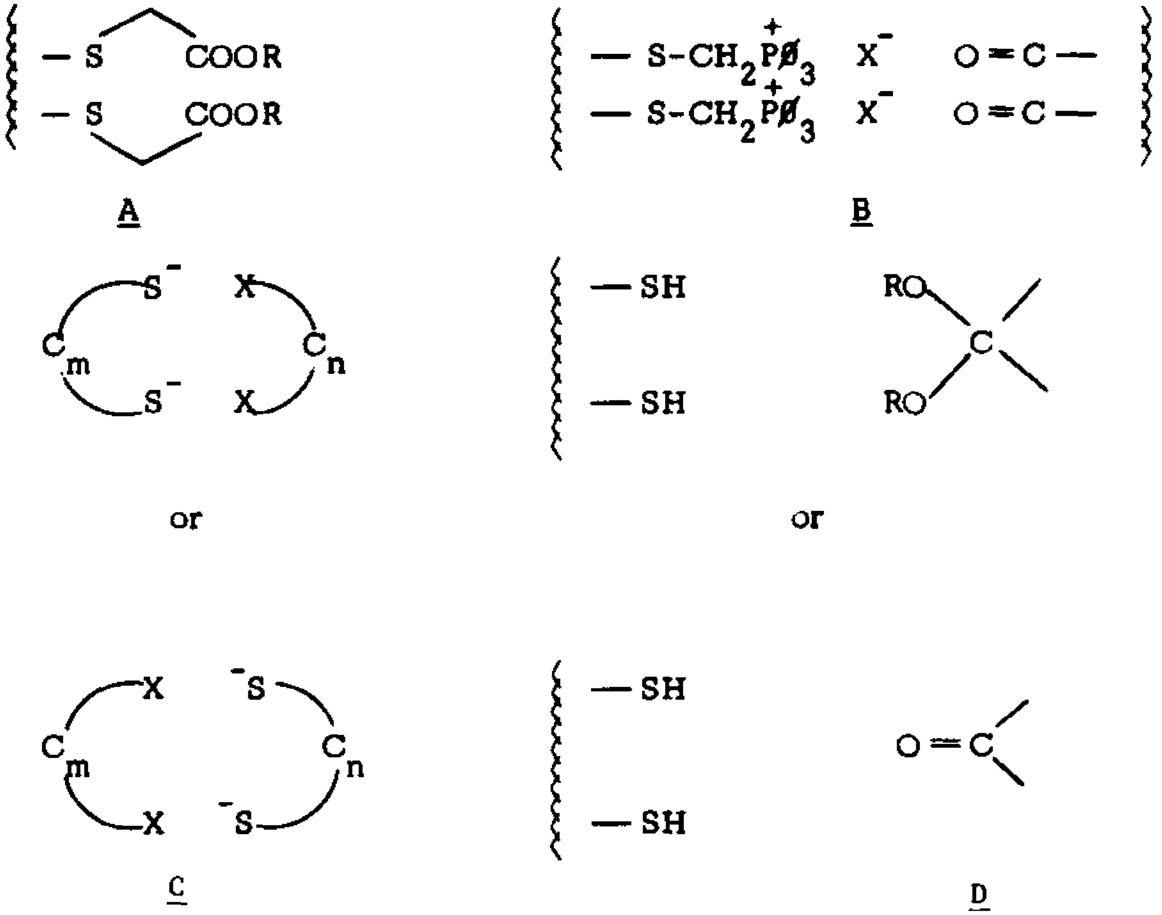
CA method



44

H-W method

Generally dithia-heterocycles can be synthesized by several methods: Method A: One could start from bis-esters via Dieckmann condensation followed by hydrogenation and decarboxylation; Method B: One could use bis-Wittig reaction; Method C: W. Schroth and coworkers[36] developed the cyclization of the disodium or dipotassium salts of dithiol and bishalides; Method D: Corey and Seebach[37] used the acid catalyzed ketalization of dithiols and acetals or ketones. This thiolacetalization is only applicable for the synthesis of 1,3-dithiaheterocycles and has been widely used in protection of carbonyl group and alkylation of ketones or aldehydes.[38] (See Scheme II).

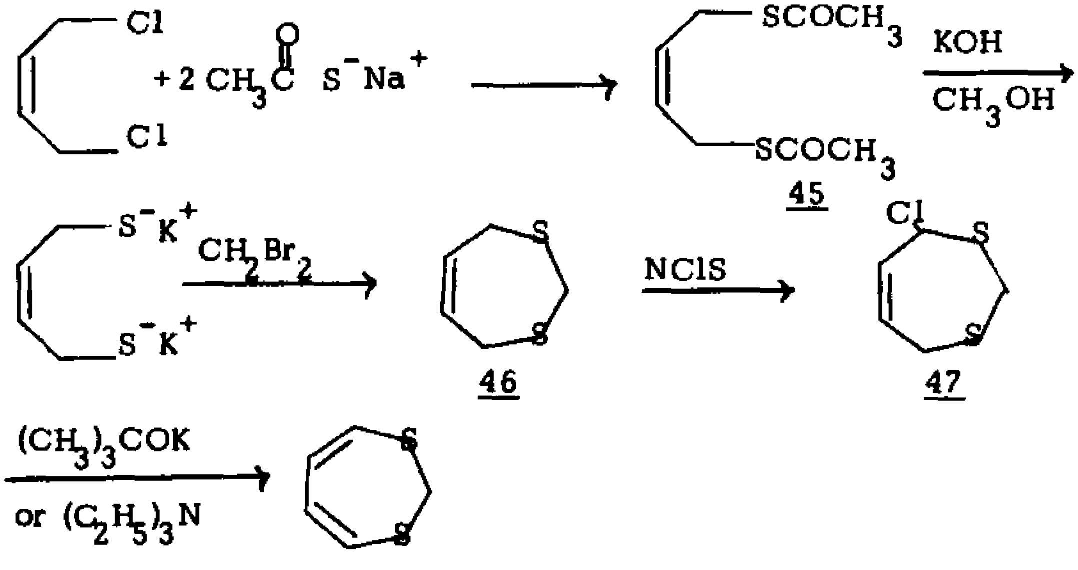


Scheme II

I. THE SYNTHESIS AND THE CHARACTERIZATION OF 1,3-DITHIA-4,6-CYCLOHEPTADIENE

The synthesis of 1,3-dithia-4,6-cycloheptadiene 43 was carried our by the following straightforward route, as shown in Scheme III.

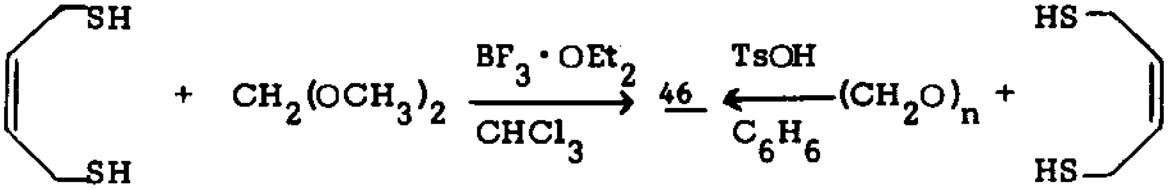
The reaction of cis-1,4-dichloro-2-butene with 2 equiv. of sodium thiolacetate at reflux under nitrogen yielded the corresponding dithiolacetate 45, which has a very unpleasant ordor and could cause headache; bp 135-140°/9 mm; nmr (CCl_4, TMS): δ 2.30 (s, 3H), δ 3,6 (d, 2H), and δ 5.51 (t, 1H). Without isolation, the dithiolacetate 45 was hydrolyzed with potassium hydroxide in methanol and the resulting dipotassium salt of cis-2-butene-1,4-dithiol was treated with dibromomethane to give the known 1,3-dithia-5-cycloheptene 46,[39] as white needle-like crystals, mp 53-54° after chromatography on silica gel (eluted with 10% benzene in pet. ether) and recrystallization from pet. ether, in 20-30% yield.



43

Scheme III

Method D, acid catalyzed ketalization, was applied to the synthesis of 46 by treating cis-2-butene-1,4-dithiol with either dimethoxymethane in the presence of boron fluoride etherate as catalyst or paraformaldehyde in the presence of p-tolunesulfonic acid in a Dean-Stark apparatus and gave erratic yields and considerable amounts of polymers,[40] as shown below:



1,3-Dithia-5-cycloheptene 46 was chlorinated with N-chlorosuccinimide in dry carbon tetrachloride (or dry benzene) at 5° C under nitrogen to give the very unstable 4-chloro-1,3-dithia-5-cycloheptene 47, which without isolation was treated with potassium t-butoxide in dry ether (or triethylamine in benzene) giving the desired diene 43 in 30-40% yield. Diene 43 is a pale yellow liquid, bp. 30° C (0.05 mm); mp. 29° C from pentane; its structure is fully established from its mass spectrum, ^{1}H nmr, ^{13}C nmr, UV and by trapping it with a dienophile.

High resolution mass spectrum: calc. $C_5H_6S_2 = 129.9911$; found 129.9903 ; M^+ at m/e = 130, 40%; base peak at m/e = 84 (M^+-46, loss of $CH_2{=}S$). After that fragmentation the mass spectrum of 43 closely resembles that of thiophene.[41]

^{1}H nmr ($CDCl_3$, TMS): δ 6.28 (AA'BB' system, 4H), δ 4.13 (s, 2H).

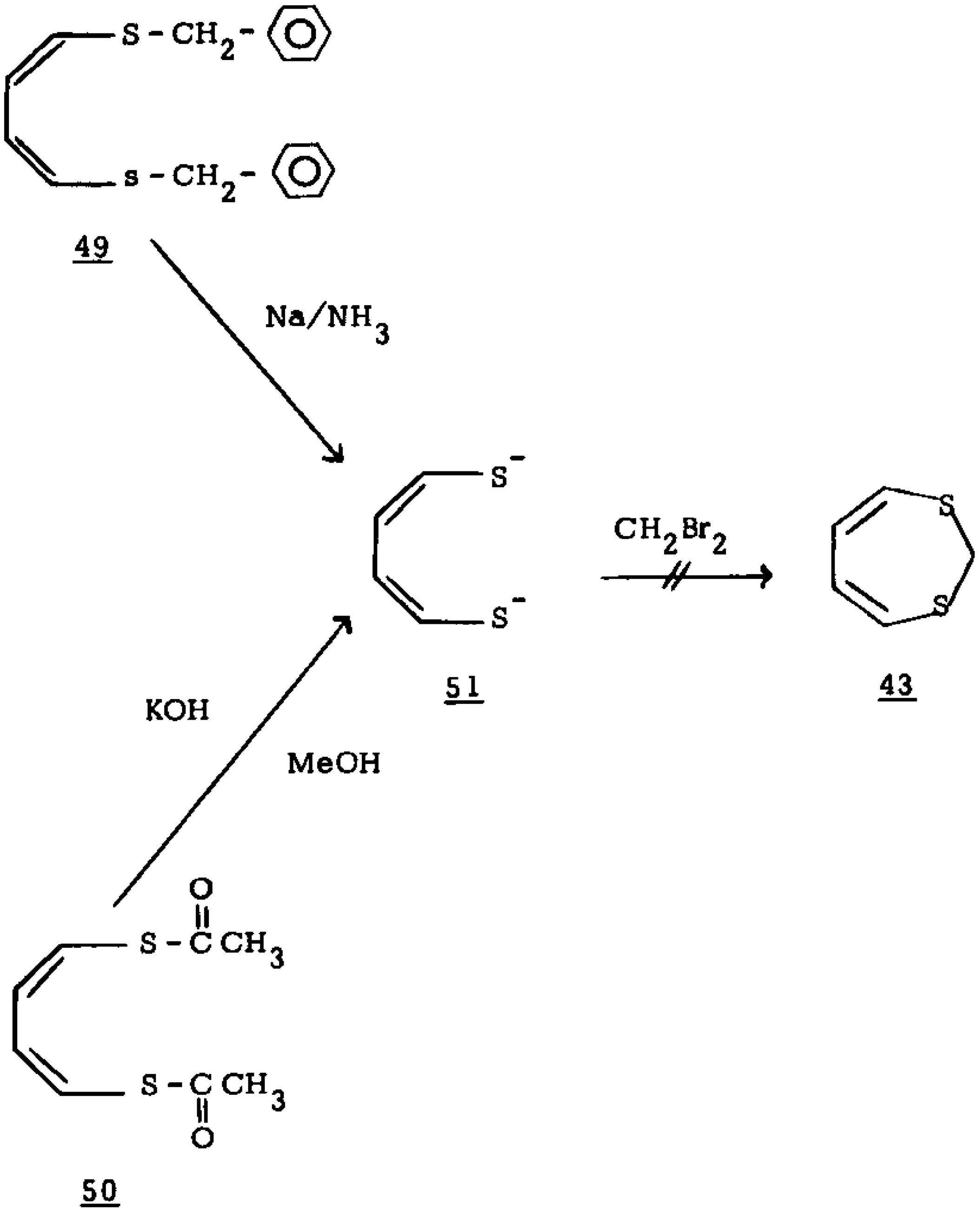
^{13}C nmr (^{1}H decoupled and off resonance decoupled): 39.7 ppm (C_2), 124.7 ppm (C_5/C_6) and 128.3 ppm (C_4/C_7).

UV: λ_{max}^{EtOH} = 257 nm (ε 4010) and 340 nm (ε3310).

Upon heating with N-phenymaleimide to 140° for 16 hours 43 could be converted into a Diels-Alder adduct 48, mp. 196-198°C, after chromatography and recrystallization from methanol, its nmr ($CDCl_3$, TMS) consists of an AB system centered at δ 3.5, 2H, J_{AB} = 14 Hz; a broad singlet at δ 3.75, 2H; AA'BB' system at δ 4.1, 2H and δ 6.2, 2H; a multiplet at δ 7.3, 5H.

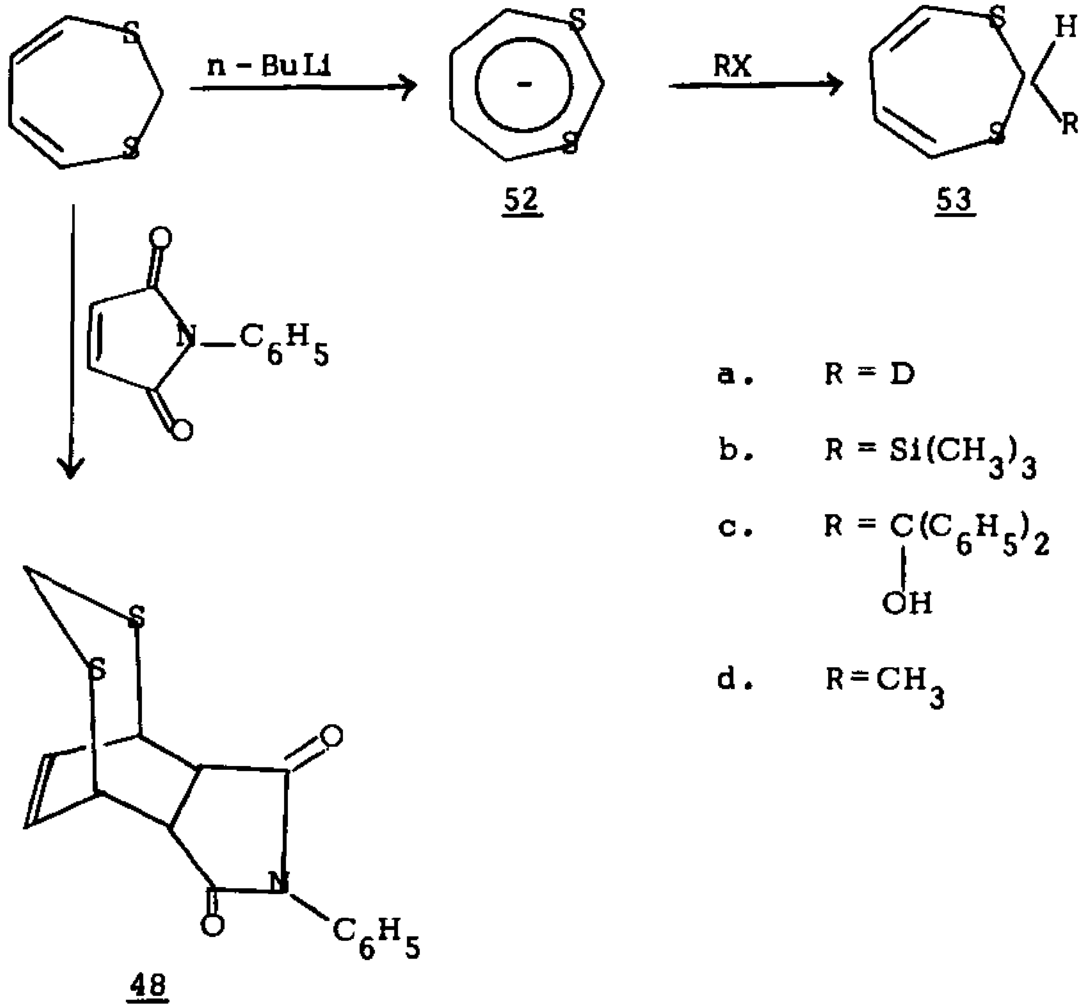
A one step synthesis of diene 43 has been attempted. Treatment of the disodium (or dipotassium) salt of cis-1,4-dithiol-butadiene 51, which can be generated from either treating cis, cis-1,4-bis(benzylthio)butadiene 49[42] with base, with dibromomethane should afford diene 43. However, only resins were obtained, from which no 43 could be isolated in either reaction. (See Scheme IV.)

Reaction of 43 with n-butyllithium in tetrahydrofuran under nitrogen at -40°C produced a deep red solution of the anion 52, which has quenched with D_2O, trimethylsilyl chloride, benzophenone and methyl iodide to give respectively: 2-deutero-1,3-dithia-4,6-cycloheptadiene 53a, M^+ at m/e 131, base peak at $M^+ - 47$ = m/e 84


S - CH2 -
s - CH2 -
49
Na/NH3
S-
S-
51
CH2Br2
S
S
43
KOH
MeOH
O
S - C CH3
S - C CH3
O
50

Scheme IV

(loss of CHD=S); 2-trimethylsilyl-1,3-dithia-4,6-cycloheptadiene 53b, M^+ at m/e 202, base peak at M^+-73-32 = m/e 97, suggesting the loss of $-Si(CH_3)_3$ (m/e = 73) and -S (m/e = 32) to give the aromatic thiapyrilium cation $C_5H_5S^+$;[41] diphenyl-(1,3-dithiepin-2-yl)-carbinol 53c and 2-methyl-1,3-dithia-4,6-cycloheptadiene 53d. Their nmr spectra are summarized in Table II.



52

53

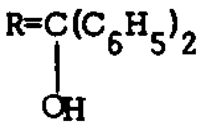
48

a. $R = D$

b. $R = Si(CH_3)_3$

c. $R = \underset{OH}{\underset{|}{C}}(C_6H_5)_2$

d. $R = CH_3$

Compound	bp (°C/mm)	δ H_2	δ Olefinic protons	δ Substituent group
53a*, R=D	30/0.05	4.12 (1:1:1 triplet)	6.28 (AA'BB')	
53b*, $R{=}Si(CH_3)_3$	40-45/0.05	3.11 (s)	6.25 (AA'BB')	0.25 (s)
53c*,  $R{=}C(OH)(C_6H_5)_2$	—	4.97 (s)	6.26 (s)	3.53 (exchanged with D_2O) 7.2-7.7 (m, 10H)
53d**, $R{=}CH_3$	35/0.05	4.43 (q)	6.19 (s)	1.73 (d)

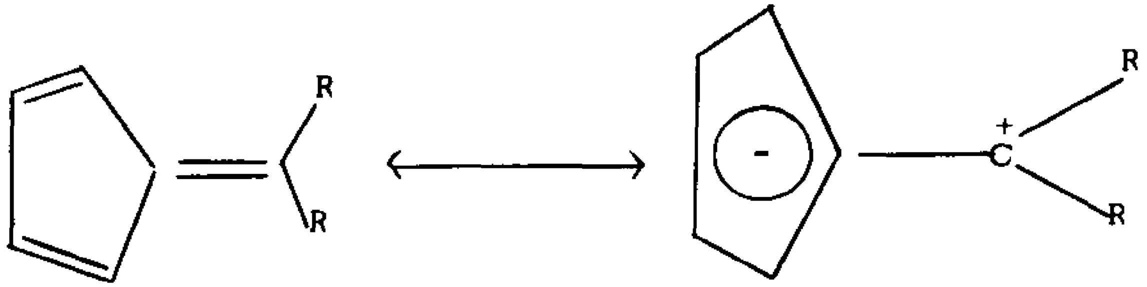
*solvent : $CDCl_3$; **solvent : CCl_4

Table II: The Nmr Spectra of 2-Substituent-1,3-Dithia-4,6-Cycloheptadiene.

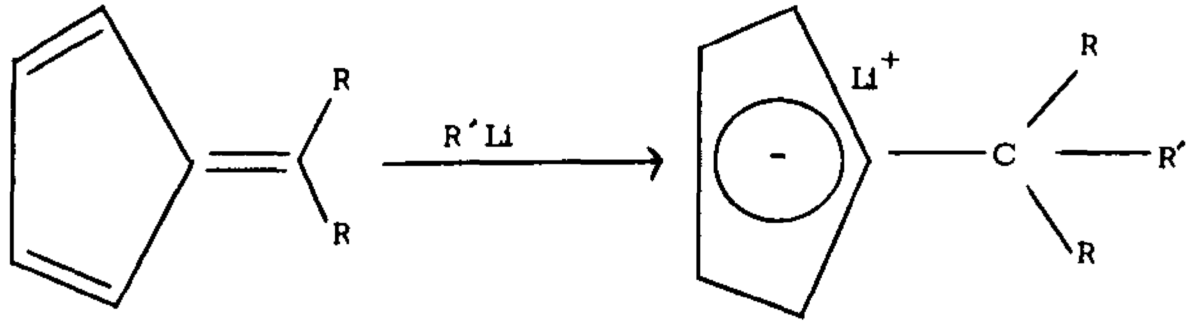
II. THE INVESTIGATION OF THE POTENTIAL TEN π-ELECTRON HETEROAROMATIC 1,3-DITHIA-4,6-CYCLOHEPTADIENYL ANION

A) THE STUDIES OF FULVENES OF 1,3-DITHIA-4,6-CYCLOHEPTADIENE

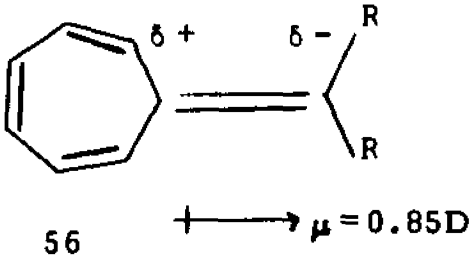
In fulvenes of cyclopentadiene the ring tends to form a stable anion, possessing a group of aromatic six π-electrons. Therefore, the exocyclic double bond is polar and the terminal carbon is positive.[43]



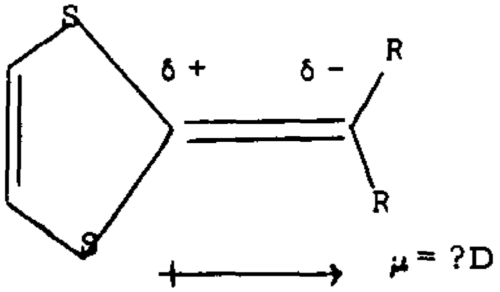
The polar character of the exocyclic double bond is expressed in a number of unusual reactions.[44,45] Organometallic compounds add to the exocyclic double bond in the expected manner, forming a carbanion at the central atom of the fulvene system as shown below:



More recently, J. Meijer and coworkers[46] have reported that the fulvene of 1,3-dithiol 54, being particularly sensitive to acid, dimerised under the influence of traces of acids. Traces of base inhibit this dimerisation. This behavior is very similar to that of heptafulvenes 56.[47]

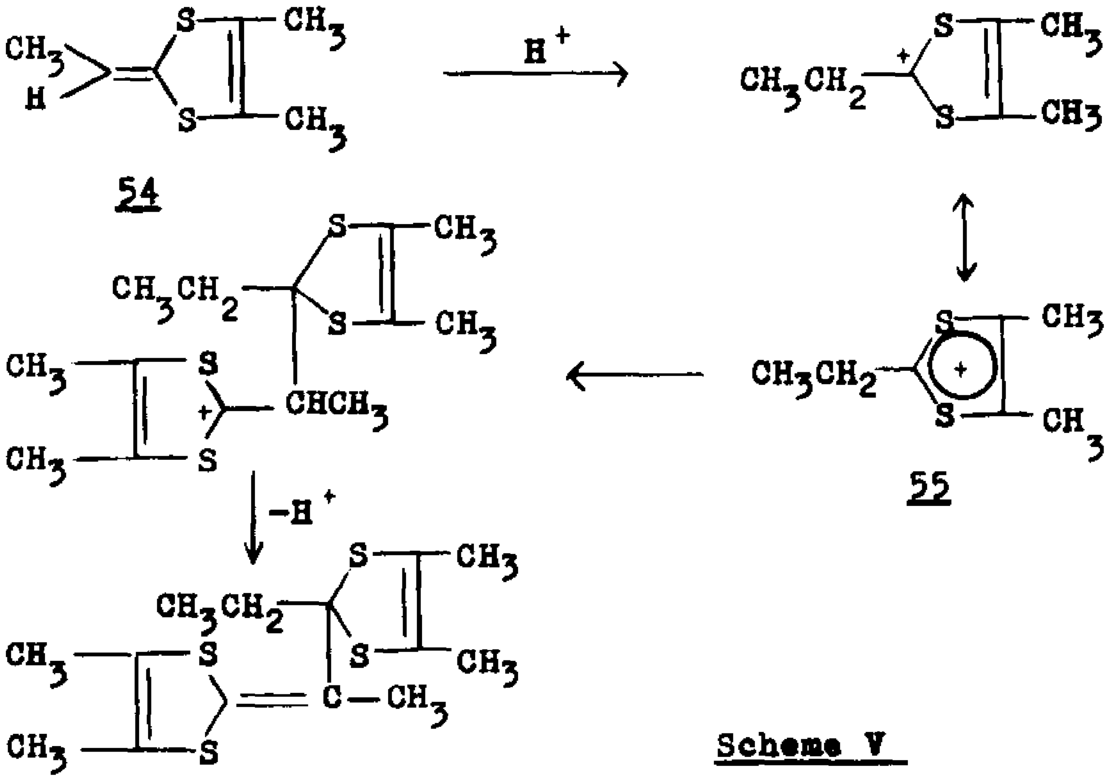


56



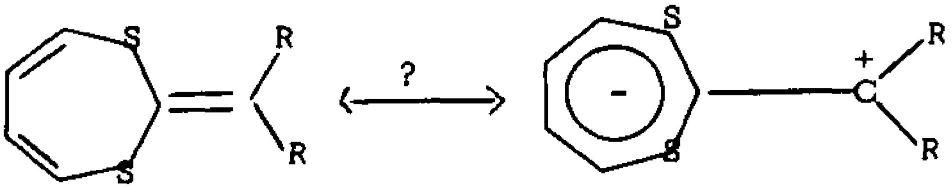
57

Although the dipole moment of 57 is still not reported, the following Scheme V, via heteroaromatic 1,3-dithiolium cation ring 55, might explain the dimerization of the fulvene of 1,3-dithiol 54.



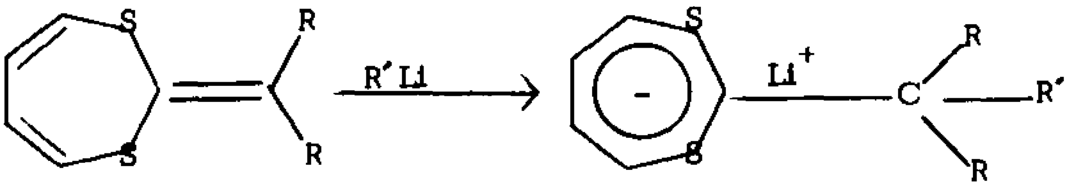
Scheme V

Fulvenes of 1,3-dithia-4,6-cycloheptadienes, resembling the fulvenes of cyclopentadiene, should exhibit a high dipole moment as indicated by the resonance structure 58, if the 1,3-dithia-4,6-cycloheptadienyl anion 52 has a high degree of aromaticity.



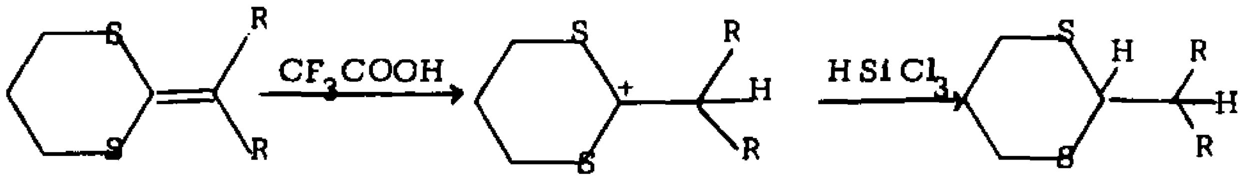
58 58'

Organometallic compounds should also add to the exocyclic double bond of fulvene 58, and form a stable anion ring possessing a group of 10 π-electrons. Consequently, the adduct 59 might be the expected reaction product.

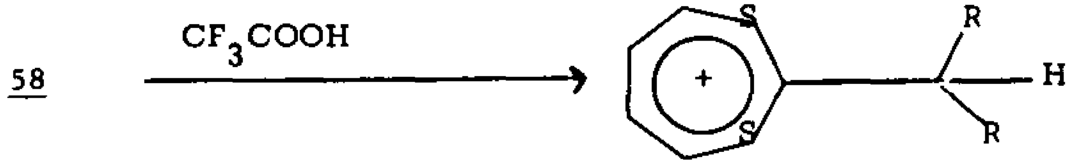


58 59

On the other hand, protonation of ketenethioacetals leading to sulfur stabilized carbonium ions such as 60 is also known.[48] Thus, fulvenes as 58 might be protonated, forming the interesting carbonium ion 61. However, since this ion represents an 8 π-electron system, and therefore should be antiaromatic, it is less likely.

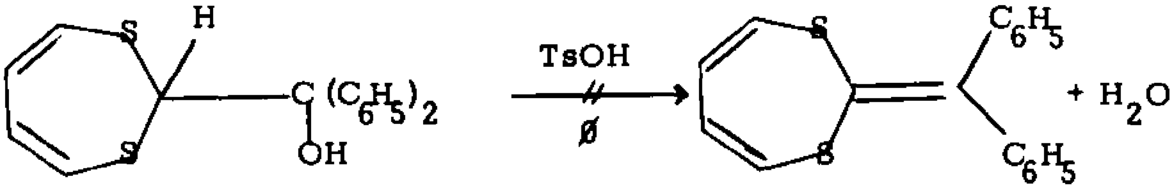


60



61

As reported by Seebach,[38] the diphenyl ketenethioacetal of 1,3-dithia-4,6-cycloheptadiene, 58a, should be available from the carbinol 53c by acid catalyzed dehydration in Dean-Stark trap. However, the dehydrated product did not give the expected compound 58a, but instead gave an isomeric ring-enlarged product. (The details are discussed on page 62).



53c

58a

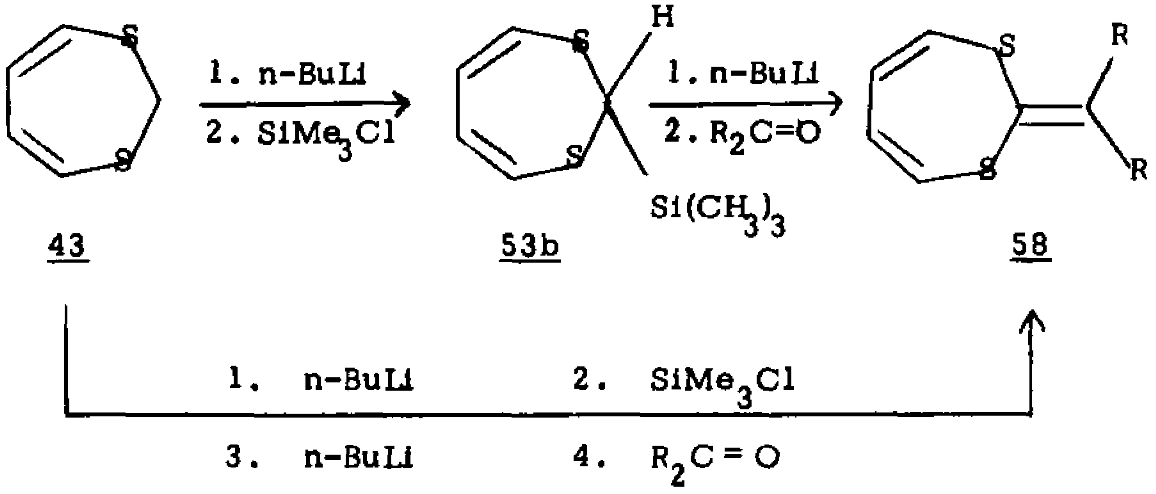
Alternatively, the reaction of the anion derived from silylated dithiacycloheptadiene with carbonyl compounds (Peterson reaction or silyl-olefination[49]) is expected to provide a more direct and milder route to the fulvenes of 1,3-dithia-4,6-cycloheptadiene.

Treatment of 2-trimethylsilyl-1,3-dithia-4,6-cycloheptadiene <u>53b</u> with n-butyllithium in tetrahydrofuran under nitrogen at -70°C produced the silylated anion which was quenched with benzophenone and acetone to give diphenyl ketenethioacetal <u>58a</u> and dimethyl ketenethioacetal <u>58b</u> in quantitative yield, respectively.

Compound <u>58a</u> formed as a yellow crystal, mp 88-89°C, ^1H nmr ($CDCl_3$, TMS): δ 7.26 (broad s, 10H), δ 6.35 (AA'BB' system, 4H); ^{13}C nmr ($CDCl_3$, TMS): eight signals as expected, δ 148.24, δ 142.4, δ 130.66, δ 129.48, δ 129.22, δ 128.3, δ 128.04, δ 127.84; UV: no definite maxium, but a broad tailing absorption into the visible region.

Compound <u>58b</u> , as a yellow liquid has a pleasant smell, bp. 72°C (0.16mm); nmr ($CDCl_3$, TMS): δ 2.03 (s, 6H) and δ 6.27 (s, 4H); mass spectrum: M^+ at m/e 170 (34.8%), m/e = 155 (M^+-CH_3, 14.7%), m/e = 103 (, 21.2%), m/e = 97 (, 26.2%), m/e = 86 (91.5%), m/e = 71 (100%) and m/e = 45 ($S{=}CH^+$, 51.1%). UV: λ_{max}^{EtOH} 342 nm (ϵ1181), 270 (shoulder, ϵ1104), 255 nm (sh., ϵ2053), 240 nm (sh., ϵ3312) and 220 nm (sh., ϵ11,039).

The fulvenes <u>58a</u> and <u>58b</u> can also be obtained directly from the parent compound <u>43</u>, without isolation of trimethylsilyl compound <u>53b</u>, as shown in Scheme VI.

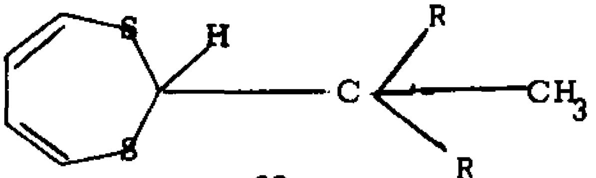


58a, R,R = C_6H_5, C_6H_5

58b, R,R = CH_3, CH_3

Scheme VI

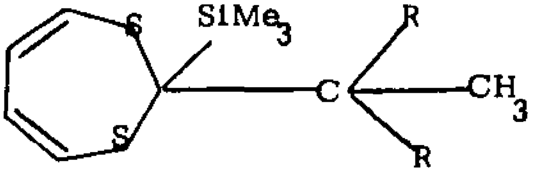
Ketenethioacetals 58a and 58b were treated with methyllithium in tetrahydrofuran under nitrogen at -70° C followed by warming to room temperature and quenching with water. Adducts, such as 62, were not observed, but instead the starting materials were recovered.



62

a. R = R = C_6H_5

b. R = R = CH_3

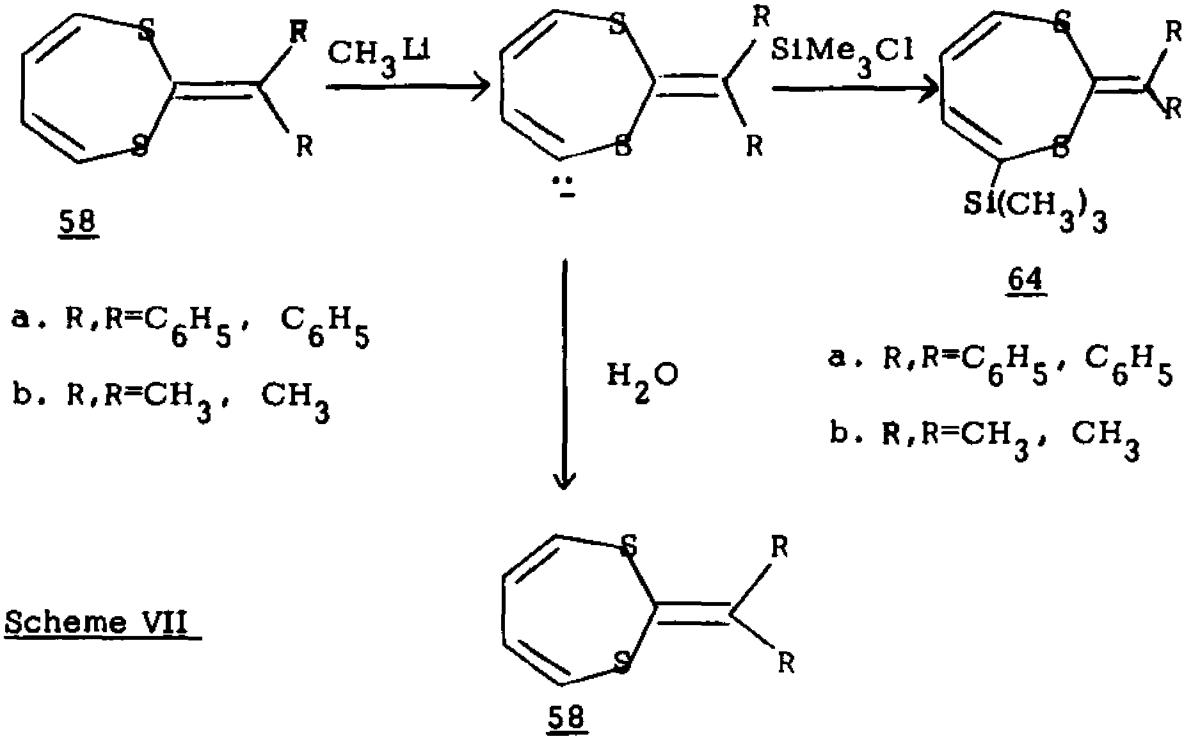


63

a. R = R = C_6H_5

b. R = R = CH_3

However, quenching the resulting anion solutions with trimethylsilyl chloride produced a corresponding trimethylsilyl compound. Based upon nmr analysis, no additional methyl group was detected; therefore, the structures such as 63 were ruled out. The narrow or sharp AA'BB' system of olefinic protons in ketenethioacetals are split into two areas in a ratio of 1 : 2 . Hence, the structures of trimethylsilyl adduct were proposed as 64, as shown in Scheme VII.

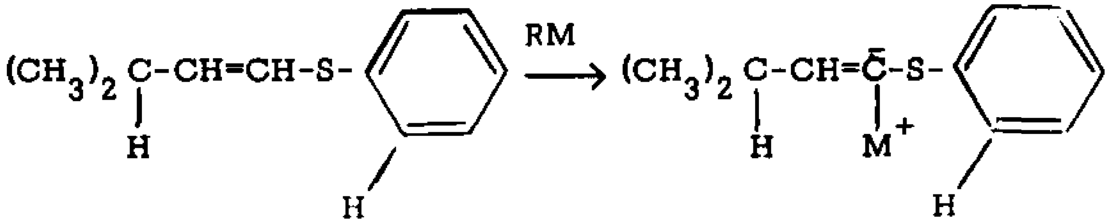


Scheme VII

Compound 64a formed as a yellow crystals, mp. 96-98° C after recrystallization from pet. ether: nmr ($CDCl_3$, no TMS): δ 0.00 (s, 9H), δ 6.46 - 6.95, split into two areas (1 : 2) (3H), δ 7.38 (broad s, 10H). Compound 64b as a yellow liquid, nmr ($CDCl_3$, TMS): δ 0.18 (s,9H), singlet at δ 2.05 and δ 2.09 (6H), δ 6.24 - δ 6.70, split into two areas (1:2) (3H).

This behavior is in striking contrast to the behavior of fulvenes of cyclopentadiene, (see page 28).

A recent report by Muthukrischman and Schlosser[50] shows that the acidity of olefinic protons adjacent to the sulfur atoms is considerable relative to that of allylic proton or phenyl protons. Thus, 1-(3-methylbut-1-enyl)phenyl sulfide is metallated exclusively at the vinylic α-position.

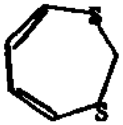


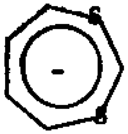
As pointed out, fulvenes of 1,3-dithia-4,6-cycloheptadiene should exhibit a high dipole moment. The methyl group should therefore add to the exocyclic bond if the parent anion has high degree of aromaticity. Based upon these results, it is proposed that either 1,3-dithia-4,6-cycloheptadienyl anion can not be considered to have a high degree of 10π-electron heteroaromatic stabilization, or vinyl metallation is much faster than nucleophilic addition due to the strong acidity of vinyl protons α to sulfur.

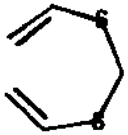
B) INVESTIGATION OF THE DIAMAGNETIC RING CURRENT OF 1,3-DITHIA-4,6-CYCLOHEPTADIENYL ANION

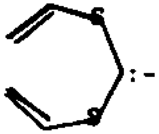
Aromatic systems sustain a diamagnetic ring-current in an applied magnetic field and cause a deshielding effect. ^1H and ^{13}C nmr spectra are the most important method used detect dia-or paramagnetic ring-currents, and to give some experimental values for the charge densities in cyclic conjugated system. In order to obtain some information concerning the possible presence of an induced diamagnetic ring-currents, we have measured the ^1H nmr and ^{13}C nmr spectra of anion 52 and compared them with those of the anion (74) of bis-(vinylthio)methane 67 (the synthesis and characterization of compound 67 are discussed on page 45 - 48). (Note: anion 74 lacks cyclic conjugation.)

One equivalent of 2.4M n-butyllithium in n-hexane was injected into the nmr tube under nitrogen, the solvent was then evaporated slowly under vacuum. To the nmr tube was added, one equivalent of compound 67 or 43 in THF-d_8 (containing tetramethylsilane as reference) at -70°C under nitrogen. The reaction mixture was warmed at 0°C for ca 10 minutes. While maintaining an atmosphere of nitrogen the tube was cooled in a dry ice/acetone bath, and then carefully sealed. The sealed nmr tube was then immediately scanned by nmr. Their ^1H and ^{13}C nmr chemical shifts are summarized in Table III.


43


52


67


74

	^1H nmr spectrum			^{13}C nmr spectrum		
Compound	δH_2	$\delta H_4/H_7$ (center)	$\delta H_5/H_6$ (center)	δC_2	δC_α	δC_β
43*	4.13	6.28	6.28	39.7	128.3	124.7
52**	1.48	6.63	5.80		146.7	121.6
$\Delta\delta$ (ppm)	-2.65	+0.35	-0.52		+18.4	-3.1
67*	3.92	6.41	5.26	34.6	131.5	112.8
74**	2.40	6.59	4.75		148.7	102.9
$\Delta\delta$ (ppm)	-1.52	+0.18	-0.51		+17.2	-9.9

*solvent : $CDCl_3$; **solvent : THF-d_8

+ : shift downfield ; - : shift upfield

all units in δ (ppm)

Table III : ^1H and ^{13}C NMR Chemical Shifts of 1,3-Dithia-4,6-Cycloheptadiene, Bis(vinylmercapto)methane and their Anions.

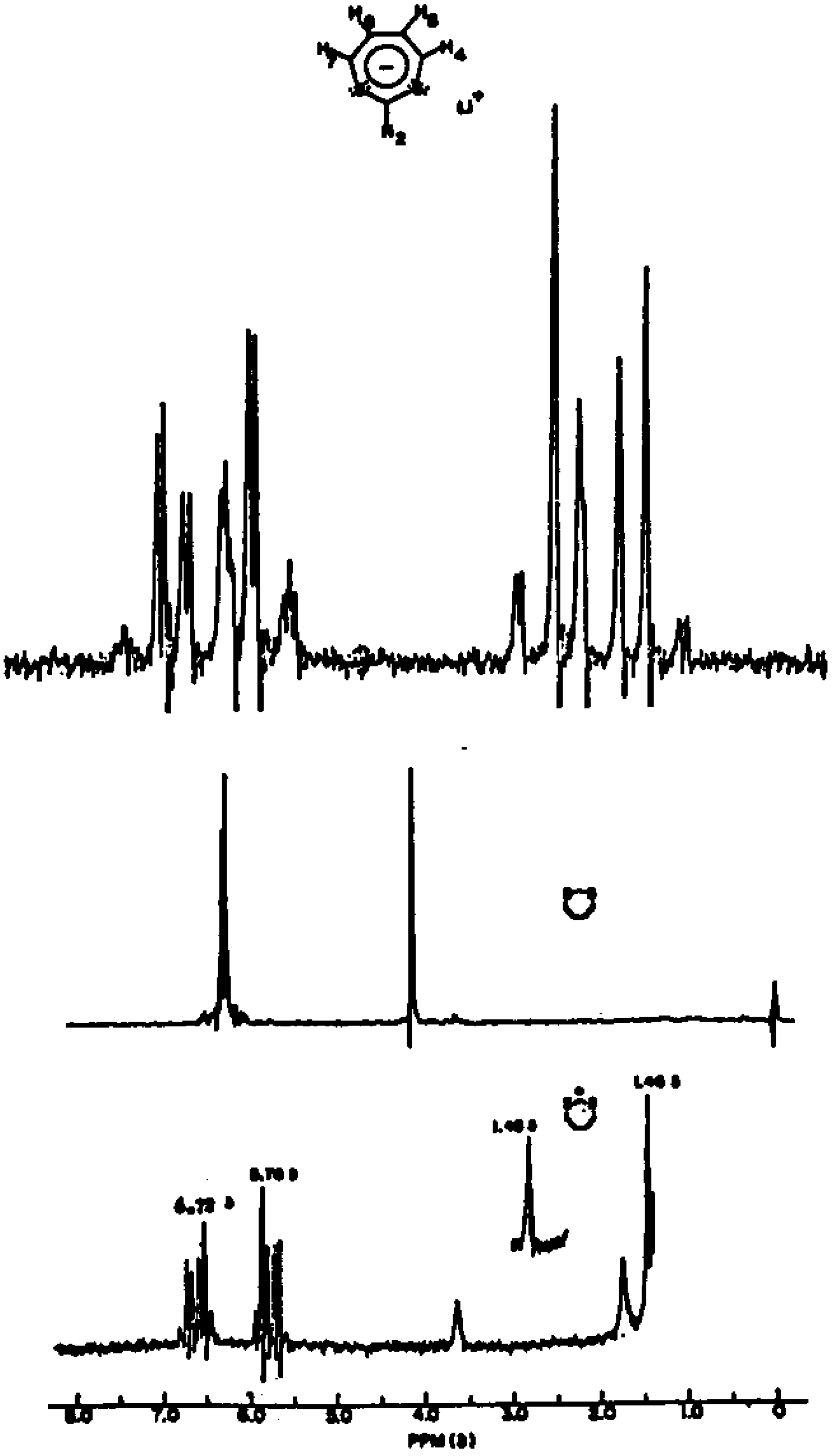


Fig. XII

From the results, it is difficult to estimate the magnitude of the "aromatic" deshielding effect in the 1,3-dithia-4,6-cycloheptadienyl anion 52, because of the several factors affecting the chemical shifts, such as the diamagnetic ring-current, the charge distribution in the system and the anisotropy of the sulfur atoms. As indicated in Table III, the values of $\delta_{43} - \delta_{52}$ and $\delta_{67} - \delta_{74}$ are not remarkably different either in the ^{1}H nmr and ^{13}C nmr spectra.

It should be noted that the narrow AA'BB' pattern of 43 is split to an AA'XX' system in the lithio-derivative 52. The analysis of the AA'XX' system is given in Table IV.[98]

AA'XX' - Analysis for the anion 52

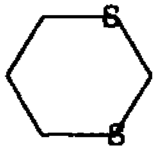
$H_{4/7}$	δ 6.63 ppm
$H_{5/6}$	δ 5.80 ppm
$J_{4,5}$	11.08 Hz
$J_{5,6}$	8.33 Hz
$J_{4,6}$	0.78 Hz
$J_{4,7}$	0.78 HZ

Table IV

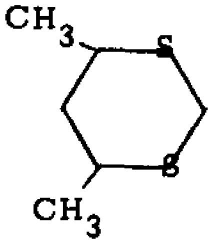
The low field part of the spectrum, shows each line split into a doublet ($J_{2,4}$ = 0.8 Hz). The same coupling constant is seen in the triplet for H_2 at δ 1.48. The well documented W-coupling[51] assigns the low field part of the AA'XX' pattern to H_4 and H_7, with a downfield shift of ca. 0.35 ppm relative to <u>43</u> despite the negative charge at C_2 in anion <u>52</u>. Protons H_5 and H_6, further away from the anionic center C_2, are shifted upfield by ca. 0.52 ppm, which indicates considerable charge density at these positions.

The observed W-coupling suggests a planar structure for anion <u>52</u>. The coupling constants, $J_{4,5}$ = 8.25 Hz can be interpreted as an increase in double bond character for C_4- C_5 bond.[52] However, it is at this time difficult to assess the effect of the sulfur atoms on the coupling constants.

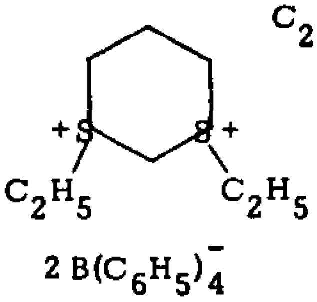
It is interesting to note that the chemical shift of the remaining proton H_2 of <u>52</u>, δ 1.48 is substantially higher than that observed for H_2 in the related 2-lithio-1,3-dithianes investigated by Eliel, et al.[53] Even the ylid salt <u>69</u>, reported by Gosselck,[54] shows a higher chemical shift for H_2 than in the lithiodithianes. (See Table V).



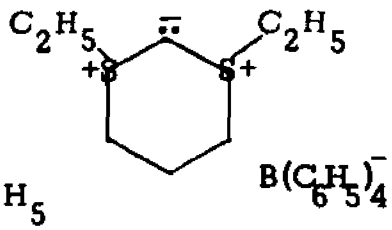
<u>65</u>



<u>66</u>



<u>68</u>



<u>69</u>

Compound	δH_2	Anion	δH_2	$\delta H_2 - \delta H_2$(anion)
65*	3.68	2-Li-deriv.	2.78	0.90
66*	4.03_{ax}; 3.40_{eq}	2-Li-deriv.	2.58_{ax}	1.45_{ax}; 0.82_{eq}
67**	3.92	anion 74	2.40	1.52
68***	5.35	ylid-salt 69	1.97	3.38
43**	4.13	anion 52	1.48	2.65

*THF-d_8; E. Eliel, personal Comm.;

**THF-d_8; see experimental section

***DMSO-d_6; counter ion $B(C_6H_5)_4^-$ see ref.

Table V: ^{1}H NMR Chemical Shift Data

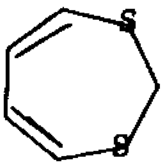
A possible interpretation of these data is that in the lithiodithianes, we see tetrahedral carbanions stabilized by polarization of the sulfur atoms.[34,55] Anion 52 and the ylid salt 69 are probably planar and delocalized systems (10π-aromatic delocalization for 52 and possibly d-orbital acceptance at the sulfurs for 69) with completely different anisotropy effects of the sulfur on proton H_2. On the basis of these results the postulate, that anion 52 be considered a planar delocalized 10π-heteroaromatic system, is proposed.

C) KINETIC AND EQUILIBRIUM ACIDITY STUDY

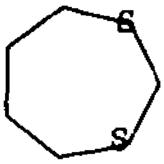
In the preceeding discussion, we concluded that anion 52 could be considered as a 10π-heteroaromatic anion on basis of its ^{1}H nmr spectrum. However, because of the complexity of the factors affecting the chemical shifts, diamagnetic ring current, charge distribution, anisotropy and geometry at the heteroatom, no clear decision concerning the aromaticity of 52 could be made.

An alternative experimental approach towards answering the question as to whether 52 is an aromatic system consists, according to Breslow, of establishing a greater stabilization by π-electron delocalization in 52 as compared to a suitable model lacking this cyclic delocalization.[16] An indication for the stability of the 1,3-dithia-4,6-cycloheptadienyl anion 52 as compared to other compounds would be the relative acidity of its conjugate acid 43 compared to suitable models lacking cyclic conjugation.

The compounds which we chose to study are the saturated 1,3-dithiacycloheptane 70 and the open chain model bis-(vinylmercapto)-methane 67. Their syntheses and characterizations are described below.



43



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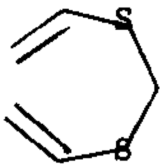
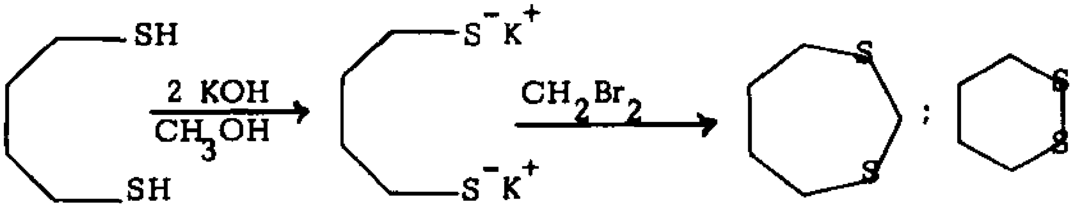


67

Syntheses and Characterizations: we synthesized the saturated compound 70 by using the same procedure as for the preparation of 46, rather than the published procedure of Oae[56] (which used the acid catalyzed procedure we found unsatisfactory for 46; see page 23).

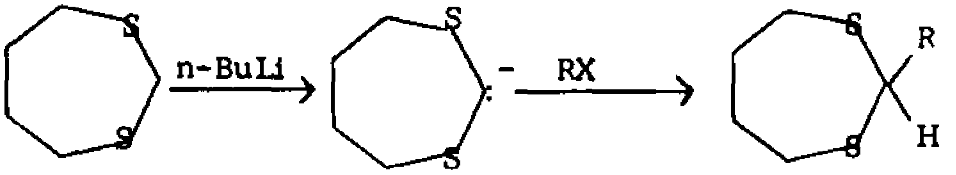
Treatment of the commercially available 1,4-butandithiol with 2 equivalents of potassium hydroxide in methanol, followed by alkylation with dibromomethane afforded compound 70 in 30% yield. Compound 70 was formed as a colorless liquid, bp. 58-65°C (1.8mm). Its nmr ($CDCl_3$, TMS) consists of two broad multiplets centered at δ 2.00 (4H) and δ 2.80 (4H) and a singlet at δ 3.85 (2H).



70 71

A lower boiling point compound 71, as a colorless liquid, bp. 42-50°C (1.8mm), has been isolated from this reaction. 71 has an nmr similar to that of compound 70, but without the singlet protons: its nmr ($CDCl_3$, TMS) shows two broad multiplets centered at δ 1.98 and δ 2.80 in a ratio of 1 : 1. The by-product 71 was formed probably through the oxidation of dipotassium salt of 1,4-butandithiol.

Treatment of the saturated compound 70 with n-butyllithium in tetrahydrofuran under nitrogen at -70°C produced a colorless anion solution. This was quenched with methyl iodide, benzophenone and trimethylsilyl chloride to give 2-methyl-1,3-dithiacycloheptane 72a, diphenyl carbinol 72b and 2-trimethylsilyl-1,3-dithiacycloheptane 72c, respectively. Their structures were characterized by their nmr spectra (summarized in Table VI). In all these derivatives, the broad multiplet of $H_{4,7}$ was split into two very broad multiplets, while the signal-complex for $H_{5,6}$ stayed the same.



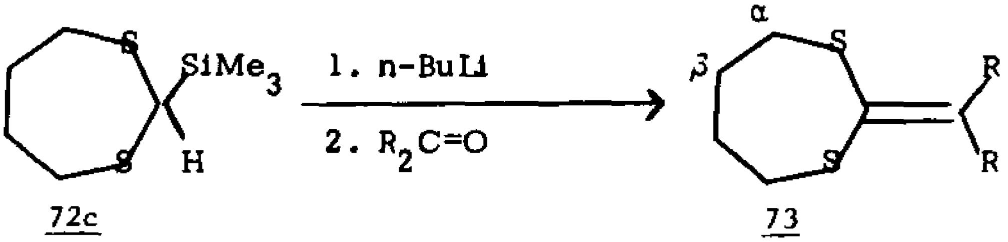
72

Compound	δH_2	$\delta H_4/H_7$ (center)	$\delta H_5/H_6$ (center)	δR
72a*, R=CH_3	4.23 (q)	2.79	1.98	1.50 (d)
72b*, R=$C(C_6H_5)_2$ with OH	5.56 (s)	2.85	1.87	3.65 (s, exchanged with D_2O), 7.22-7.72 (m, 10 H)
72c**, R=$Si(CH_3)_3$	3.26 (s)	2.70	1.85	0.00

*solvent: $CDCl_3$, TMS; **solvent: CCl_4, no TMS

Table VI: The NMR Chemical Shifts of 2-Substituted-1,3-dithiacycloheptanes.

Upon treating with n-butyllithium in tetrahydrofuran at -70° C under nitrogen, followed by quenching with acetone and benzophenone, 2-trimethylsilyl-1,3-dithiacycloheptane 72c could be converted into dimethyl fulvene 73a and diphenyl fulvene 73b, respectively. (See Table VII.)

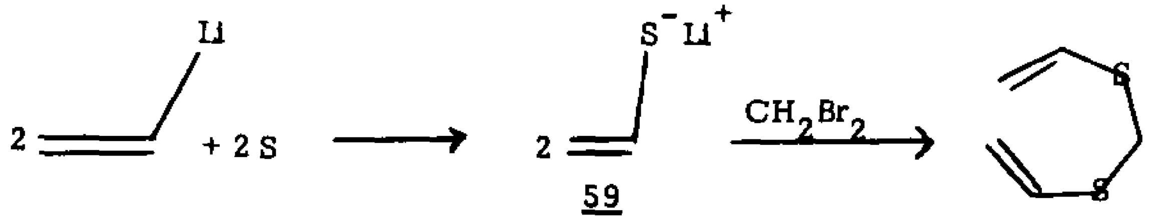


Compound	δ H_α (center of m.)	δ H_β (center of m.)	δ_R
73a , R=R=CH_3	2.90	1.93	1.98 (s)
73b , R=R=C_6H_5	2.97	1.97	7.22 (br.s)

solvent: $CDCl_3$

Table VII: The NMR Chemical Shifts of Keteneacetals of 1,3-Dithiacycloheptane.

The synthesis of bis(vinylmercapto)methane 67 has been reported in the literatures,[57,58] but we developed a simpler route leading to 67. The synthesis was performed by reacting sulfur with the commercially available vinyllithium in tetrahydrofuran under nitrogen at -70° C to yield lithium vinyl thiolate,[59] followed by alkylation with dibromomethane, as shown below:



59

After work-up in the usual manner, the reaction mixture was so clean (only one spot showed on the tlc plate) that one could use simple distillation to isolate the desired compound 67. The divinyl mercaptomethane 67 was obtained in 40-45% yield as a colorless liquid, bp. 78-79° C (9 mm); its structure is fully confirmed by ^{1}H nmr, ^{13}C nmr, IR, UV and mass spectrum.

^{1}H nmr (CCl_4, TMS): δ 3.92 (s, 2H), ABX type at δ 5.08-5.37 (m, 4H)
and δ 6.19 - 6.63 (m, 2H)

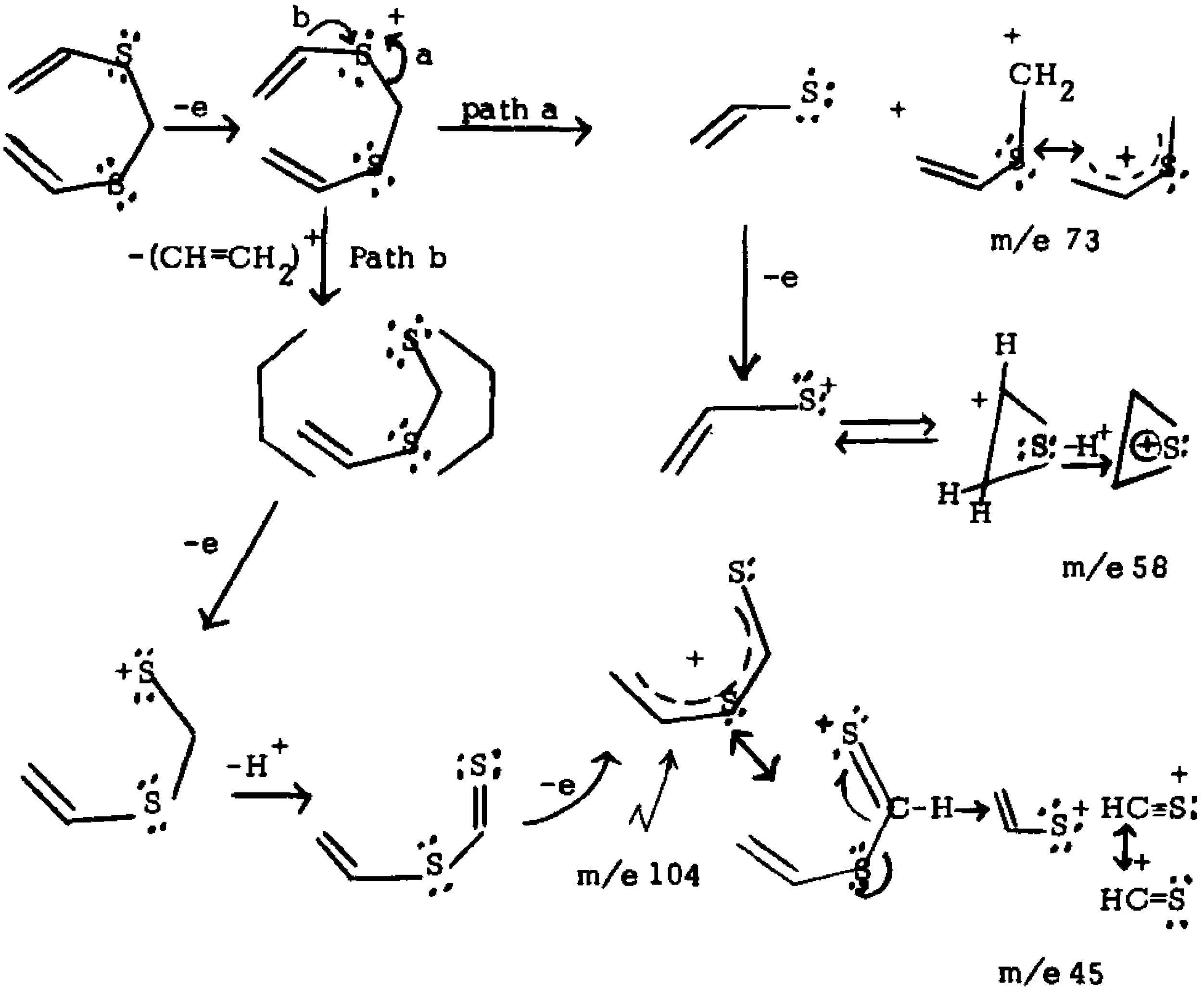
^{13}C nmr (CCl_4, TMS): δ 131.5 ppm (d, $C_{4,7}$), δ 112.8 ppm (t, $C_{5,6}$)
and δ 34.6 ppm (t, C_2)

IR (CCl_4): 3100 cm^{-1}, 1580 cm^{-1}

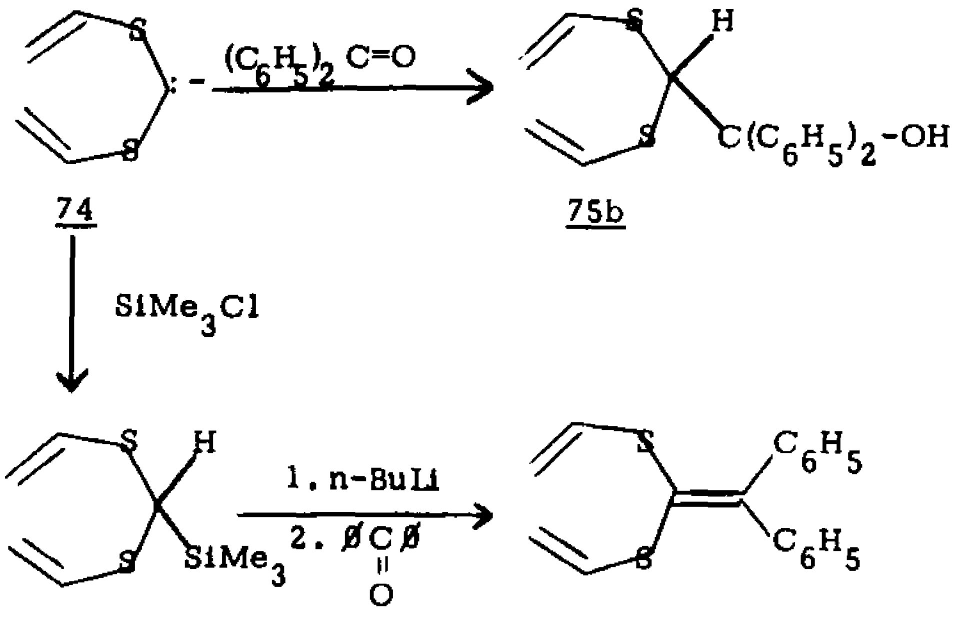
UV: λ_{max}^{EtOH} = 227 (ε 4759)

mass spectrum: m/e = 132 (M^+, 11.5%), 104 (21.5%), 73 (83.1%)
58 (24%), 45 (100%).

For the bis(vinylmercapto)methane 67 two major routes of fragmentation were proposed as shown below:



Treatment of 67 with n-butyllithium in tetrahydrofuran under nitrogen at -70° C yielded a straw-yellow solution of anion 74 which was quenched by trimethylsilyl chloride and benzophenone to give the corresponding trimethylsilylated compound 75a and diphenyl carbinol 75b, respectively. Compound 75a was further treated with n-butyllithium in tetrahydrofuran at -70° C, followed by quenching with benzophenone. 75a was thus converted into the expected diphenyl ketene thioacetal 76.



74 75b 75a 76

The structures were characterized by nmr and the outlines are shown below:

Compound 75a : nmr (CCl_4, no TMS): δ 0.00 (S,9H), δ 3.17 (s,1H), ARX type at δ 4.96-5.25 (m,4H) and δ 6.11-6.55 (m,2H)

Compound 75b : nmr (CCl_4,TMS): δ 3.32 (s,1H, exchanged with D_2O), δ 4.90 (s,1H), ARX type at δ 5.03-5.32 (m,4H) and δ 6.03-6.47 (m,2H), δ 7.12-7.57 (m,10H)

Compound 76 : nmr ($CDCl_3$, TMS), ABX type at δ 5.09-5.37 (m,4H) and δ 6.31-6.74 (m,2H), δ 7.20 (s, 10H).

Kinetic Acidity: equimolar mixtures of 43 and 70 and 43 and 67 were subjected to competitive H/D-exchanges in t-butanol-OD with a catalytic amount of potassium t-butoxide. The reactions were carried out at constant temperature and the work-up involved quenching with ice water, extraction with ether and vacuum distillation. The products were analyzed by nmr and gas-chromatography/mass spectroscopy using a Finnegan 3300 instrument.[60] The results are summarized in Table VIII.

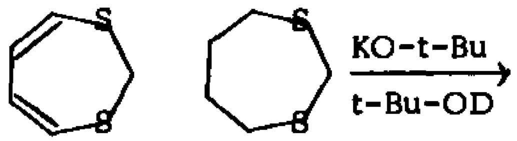
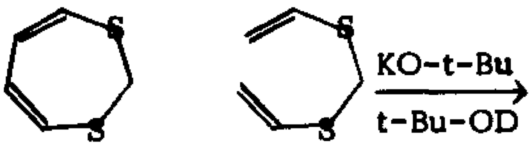
 43 70	24 hrs/85°	43 - D_4	70 - D_2
	4 hrs/85°	43 - D_2 43 - D_3 (30%)	70 - H_2 (32%) 70 - D_1 (50%) 70 - D_2 (18%)
	2 hrs/85°	43 - D_2	70 - H_2
	10 min/85°	43 - D_2	70 - H_2
	30 min/35°	43 - D_2 (51%) 43 - D_1 (41%) 43 - H_2 (8%)	70 - H_2
 43 67	30 min/50°	43 - D_2 (90%)	67 - H_2 67 - D_1 (traces)

Table VIII: Base Catalyzed H/D-Exchange Result for 43, 70 and 67.

It is apparent from Table VIII the three compounds investigated show very different kinetic acidities under the conditions employed. In refluxing t-butanol-OD compound <u>43</u> exchanges completely both protons in position 2 within 10 minutes. The saturated model <u>70</u> under the same conditions does not exchange at all, while after 24 hours at 85° C both compound <u>43</u> and <u>70</u> exchange completely their protons in position 2. On basis of these results one can approximately estimate a relative acidity of <u>43</u> and <u>70</u> as follows:

first order kinetic rate, $k = 2.303 \times 1/t \times \log C_o/C$

where C_o is the initial concentration and C is the final concentration.

After 10 min. <u>43</u> is completely deuterated and after 24 hrs. <u>70</u> is completely deuterated.

$$k_{\underline{43}} = 2.303 \times 1/600 \times \log (C_o/C)_{\underline{43}}$$

$$k_{\underline{70}} = 2.303 \times 1/24 \times 3600 \times \log (C_o/C)_{\underline{70}}$$

assume: $(C_o/C)_{\underline{43}} \simeq (C_o/C)_{\underline{70}}$

hence:

$$k_{\text{relative}} = \frac{k_{\underline{43}}}{k_{\underline{70}}} = \frac{24 \times 3600}{600} = \sim 150$$

The relative acidity at 85° C for <u>43</u> and <u>70</u> is about 150.

We should like to interpret the increased acidity of 43 as an indication of the increased stability (aromaticity) of the planar 1,3-dithia-4,6-cycloheptadienyl anion 52, stabilized by π-electron delocalization with a "resonance energy" of approximately 3 Kcal/mol.

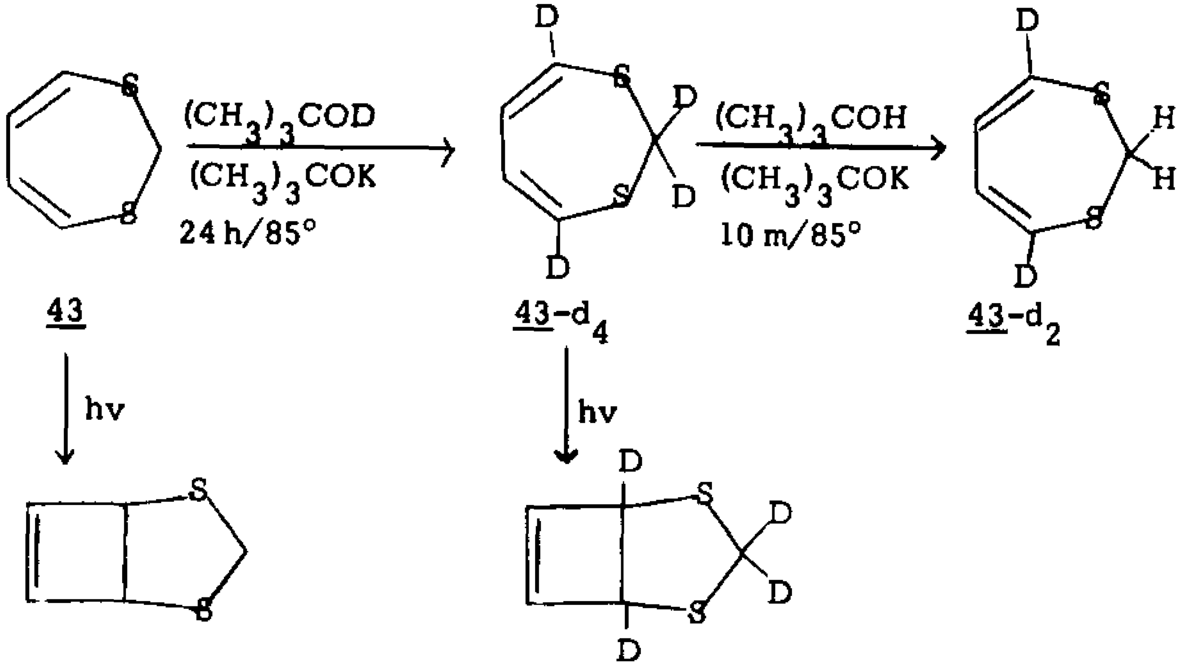
However, in view of a recent publication by Streitwieser and Ewing,[34] who attribute the stability of a carbanion next to sulfur to polarization at the heteroatom, one could argue that the increased stability of unsaturated anion 52 as compared with the saturated anion derived from 70 is the result of better polarization at the sulfur in 52, due to the presence of polarizable π-electrons at the adjacent carbon atom. The anion of model compound 67 should exhibit the same or an even greater polarizability than the cyclic unsaturated anion 52. Therefore, if 1,3-dithia-4,6-cycloheptadiene 43 and bis(vinylmercapto)-methane 67 show different acidities, the difference should clearly establish stabilization through π-electron delocalization in 52 and thus characterize anion 52 as a 10 π-heteroaromatic system.

As apparent from Table VIII, after 30 min at 50°C, 43 has nearly completely exchanged its protons at position 2, while 67 has exchanged hardly at all. This remarkable different kinetic acidity between 43 and 67 also suggests that the planar 1,3-dithia-4,6-cycloheptadienyl anion 52 is stabilized by π-electron delocalization.

The mass spectral analysis of the products obtained from the H/D-exchange at 85°C for 24 hr, show compound 43 had actually incorporated four deuterium atoms, two of them in position 2, the remaining in the diene part. An assignment of the position of the third and the fourth deuterium atom on basis of the ^{1}H and ^{13}C nmr proved to be difficult. However, this assignment was made possible through use of the photoisomer of 43.

Upon Pyrex filtered irridiation with a 450 W Hanovia Hg-lamp, compound 43 was converted into its photoisomer, 2,4-dithiabicyclo (3,2,0)heptene 77, in quantitative yield (Scheme VIII). 77 was obtained as a colorless oil, bp 30-33° (0.05 mm); its ^{1}H nmr spectrum consists of a singlet at δ 5.77 (2H), a singlet at δ 5.00 (2H) and an AB system centered at δ 3.8 (2H) with a coupling constant of 12 Hz; its ^{13}C nmr spectrum consists of three signals at δ 134.6 ppm, δ 61 ppm and δ 35.8 ppm; mass spectrum: M^{+} at m/e = 130 (22%), m/e = 103 (17%), m/e = 84 (100%), ... and etc.

Following the same sequence, the tetradeutero derivative of 43 was converted into the photoisomer 77-d_4. Its ^{1}H nmr spectrum showed only one singlet at δ 5.75. This clearly establishes the position of the additional two deuterium atoms at carbons 4 and 7, next to the sulfur (Scheme VIII). This result compares well with similar observations made during the deuteration of thiophene and vinylthioethers.[61]



Scheme VIII

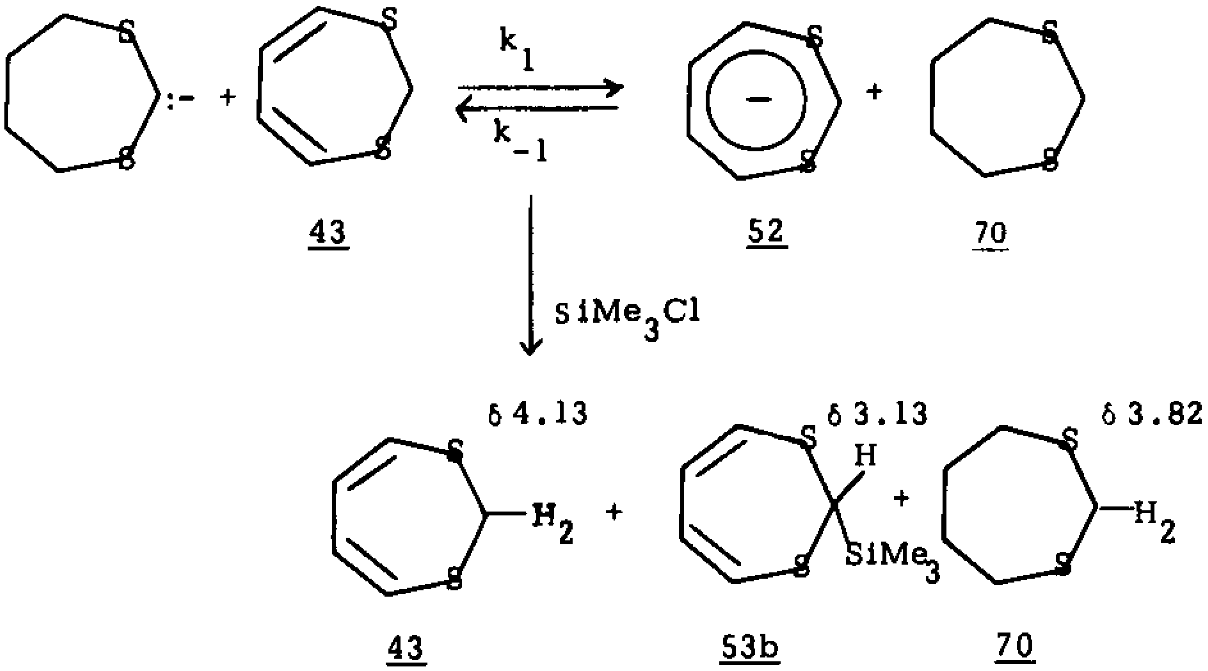
The two deuteriums at position 2 of compound 43-d$_4$ have been completely exchanged in t-butanol with a catalytic amount of potassium t-butoxide at 85° C for 10 minutes to give 43-d$_2$ (Scheme VIII) the ^{1}H nmr spectrum of which showed a singlet at δ 4.13 (2H) and a broad singlet at δ 6.30 (2H); the ^{13}C nmr spectrum (^{1}H decoupled and off resonance decoupled) showed three signals at δ 127.9 (peak height = 12%), δ 124.2 (58%) and δ 39.3 (37%). The higher peak at δ 124.2 should be assigned to C_β, because the height increase is from the collapse of C-H spin multiplets.[62] Thus, this ^{13}C nmr spectrum is found to be useful for the assignments of C_α and C_β in the spectrum of the parent compound 43. (See Table III.)

Equilibrium Acidity: in view of uncertainties associated with the interpretation of kinetic data by the existence of factors such as internal return and ion pairing.[63] We also studied the equilibrium acidity of <u>43</u>, <u>67</u> and <u>70</u>.

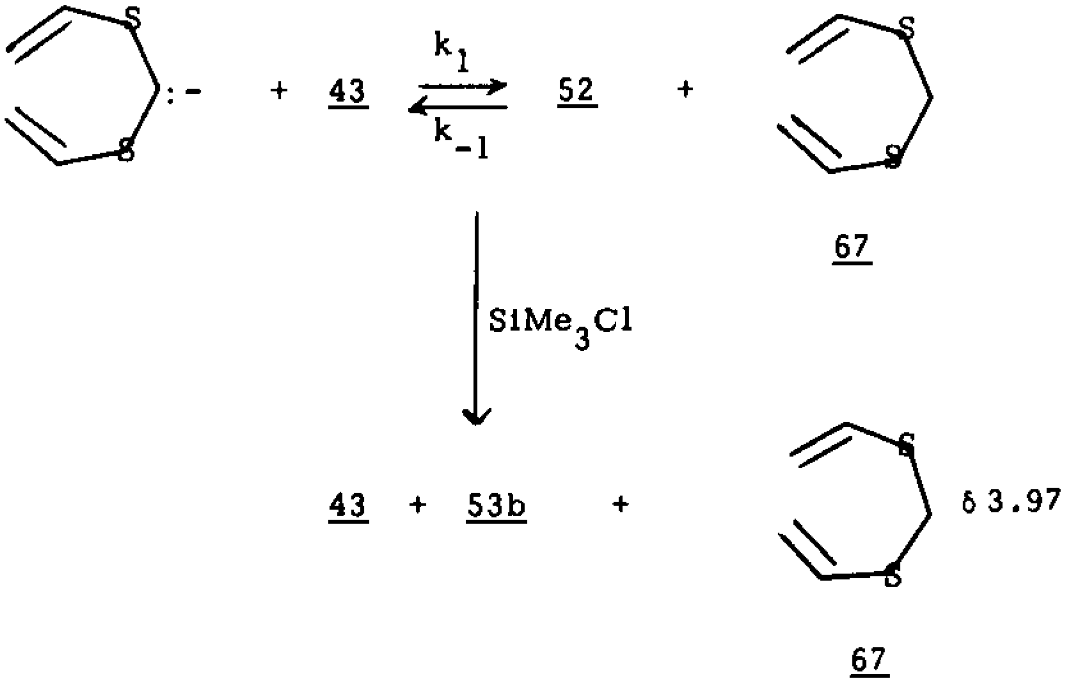
Addition of an equimolar amount of the diene <u>43</u> to the <u>colorless</u> solution of anion derived from <u>70</u> at -70° C, then holding the reaction mixture at 0° C for 2 hours, produced a <u>deep red</u> solution of the anion <u>52</u> (see page 24) which was quenched at -70° C with freshly distilled trimethylsilyl chloride.

After work-up in the usual manner and distillation under vacuum, the nmr spectrum of the reaction mixture was recorded. From the spectrum shown, the reaction gave exclusively the 2-trimethylsilyl-1,3-dithia-4,6-cycloheptadiene <u>53b</u> and no trimethylsilyl derivative from the saturated anion. The relative areas of the nmr singlets at δ 3.13 in compound <u>53b</u>, at δ 3.82 in compound <u>70</u> and at δ 4.13 in compound <u>43</u> are 19.5, 110 and 42.1, respectively. In other words, the reaction mixture contained 22% of <u>43</u>, 57.5% of <u>70</u> and 20.4% of <u>53b</u>.

The experiment with bis(vinylmercapto)methane <u>67</u> had the same result that the reaction gave exclusively the compound <u>53b</u>. Based on NMR spectrum analysis, the relative areas of nmr singlets at δ 4.15 in compound <u>43</u>, at δ 3.97 in compound <u>67</u> and at δ 3.18 in compound <u>53b</u> are 21, 35 and 9.1, respectively. In other words, the reaction mixture contained 28.3% of <u>43</u>, 47.2% of <u>67</u> and 24.5% of <u>53b</u>.



:-
+
k1
k-1
43
52
+
70
SiMe3Cl
δ 4.13
H2
+
δ 3.13
H
SiMe3
+
δ 3.82
H2
43
53b
70



:-
+
43
k1
k-1
52
+
67
SiMe3Cl
43
+
53b
+
δ 3.97
67

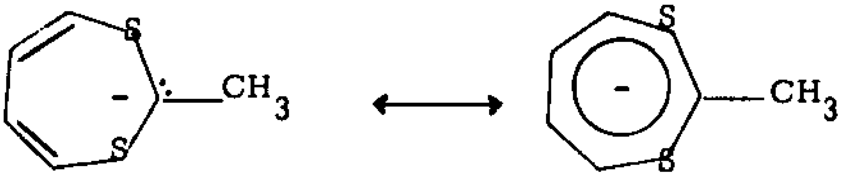
As the results indicated, in the above equilibrium equation, the rate constant k_1 is much larger than the rate constant k_{-1} in both cases because the stronger acid 43 is metalated completely by the stronger base derived from 70 or 67 .

A. Streitwieser[63a,64] has shown that hydrocarbons whose thermodynamic acidity is proportional to the difference in π-delocalization energy (ΔE_π) between the carbanion $(E_\pi)_{A^-}$ and the parent hydrocarbon $(E_\pi)_{AH}$. It appears from these results that the increased thermodynamic acidity of 43 relative to 67 or 70 is due to the π-delocalization energy of anion 52 which is much larger than the π-delocalization energy of the anions derived from 67 or 70 . (Note: π-delocalization energy, ΔE_π , is expressed by β which is a negative value). The greater resonance stabilization energy of anion 52 must be the result of its aromaticity. Thus, 1,3-dithia-4,6-cycloheptadienyl anion 52 represents a 10 π-electron heteroaromatic system, although the degree of aromaticity seems to be small.

D) KINETIC ACIDITY OF SUBSTITUENT 1,3-DITHIA-4,6-CYCLOHEPTADIENE

A. Streitwieser[34] has shown that 2-methyl-1,3-dithiane is less acidic than the parent compound by a factor of 10^6 due to the electron donating substituent effect of a methyl group. Thus, one would predict 2-methyl-1,3-dithia-4,6-cycloheptadiene <u>53d</u> is also less acidic by a factor of about 10^6 than the parent compound <u>43</u> if the system is without π-delocalization, and only the inductive substituent effect of a methyl group is involved. In view of the previous kinetic acidity study, compound <u>53d</u> would then be expected to be much less acid than the saturated model <u>70</u> or the acyclic model <u>67</u>.

On the other hand, if the negative charge in carbanion <u>78</u> tends to be delocalized through sulfur atoms and forms a 10 π-electron system, the substituent effect effects on the acidity of <u>53d</u> should be less important.



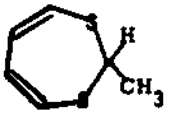
<u>78</u>

Thus, the study of the kinetic acidity of 2-methyl-1,3-dithia-4,6-cycloheptadiene and the related models, 67 and 70, is yet another approach to solve the question of whether or not 1,3-dithia-4,6-cycloheptadienyl anion 52 represents a 10 π-electron heteroaromatic system.

The equimolar mixture of 53d and 70, and the equimolar mixture of 53d and 67 were subjected to competitive H/D exchange in t-butanol-OD with a catalytic amount of potassium t-butoxide. The reactions were carried out at constant temperature. After work-up in the usual way, the reaction mixture was distilled under vacuum, and the products were careful analysis by nmr integration. The results are summarized in Table IX and X. (For the calculations see the experimental part.)

For the double check, the equimolar mixture of 70 and 67 were subjected to competitive H/D exchange in the same manner. The result (see Table XI, the calculation see experimental part) indicated that the slightly more acidic of compound 67 relative to compound 70 (5.5 : 1) is in agreement with the results obtained from Table IX and X.

From Table IX and X, these results indicated that 2-methyl-1,3-dithia-4,6-cycloheptadiene is still more acidic than the saturated compound 70 and now slightly less acidic than the acyclic compound 67. An expected large substituent effect of the methyl group in the

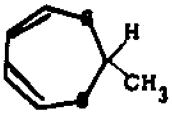

53d


70

	H_2	vinyl	CH_3	H_2	$(CH_2)_2$
Actual Ratio of integration units	* 16, 14 ** 0.45	145, 149 5.4	 5.8	19, 17	155, 155
Theoretical Ratio of integration units	* 1 (36.3, 39) **1 (1.933)	4 (145, 149) 4 (7.73)	 3 (5.8)	1 (77.5)	2 (155)
% of Deuterium Exchanged for 1 H	* 61.7 % ** 76.7 %			38.4%	
% of Unexchanged Material	* 38.3 % ** 23.3 %			61.6%	
Relative Rate	$2^{*} - 3^{**}$			1	

* based on vinyl ** based on CH_3

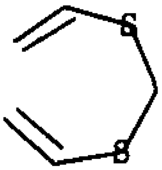
Table IX: H/D Exchange of 2-Methyl-1,3-dithia-4,6-cycloheptadiene and 1,3-Dithiacycloheptane at 75° C for 3.5 hours.

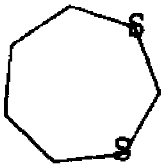

53d


67

	H_2	CH_3	H_2	CH_2=
Actual Ratio of integration units	17, 17	55, 56	11, 11	51, 50
Theoretical Ratio of integration units	1 (18.33, 18.67)	3 (55, 56)	1 (25.5, 25)	2 (51, 50)
% of Deuterium Exchanged for 1 H	8.1%		28.2%	
% of Unexchanged Material	91.9%		71.8%	
Relative Rate	1		3.93	

Table X: H/D Exchange of 2-Methyl-1,3-dithia-4,6-cycloheptadiene and Bis-(vinylmercapto)methane at 50° C for 1 hour.


67


70

	H_2	$CH_2=$	H_2	$(CH_2)_2$
Actual Ratio of integration units	20	194	54, 55	146, 145
Theoretical Ratio of integration units	1 (97)	2 (194)	1 (73, 72.5)	2 (146,145)
% of Deuterium Exchanged for 2 H	79.4%		25%	
% of Unexchanged Material	20.6%		75%	
Relative Rate	5.5		1	

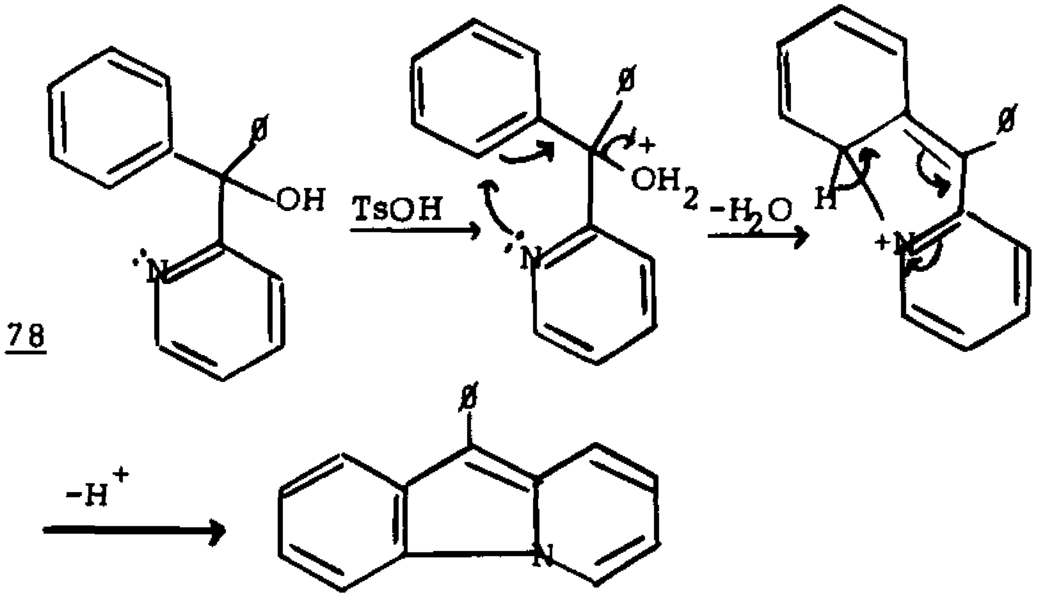
Table XI: H/D Exchange of Bis(vinylmercapto)methane and 1,3-Dithiacycloheptane at 50° C for 2 hours and 40 minutes.

1,3-dithia-4,6-cycloheptadiene system is not observed. A possible explanation for this small substituent effect is that the negative charge in carbanion 78 could be electron-through conjugated with sulfur and the carbon-carbon double bonds and therefore is a 10π-electron heteroaromatic 1,3-dithia-4,6-cycloheptadienyl anion.

III. RING ENLARGEMENT OF CARBINOL DERIVATIVES OF 1,3-DITHIACYCLES.

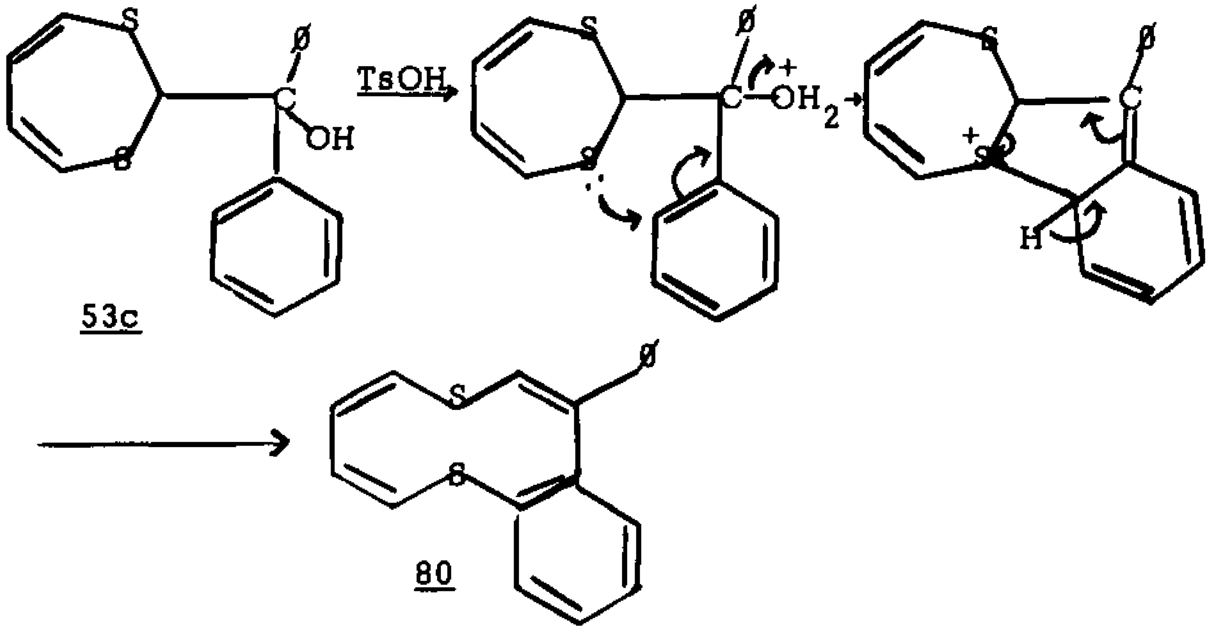
As mentioned before, in order to obtain diphenyl ketene thioacetal 58a, we have attempted the dehydration of diphenyl 2-(1,3-dithiepinyl) carbinol 53c in the presence of a catalytic amount of p-toluenesulfonic acid in a Dean-Stark trap. The reaction did not give the expected product ketene thioacetal 58a (see page 31), but instead gave an isomeric compound which formed white crystal having mp. 101-102°C; nmr ($CDCl_3$, TMS): δ 6.75 (s,1H), δ 7.21 (broad s, 5H), δ 7.4 (broad s, 4H) and an underlying multiplet of about 4H between δ 6.85 and δ 7.5; UV: λ_{max}^{EtOH} 229 nm (ϵ 21,700), 298 nm (ϵ 15,340); mass spectrum: M^+ at 294 (100%).

H. Wasserman[68] has reported that the carbinol 78 underwent cyclodehydration to give the ring closed product 79 as shown below:

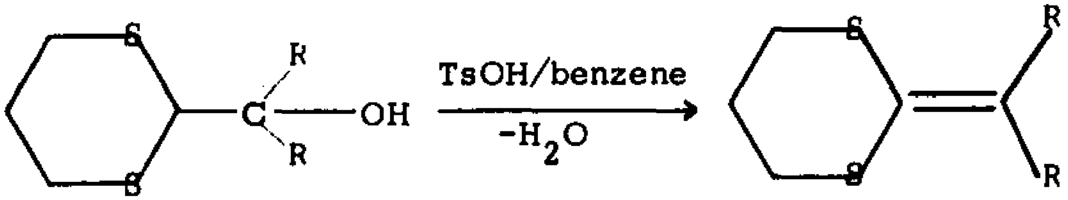


79

Based on the obtained spectra and following the same mechanism as reported by Wasserman, we propose the structure of this isomeric product as a ring enlarged compound 80.



However, the carbinol derivatives of 1,3-dithiane 81 can undergo dehydration in the presence of p-toluenesulfonic acid to give ketene thioacetal 82 in 97% yield, as reported by Corey and Seebach.[37,38,66]



81

a. $R=R=CH_3$

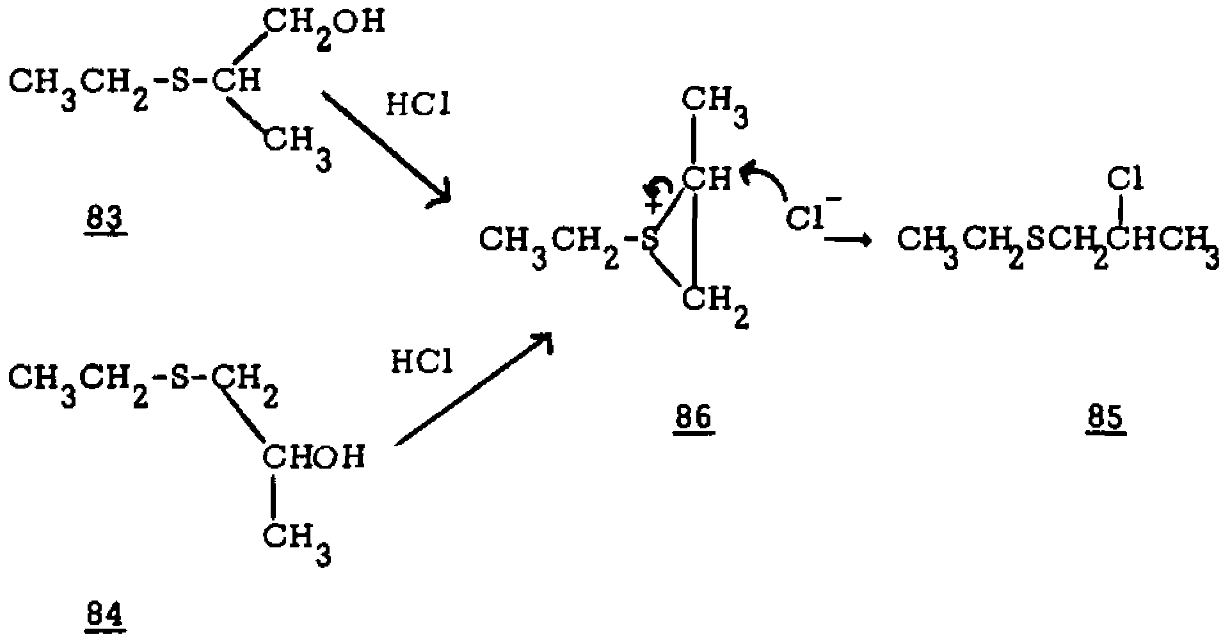
b. $R=R=C_6H_5$

82

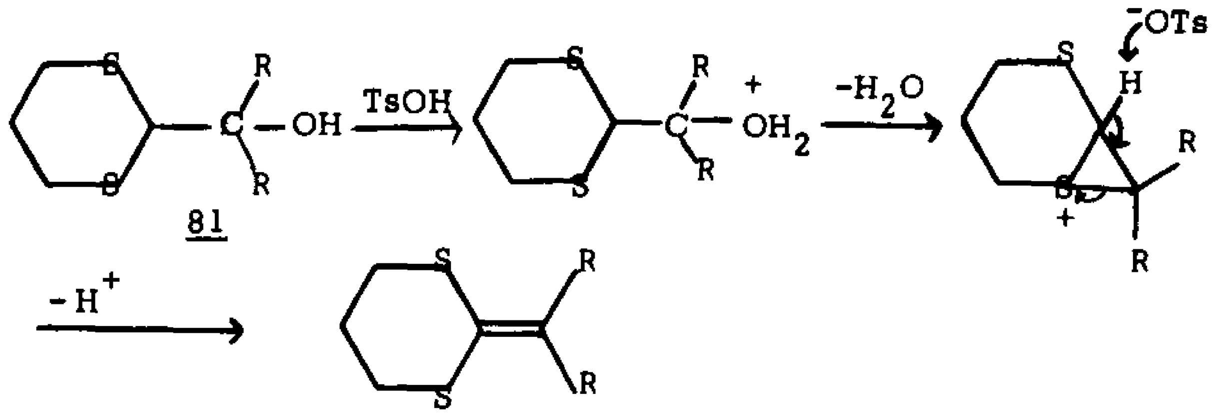
a. $R=R=CH_3$

b. $R=R=C_6H_5$

In the sulfur compounds containing a leaving group β to the sulfur atom, the heteroatom will generally interact with the electron difficient carbon bearing the leaving group to form a cyclic sulfonium ion. Consequently, the reaction rate is accelerated. The evidence for the formation of a cyclic sulfonium ion in a related case is the observation that both 83 and 84 are transformed to the same chloride 85 on treatment with HCl. This is expected if the isomeric starting alcohols are transformed to a common intermediate, the cyclic sulfonium ion 86.[65]

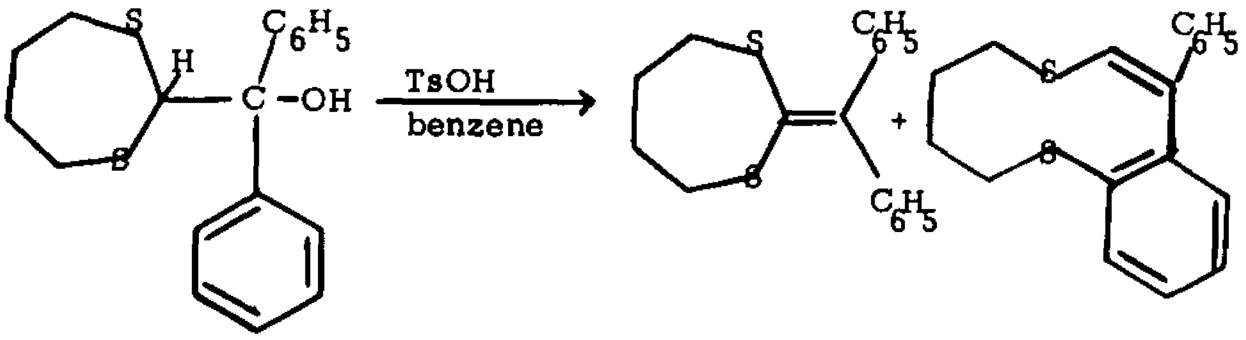


Therefore, the dehydration mechanism in the case of carbinol 81 could be formulated as below:

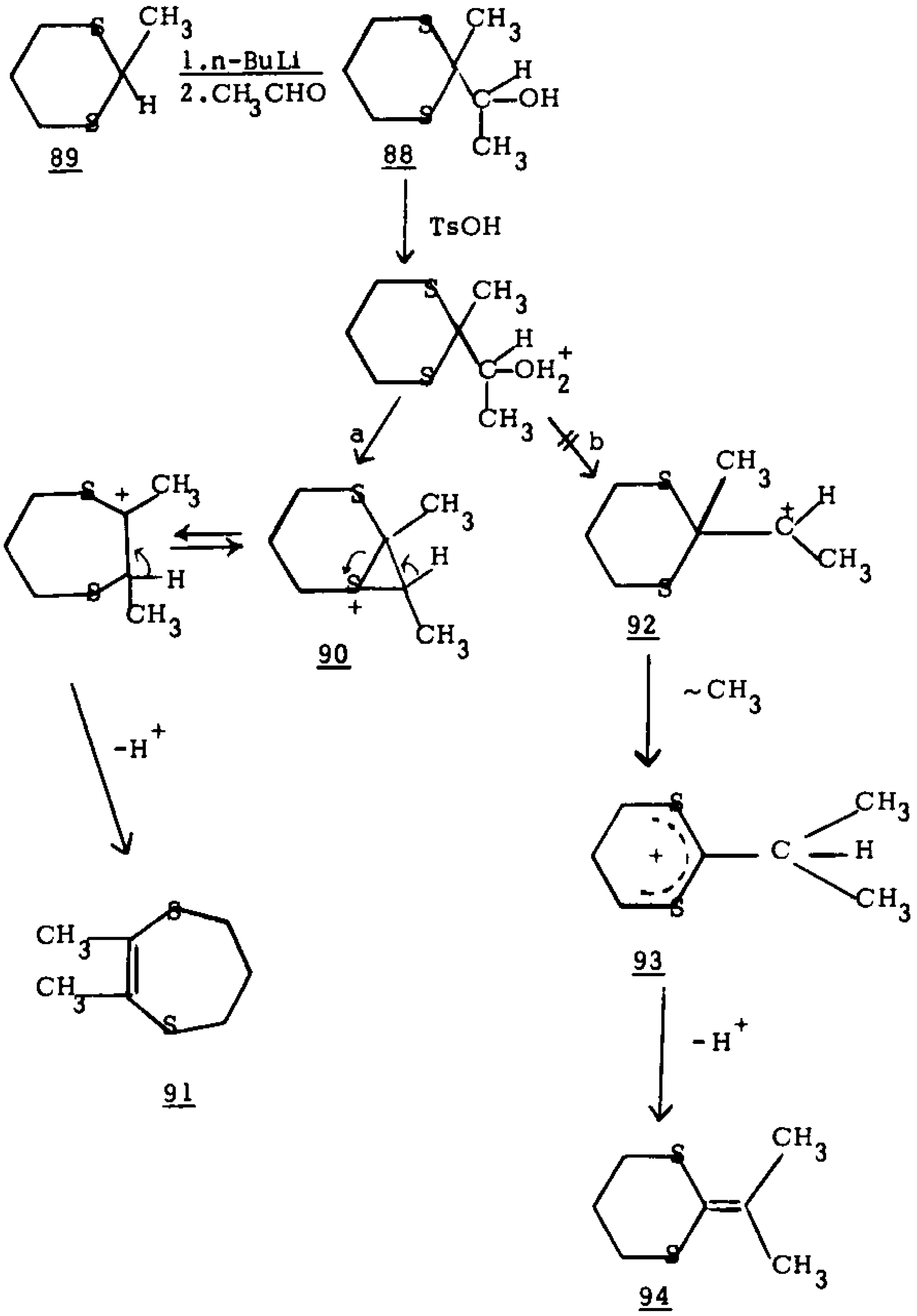


In order to answer whether the ring enlargement of diphenyl 2-(1,3-dithiepinyl) carbinol is a special case, we have investigated some other carbinol derivatives of 1,3-dithiacycles under the same conditions.

Treatment of carbinol 72b in the same way gave two dehydration products. One is ketene thioacetal 73b and the other one is the ring enlarged compound 87 which is proposed based on nmr and mechanistic considerations; nmr ($CDCl_3$, TMS) : δ 1.75 (broad m., 4H), δ 2.68 (center of broad m., 4H), δ 6.57 (s, 1H), δ 7.23 and δ 7.35 (s,s, ca 9H).



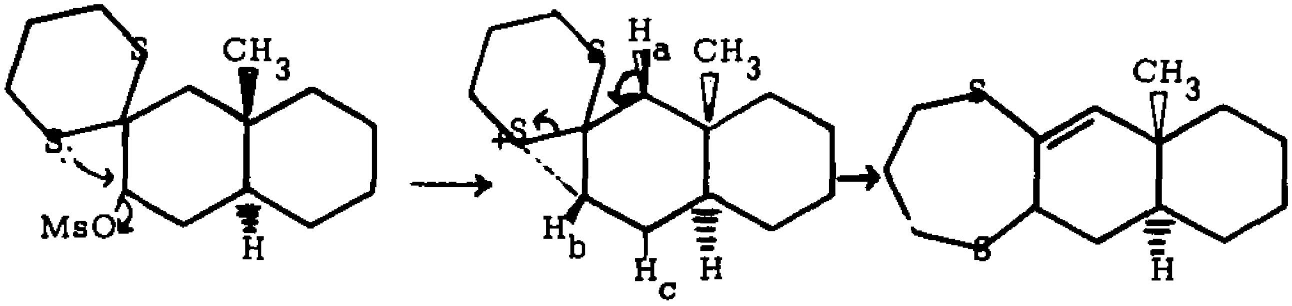
72b 73b 87



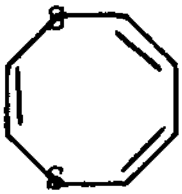
SCHEME IX

In the presence of p-toluenesulfonic acid the carbinol 88 was obtained by treating 2-methyl-1,3-dithiane 89 with n-butyllithium at -70°C followed by quenching with acetaldehyde, then dehydration in a Dean-Stark apparatus, giving, in 70% yield, 2,3-dimethyl-1,4-dithia-2-cycloheptene 90 as a colorless liquid, bp. 52-53°C (0.05 mm). This compound has the identical nmr spectrum with the product of methylation of 2-methyl-1,4-dithia-2-cycloheptene (see part II, page 99); nmr (CCl_4, TMS): δ 3.30 (t, 4H, J's 7 Hz), δ 2.06 (quintet, 2H, J's 7 Hz), δ 1.78 (s, 6H). ir (neat): 1613 cm^{-1} (C=C). Obviously, the dehydration of carbinol 88 proceeds via cyclic sulfonium ion 90 followed by loss of a proton to give exclusively the ring enlarged product 91.

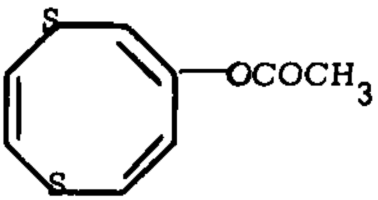
The example of transformation of a 1,3-dithiane derivative to a seven-membered ring has been reported by Marshall and Roebke.[67] The cyclic sulfonium ion was opened by loss of H_a instead of H_b or H_c.



Several attempts have been made to synthesize the interesting 1,4-dithiocin <u>13</u>[20,23,25,69] which is considered to be the best candidate for a 10 π-heteroaromatic sulfur-compound.[20,70] So far only the enolacetate <u>20</u> with the structural element of a fully conjugated 1,4-dithiocin[23] is known.

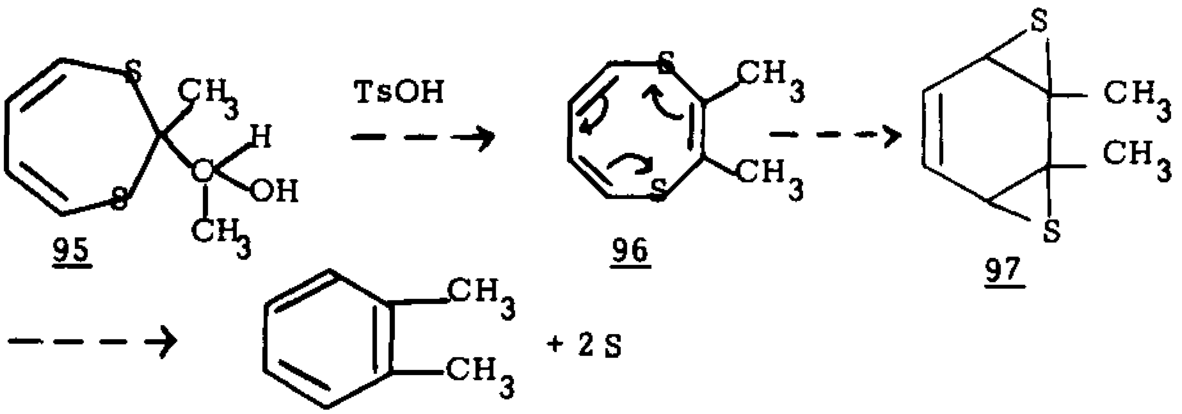


<u>13</u>

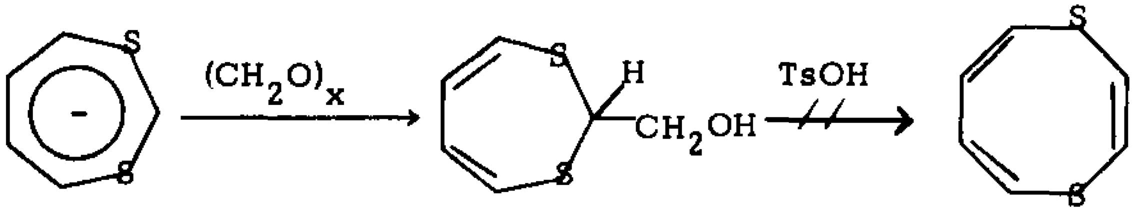


<u>20</u>

In view of our studies on the transformation of dithiane carbinol to ring enlargement product, we proposed a route to the dimethyl derivative of 1,4-dithiocin, <u>96</u>. If 1,4-dithiocin is thermally unstable, as reported by Coffen,[20] Bickelhaupt and Eggelte,[23,24] it would easily be converted into its valence isomer (an internal Diels Alder reaction), bisepisulfide <u>97</u>. Then, if this is followed by desulfurization, o-xylene will be the final product and it should be detectable by gas chromatography.

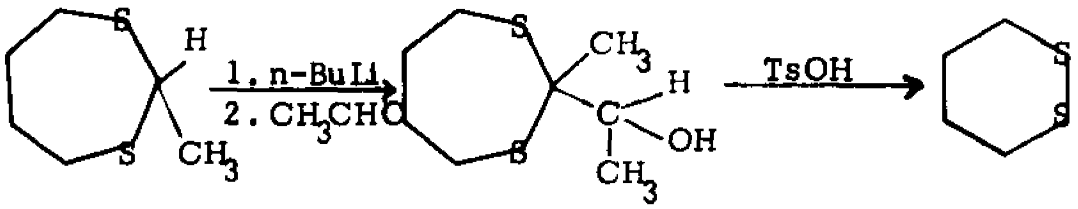


Compound 95 was prepared by treating 2-methyl-1,3-dithia-4,6-cycloheptadiene (53d) with n-butyllithium under nitrogen at -70° C, followed by quenching with acetaldehyde. Compound 95 formed as a yellow oil; bp. 83° (0.05 mm); nmr (CCl_4, TMS): δ 6.20 (broad s, 4H), δ 4.06 (q, 1H), δ 2.72 (broad s, 1H, exchanged with D_2O), δ 1.61 (s, 3H), δ 1.31 (d, 3H). The mixture of compound 95 and a catalytic amount of p-toluenesulfonic acid in benzene was refluxed for 3 hours under nitrogen at 100°, and checked by GC from time to time. Unfortunately, o-xylene was never observed and the material decomposed (a series of spots appeared on tlc plate). The same fate was observed in the case of 2-(1,3-dithiepinyl)methanol 95a, the analogue of compound 95. This was obtained in ca 85% yield through the reaction of 1,3-dithia-4,6-cycloheptadienyl anion 52 with paraformaldehyde under nitrogen at -70° C.

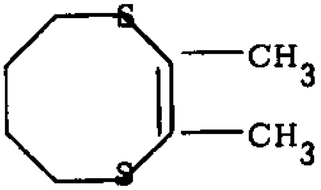


52 95a 13

The dehydration of the saturated carbinol 98 was also investigated under the same condition. The product did not give the expected eight-membered ring compound 99, but instead gave 1,2-dithiane 71 which had identical nmr, ir, R_f value of tlc and retention time on GC with an authentic sample.

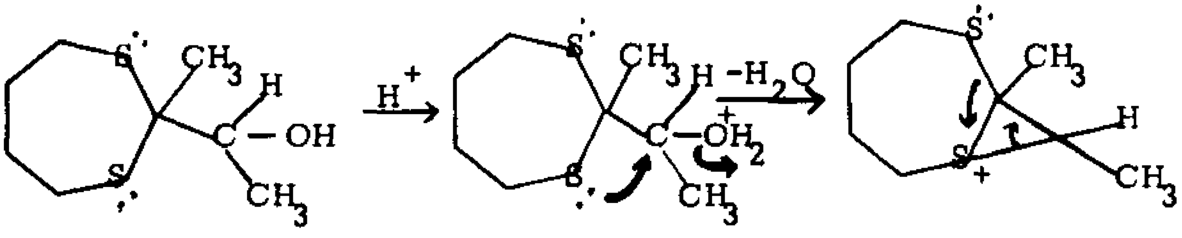


72a 98 71

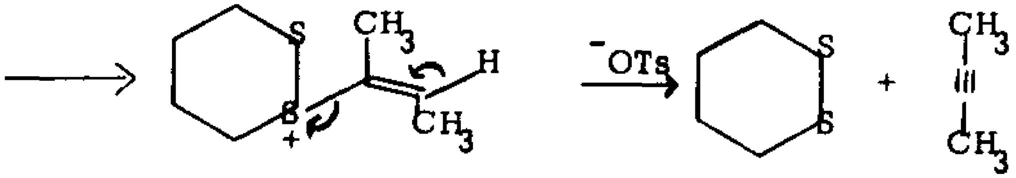


99

A possible mechanism for the dehydration of 98 leading to 71 was proposed as below:

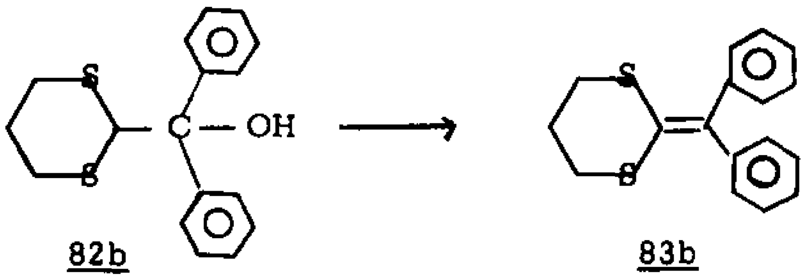


98

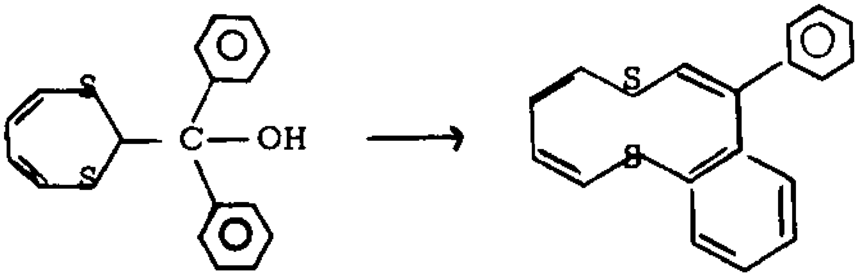


71

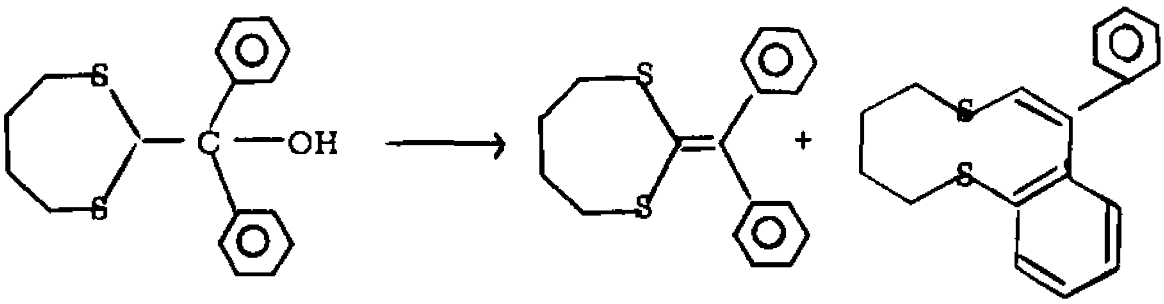
From a review of this study, we can not represent this type of dehydration by a common mechanism. As we see, the six-membered ring of diphenyl carbinol 82b undergoes dehydration to form a ketene thioacetal 83b, while the unsaturated seven-membered ring of diphenyl carbinol 53c undergoes cyclodehydration to give a ring enlarged product 93, and the saturated seven-membered ring of diphenyl carbinol 72b gives both ketene thioacetal 73b and the ring enlarged product 87.



82b 83b

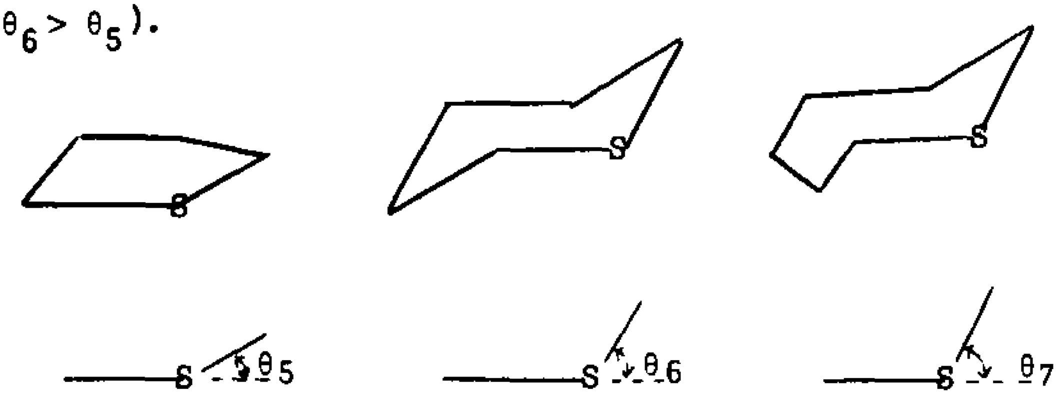


53c 93

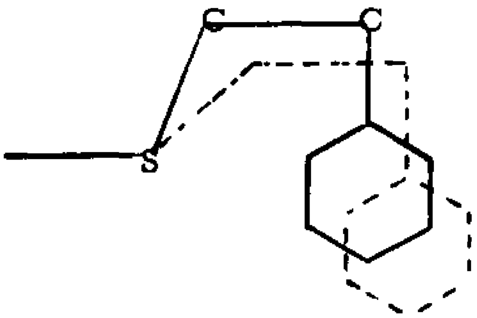


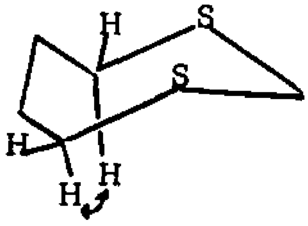
72b 73b 87

A possible reason for these different reaction pathways could be their different geometries. From the molecular models shows that the dihedral angle between C-S and S-C, θ, is getting larger when the size of ring is increasing from five to seven, (i.e., $\theta_7 > \theta_6 > \theta_5$).



Thus, we proposed that the key for understanding these different reactions lies in the distance between sulfur and the benzene ring which is attached on β-C. In the unsaturated seven-membered 1,3-dithia-4,6-cycloheptadiene ring the sulfur is closer to the benzene ring than in the saturated six-membered 1,3-dithian ring, because the molecular shape is much puckered in the seven-membered ring (see the diagram). Therefore, the sulfur attacks the benzene ring more easily in the seven-membered ring (i.e. <u>53c</u> and <u>72b</u>).





The alternative possible reason for the seven-membered ring can undergo ring enlargement is: the saturated seven-membered ring may lose the non-bonded transannular interactions upon ring enlargement, while the unsaturated seven-membered ring may flatten the molecule upon ring expansion.

PART TWO

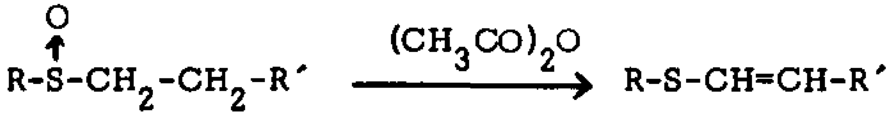
1,4-DITHIA-2,5-CYCLOHEPTADIENE

I. THE SYNTHESIS AND CHARACTERIZATION OF 1,4-DITHIA-2,5 CYCLOHEPTADIENE

1,4-Dithia-2,5-cycloheptadiene 44 has been synthesized by two independent routes: by a Pummerer reaction on 1,4-dithia-2-cycloheptene 102, and by the elimination of HX from the benzenesulfonate(110) of 1,4-dithia-2-cyclohepten-6-ol 103. The details are shown below:

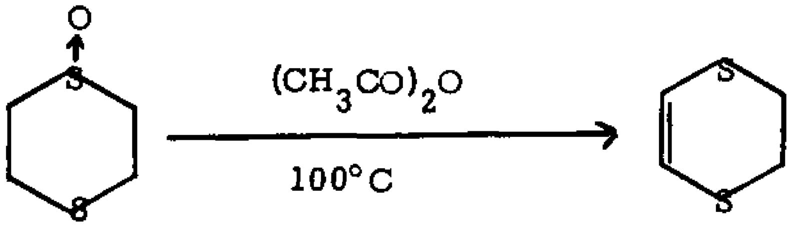
A) Pummerer Reaction

The decomposition of sulfoxides in hot acetic anhydride, a reaction analogous to that originally reported by Pummerer,[71] has been shown to be an attractive preparative route[72] to certain α,β-unsaturated sulfides.

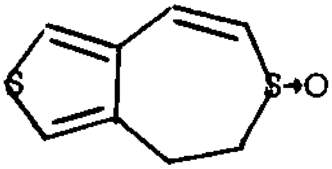


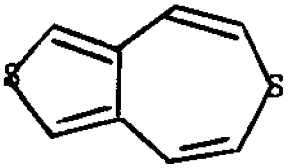
$$R\text{-}\overset{\overset{O}{\uparrow}}{S}\text{-}CH_2\text{-}CH_2\text{-}R' \xrightarrow{(CH_3CO)_2O} R\text{-}S\text{-}CH{=}CH\text{-}R'$$

This reaction could also be extended successfully to heterocyclic compounds containing more than one sulfur atom. In 1963, Parham[73] reported that 1,4-dithiane-1-oxide in acetic anhydride reacted smoothly at steam bath temperature, and 1,4-dithiene was obtained in 53% yield.

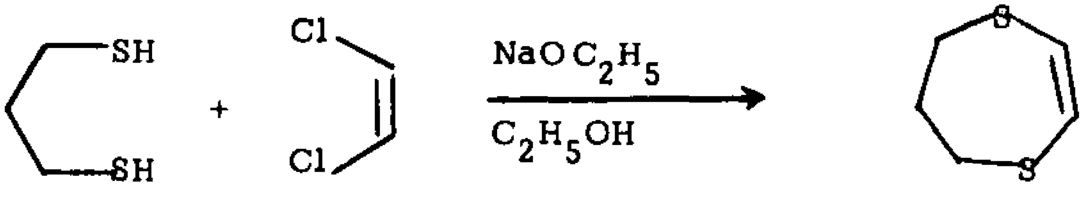


Later on, Schlessinger and Ponticello[74] successfully applied this method to synthesize the heterocyclic thiepin 101 (in 50% yield) by a brief treatment of the corresponding vinyl monosulfoxide 100 with freshly distilled acetic anhydride at 150° C, in the absence of oxygen. Therefore, one might be able to employ this reaction for the preparation of compound 44 from the corresponding mono-olefin 102.


100

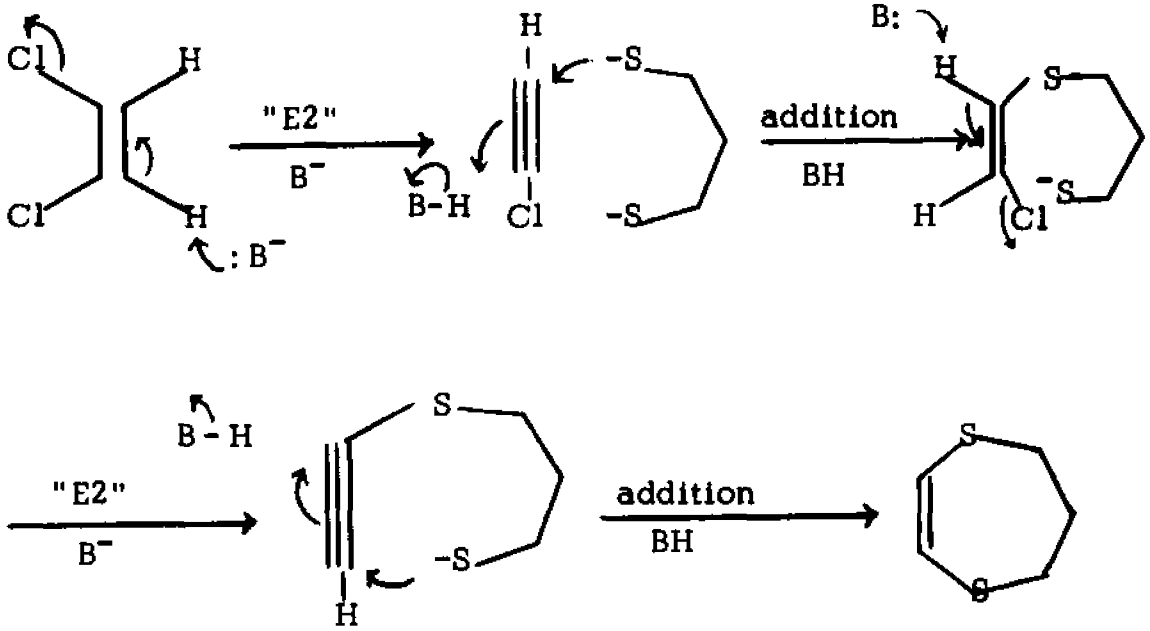

101

1,4-Dithia-2-cycloheptene 102 was obtained in 48% yield by treating 1,3-propanedithiol with base, followed by cycloalkylation with cis-dichloroethylene.



102

The mechanism of the base-catalyzed reaction of cis-dichloroethylene with thiols has been shown to proceed via the "elimination-addition" mechanism[75] shown below:



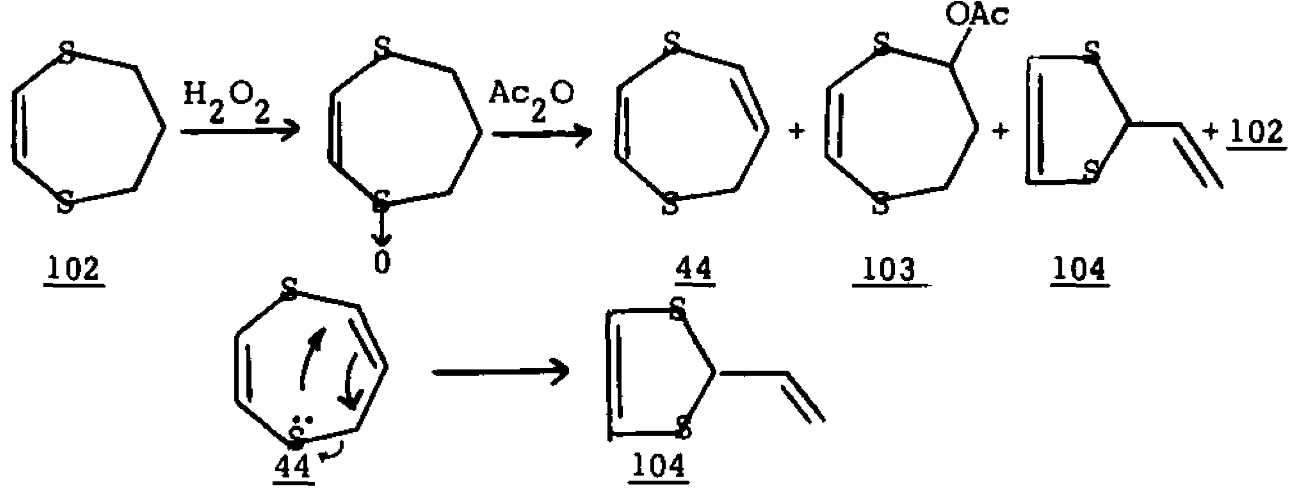
102

Compound 102 formed as a colorless oil, bp. 91-93° (15 mm), and its structure was characterized by nmr, ir, UV and mass spectrum: nmr ($CDCl_3$, TMS): δ 2.17 (quintet, 2H), δ 3.50 (t, 4H), δ 5.95 (s, 2H); ir (neat): 3018 cm^{-1}, 1530 cm^{-1}; UV: 294 nm (shoulder, ϵ4326), λ_{max}^{EtOH} 287 nm (ϵ=4805), 235 nm (shoulder, ϵ1473) mass spectrum: M^+ at m/e 132, and m/e at 103, 99, 73, 45, ... etc.

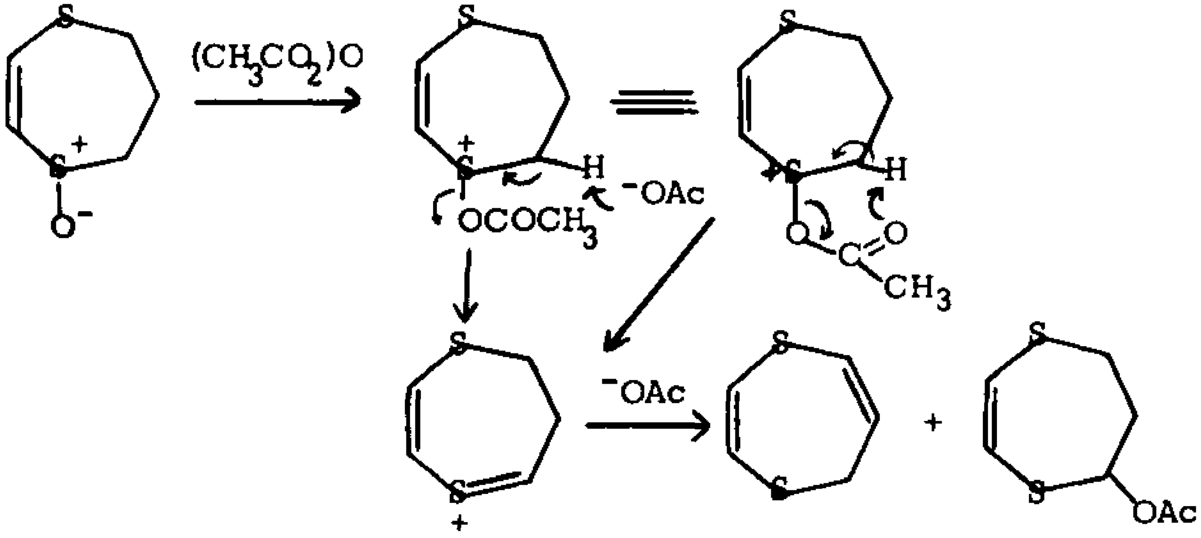
Compound 102 was oxidized with 1 equivalent of 30% hydrogen peroxide at 0° C in acetic acid or m-chloro-perbenzoic acid in chloroform at 0° C. Without isolation of the sulfoxide, the dark residue remaining after removal of solvent was dissolved in acetic anhydride and refluxed under nitrogen for 3 hours. After work-up, the residue was distilled in vacuo to give a constant boiling mixture (ca

55% yield) containing the desired diene 44 (relative yield 65%, based on GC analysis), the starting material 102 (relative yield 22%) and a by-product (relative yield 12%) for which as the structure of a vinyl-1, 3-dithiol 104 was proposed. In addition, 5-acetoxy-1,4-dithia-2-cycloheptene 103 was formed in ca 45-50% yield.

Compound 104 was formed probably as the result of a thermal rearrangement of the diene 44 .



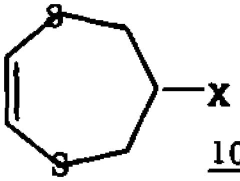
The mechanism of the Pummerer reaction is still not clear,[73] but one could propose a mechanism as indicated below:



B) Elimination of Benzenesulfonate

The Pummerer reaction always gave compound 44 contaminated by the starting mono-olefin 102. We found that the polarities and the boiling points of diene 44 and mono-olefin 102 were too close to allow purification by chromatography and fractional distillation. Hence, we decided to try another approach leading to compound 44.

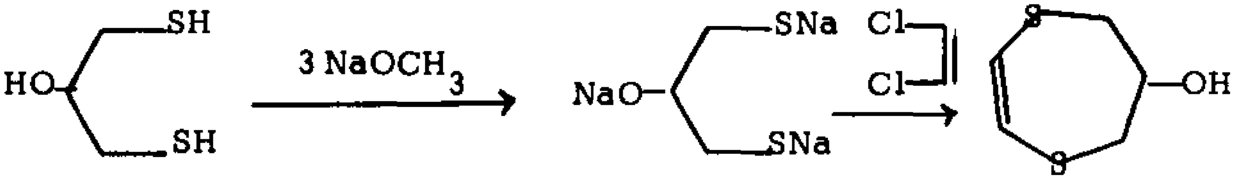
A compound of structure 105 having good leaving group such as bromine or toluenesulfonyl group on the 6 position should, after elimination with base, yield the desired diene 44 and the model 105 should exist with a difference both in polarity and boiling point suitable for later separation.



105

X = Br or OTs

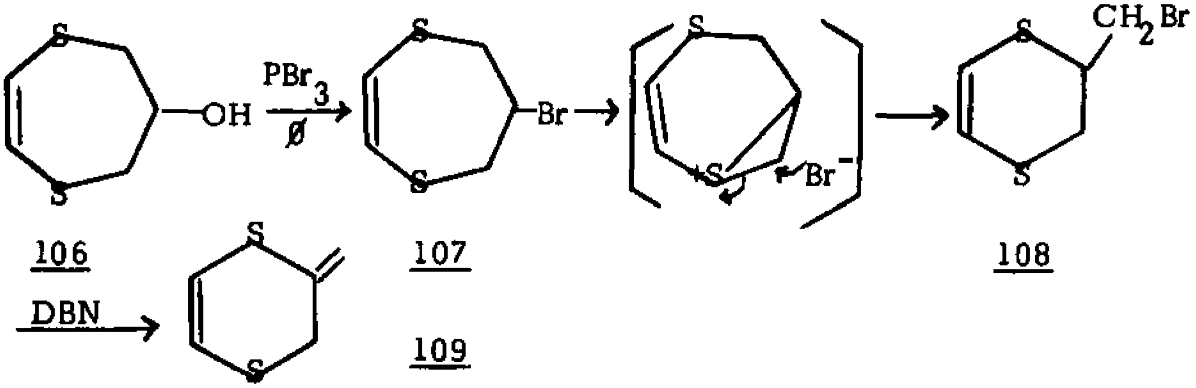
1,4-Dithia-2-cycloheptene-6-ol 106, the precursor of the model 105, has been synthesized by a manner similar to that used for the synthesis of compound 102, as shown below:



106

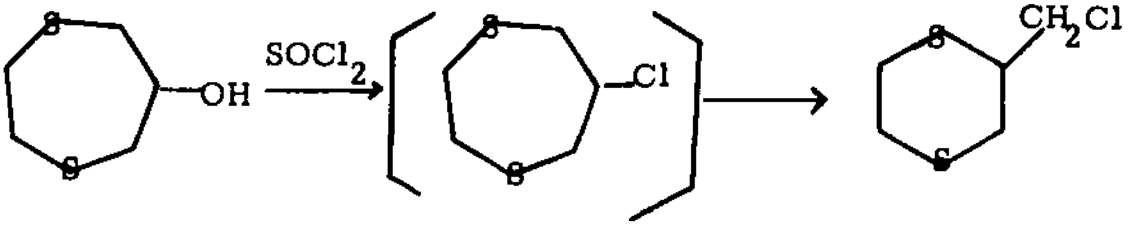
Alcohol 106 formed as a white needle crystal, mp. 53-54°C after recrystallization from benzene-pet. ether. Its ^{1}H nmr spectrum consists of a singlet at δ 3.06 (1H), a multiplet at δ 3.35-δ 3.51 (5H) and a singlet at δ 6.03 (2H); the ^{13}C nmr spectrum consists of three signals at 121 ppm, 69.5 ppm and 38.4 ppm.

Treatment of alcohol 106 with PBr_3 in dry benzene or in pyridine did not give the corresponding bromide 107, but gave a ring contracted isomer, 6-bromomethyl-1,4-dithia-2-cyclohexene 108. The same ring contraction giving 6-chloromethyl-1,4-dithia-2-cyclohexene was observed when the alcohol 106 was treated with toluenesulfonyl chloride in pyridine.



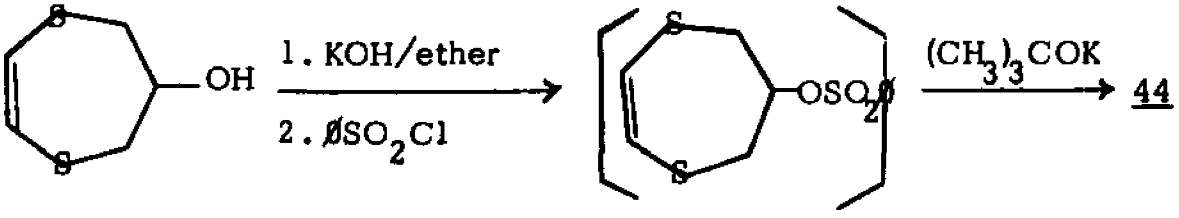
106 107 108 109

As reported by Fuson,[76] this ring contraction by rearrangement of a β-halogeno-sulfide was also observed during the reaction 6-hydroxy-1,4-dithiacycloheptane 110 with thionyl chloride,



The bromide 108 was further treated with 1,5-diazabicyclo[4,3,0]non-5-ene (DBN) to yield the exocyclic olefin 109.

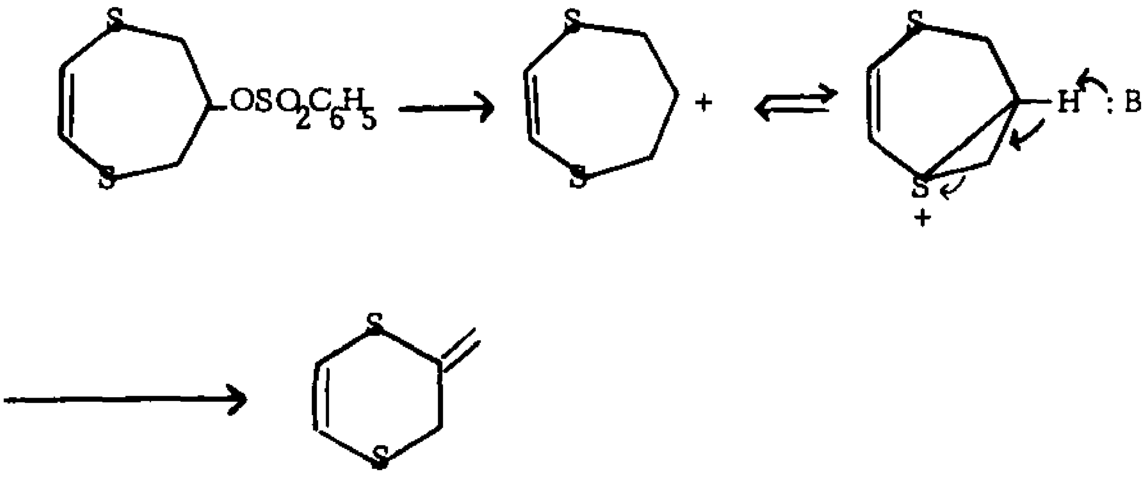
However, the corresponding benzenesulfonate 111 can be successfully obtained, without ring contraction, by treating the alcohol 106 with powdered potassium hydroxide in dry ether followed by addition of benzenesulfonyl chloride. Without isolation of the unstable benzenesulfonate 111, treatment with a suspension of potassium t-butoxide gave an excellent yield (85%) of the desired diene 44 (purity: 84% - 98%).



106

111

A trace of compound 109 (0-10%, based on G.C. analysis) was observed in this reaction (having an identical retention time on GC with the compound obtained from the reaction of 108 with DBN) and its amount in reaction products seems dependent on the amount of water in the reaction system. If the system is drier, the amount of compound 109 is less. Probably the carbonium ion or the form stabilized by lone pair electrons on sulfur could be stabilized by water (polar solvent), and therefore favor the formation of 109. (SN 1/E1 conditions.)



109

1,4-Dithia-2,5-cycloheptadiene 44 formed as yellow oil, bp. 31° (0.12 mm) and its structure was characterized by ^{1}H nmr, ^{13}C nmr, ir, UV and mass spectrum.

^{1}H nmr (60 M Hz, CDCl$_3$, TMS): δ 3.70 (d,2H), δ 5.80-δ 6.75 (m,4H).

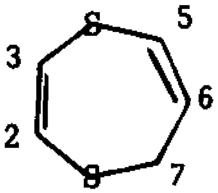
^{13}C nmr (CDCl$_3$, TMS): 135.3 ppm, 125.1 ppm, 123.2 ppm, 117.8 ppm and 33.1 ppm.

ir (CDCl$_3$): 3020 cm^{-1}, 2960 cm^{-1}, 2920 cm^{-1}, 1608 cm^{-1} .

UV: λ = 310 nm (shoulder, ε = 1393), λ_{max}^{EtOH} 285 nm (ε = 3366), λ_{max}^{EtOH} = 240 nm (ε = 2089).

mass spectrum: M$^+$ at m/e 130 (60%), m/e at 129 (M$^+$ - 1, 32%), at 103 (, 100%), at 97 (, 39%)... etc. (a proposed mechanism is discussed on page 113).

The multiplet between δ 5.80 - δ 6.75 was split in the 220 MHz spectrum, the coupling constant and the peak assignment are outlined as below:



δ 5.83 (d,d; H_3, $J_{2,3}$ = 10.2 Hz; $J_{3,5}$ = 1.74 Hz)

δ 6.03 (d,d ; H_5, $J_{5,6}$ = 9.2 Hz; $J_{3,5}$ = 1.74 Hz)

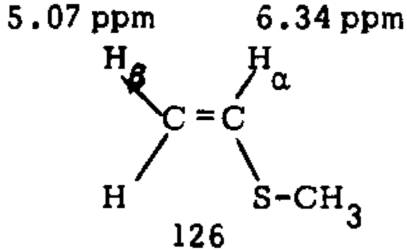
δ 6.29 (d, H_2; $J_{2,3}$ = 10.2 Hz)

δ 6.47 (center of t,d ; H_6, $J_{5,6}$ = 9.2 Hz ; $J_{6,7}$ = 7 Hz)

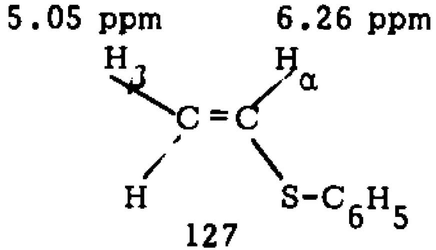
The observation of a W-coupling between H_3 and H_5 with a J = 1.74 Hz suggests the molecule is a half-chair conformation: the two sulfur atoms are coplanar with the four olefinic carbon atoms, whereas the sp^3-hybridized C_7 is out of the plane of the molecule. This W-type coupling was found to be very useful for the later structure determination of the products of alkylation of diene 44.

Both the ^1H and ^{13}C nmr spectra of 1,4-dithia-2,5-cycloheptadiene showed a strange chemical shift reversal of the usual sequence at positions 5 and 6.

In vinyl sulfides, normally, protons α to sulfur have a lower chemical shift than that of protons β to sulfur. For instance, methylmercaptoethene 126[84] and phenylmercaptoethene 127[85] the chemical shifts of the H_α are lower than those of H_β, as shown in the diagram below:



126

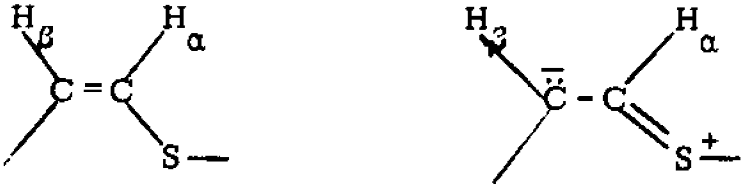


127

The shielding effects on the α and β-protons are the net result of two opposing effects, the inductive effect of the S-atom which causes a polarization of the π-electrons as shown below:

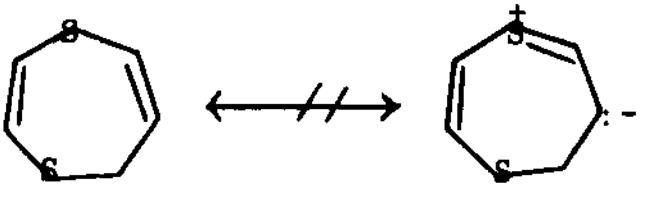
$\delta H_\alpha < \delta H_\beta$

and the resonance effect, represented in the resonance structures below which symbolize qualitatively a stabilization of the vinyl sulfide unit:



$\delta H_\alpha > \delta H_\beta$

Based upon this argument, one could say that the resonance of sulfur electron pairs with carbon π-electrons does not appear to be as significant in 1,4-dithia-2,5-cycloheptadiene, as it is in 126 or 127.



At this moment no satisfactory explanation is available. Further studies are under way in this laboratory.

II. BEHAVIOR OF 1,4-DITHIA-2,5-CYCLOHEPTADIENE TOWARDS n-BUTYLLITHIUM IN TETRAHYDROFURAN

Treatment of 1,4-dithia-2,5-cycloheptadiene 44 with n-butyllithium in tetrahydrofuran under nitrogen at -70° C produced a deep red solution from which after hydrolysis the starting material was obtained. The color of the red solution changed at ca. -15° C to brown-green and a muddy-like precipitate appeared. Again hydrolysis gave the starting material back in almost quantitative recovery.

The resulting red anion solution was stirred at 0° C for 10 minutes, then was quenched with chlorotrimethylsilane at -70° C. After work-up the reaction products contained 66% of an unexpected compound which formed as a yellow-golden oil, bp. 55° (0.12 mm) and 34% of the starting material 44 (based on GC analysis).

Based upon ^1H nmr (60 MHz and 220 MHz), ^{13}C nmr, ir, and mass spectrum, we assigned the structure of the ring opened acetylene 112 for this unexpected product.

ir (neat): 3077 cm^{-1} (C=C), 2941 cm^{-1} (alkane), 2577 cm^{-1} (S-H), 2128 cm^{-1} (C≡C) and 1613 cm^{-1} (C=C).

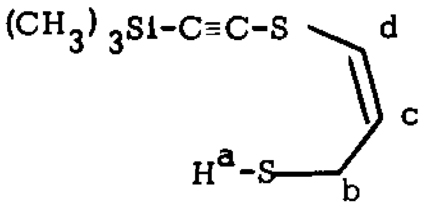
^1H nmr (60 MHz, $CDCl_3$, TMS): δ 0.20 (s, 9H), δ 1.72 (t, 1H), δ 3.39 (broad t, 2H) and δ 5.98-δ 6.54 (m, 2H).

^{1}H nmr (220 MHz, CCl_4, no TMS):

δ 1.22 (t, H_a, $J_{a,b}$ = 7.8 Hz)
δ 2.97 (d, t, 2H_b, $J_{b,c}$ = 7.8 Hz, $J_{b,d}$ = 1 Hz)
δ 5.61-5.75 (m, H_c, $J_{c,d}$ = 9 Hz, $J_{c,b}$ = 7.8 Hz)
δ 5.81 (d, t, H_d, $J_{c,d}$ = 9 Hz, $J_{b,d}$ = 1 Hz)

^{13}C nmr: 0.2 ppm ($-Si(CH_3)_3$), 22.4 ppm ($-CH_2-SH$), 91.3 ppm and 101.9 ppm (acetylene), 123.5 ppm and 131.5 ppm (olefin).

mass spectrum: M^+ at m/e 202 (10.3%), m/e 169 (M^+-SH, 7.3%) 115 (55.6%), 97 (100%), 83 ($SiMe_3$, 8.8%).



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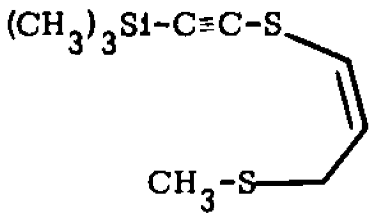
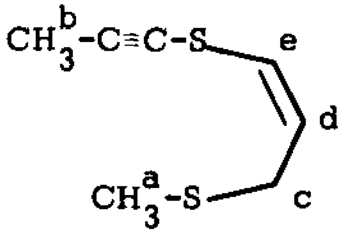


113

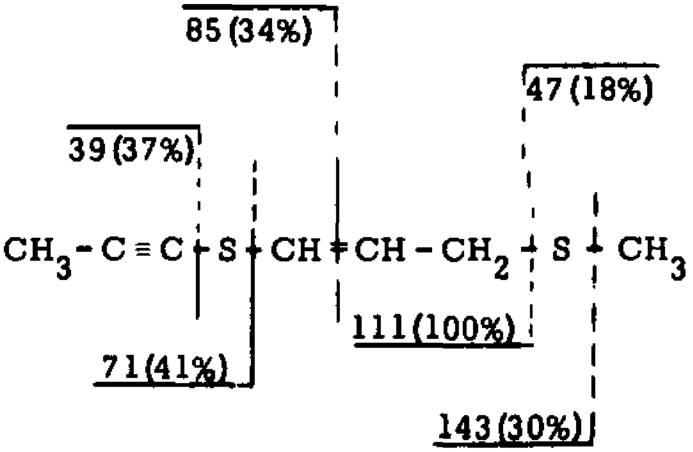
Upon treatment with n-butyllithium in tetrahydrofuran followed by methyl iodide, the S-H function of compound 112 could be methylated to give the corresponding S-CH_3 compound 113, nmr ($CDCl_3$, TMS): δ 0.18 (s, 9H), δ 2.08 (s, 3H), δ 3.19 (d, 2H) and δ 5.58-δ 6.33 (m, 2H).

The same procedure was employed, trapping the resulting anion solution generated from 44 with methyl iodide to give dimethyl compound 114. It formed as a red oil, bp. 51° (0.04 mn) and was characterized by ir, nmr and mass spectrum; ir (neat): 3077 cm^{-1} (alkene), 2941 cm^{-1} (alkane), 2128 cm^{-1} (C≡C, very weak) and 1613 cm^{-1} (C=C). nmr (100 MHz, $CDCl_3$, TMS): δ 1.92 (s,3H,$-CH_3^b$), δ 2.03 (s,3H,$-CH_3^a$), δ 3.13 (d,2H,H_c,J's 8Hz), δ 5.67 (d,t,1H,H_d, J's 8Hz and 9Hz) and δ 6.17 (d,1H,H_e, J's 9Hz). This spectrum compares well with that of its analogous, 1,3-bis(methylthio)-propene, as reported by E.J. Corey.[78]

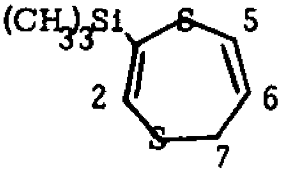
mass spectrum: M^+ at m/e 158 (27%) and the other important fragmentations are outlined as below (m/e, %).



114



Treatment of the original red solution produced from 44 and n-butyllithium in tetrahydrofuran at -70° C, and kept for 20 minutes at -40° C, with trimethylsilyl chloride gave a different trimethylsilyl compound for which we assign the structure 115a: The ir spectrum did not show any S-H or triple bond adsorbtion.



115a

δ 0.15 ppm (s, 9H, $Si(CH_3)_3$)

δ 3.75 ppm (d, 2H, H_7, $J_{6,7}$ = 7 Hz.)

δ 6.00 ppm (d, 1H, H_5, $J_{5,6}$ = 9 Hz.)

δ 6.4 ppm (s, 1H, H_2)

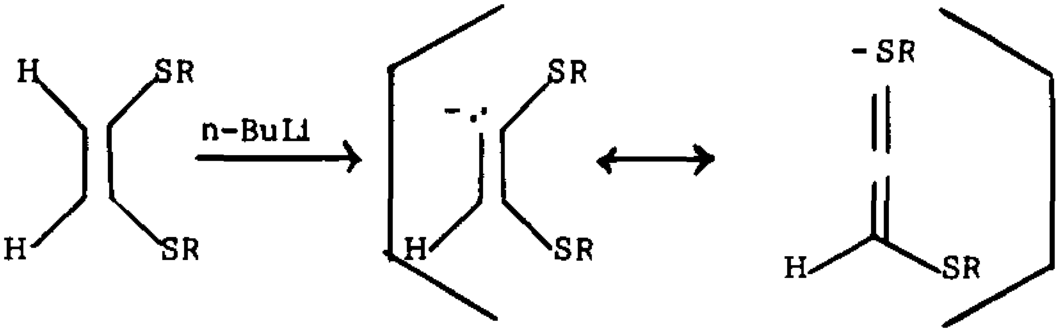
δ 6.45 ppm (center of d.t., 1H, H_6, $J_{5,6}$=9H
$J_{5,6}$ = 9 Hz, $J_{6,7}$ = 7 Hz)

The absence of any W-type long range coupling strongly suggests the position 3 as the site of trimethylsilyl group. In the same way, the reaction of anion of 44 at -40° C with methyl iodide, benzophenone and D_2O gave 3-methyl-1,4-dithia-2,5-cycloheptadiene 115b, diphenyl 3-(1,4-dithiepinyl) carbinol 115c and 3-deutero-1,4-dithia-2,5-cycloheptadiene 115d, respectively. Their nmr spectra are summarized in Table XIII.

Compound	δH_2(s)	δH_5(d)	δH_6(d,t)	δH_7(d)	δR
115a, $R=SiMe_3$	6.40	6.0	6.45	3.75	0.15 (s)
115b, $R=CH_3$	6.10	5.84	6.26	3.51	1.94 (d)
115c, $R=\underset{\displaystyle OH}{C}(C_6H_5)_2$	5.81	6.11	6.52	3.83	3.52 (s) 7.33 (m)
115d, R=D	6.29	6.03	6.47	3.75	---

Table XIII: The NMR Chemical Shifts of 3-Substituted,-,4-dithia-2,5-cycloheptadienes.

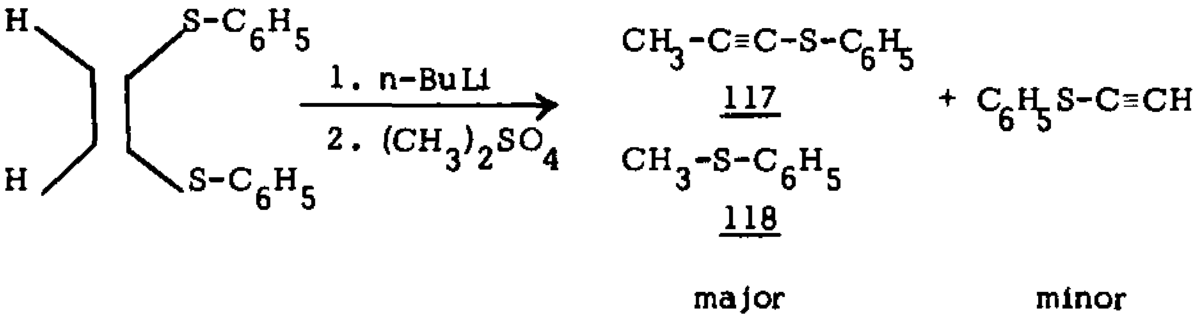
Parham and coworkers[79,80] have reported that open chain unsaturated and saturated thioethers are rapidly cleaved to substituted mercaptoacetylenes and mercaptoethenes respectively and stated that the reactions can be best explained with a β-elimination mechanism.



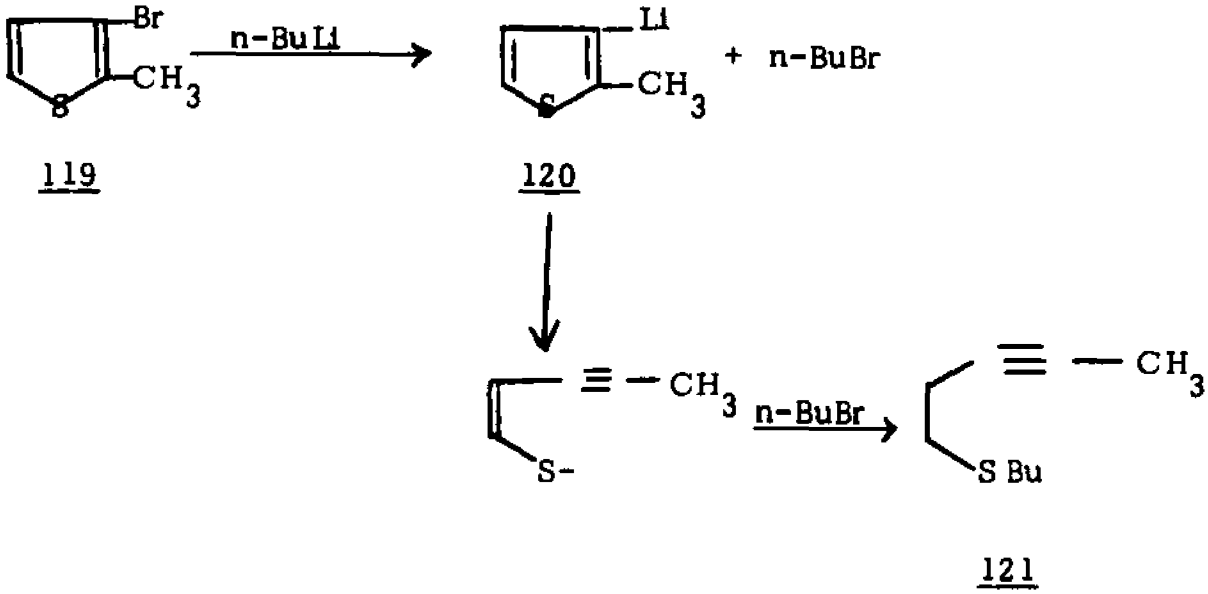
$$\longrightarrow \quad R\text{-}S\text{-}C{\equiv}C\text{-}H + RSLi$$

$$C_6H_5\text{-}S\text{-}CH_2CH_2\text{-}S\text{-}C_6H_5 \xrightarrow{\phi\text{-}Li} C_6H_5S\text{-}CH{=}CH_2 + C_6H_5SLi$$

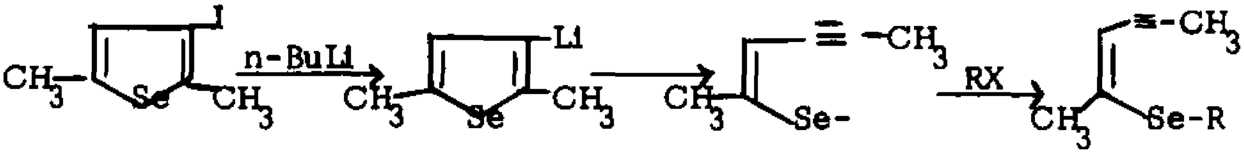
The author also reported that if the above reaction mixture was worked up with an alkylating reagent, the alkylated acetylene was isolated. Thus treatment of cis-bis(phenylmercapto)-ethene with n-butyllithium and dimethylsulfate mainly gave methylacetylene sulfide 117 and methyl-phenyl sulfide 118.



Jakobsen[81] has reported that reaction of thiophene derivative 119 with n-butyllithium in ether afforded the corresponding thienyllithium compound 120 which, on warming to room temperature, the ring opened to form product 121 which was isolated in 95% yield.

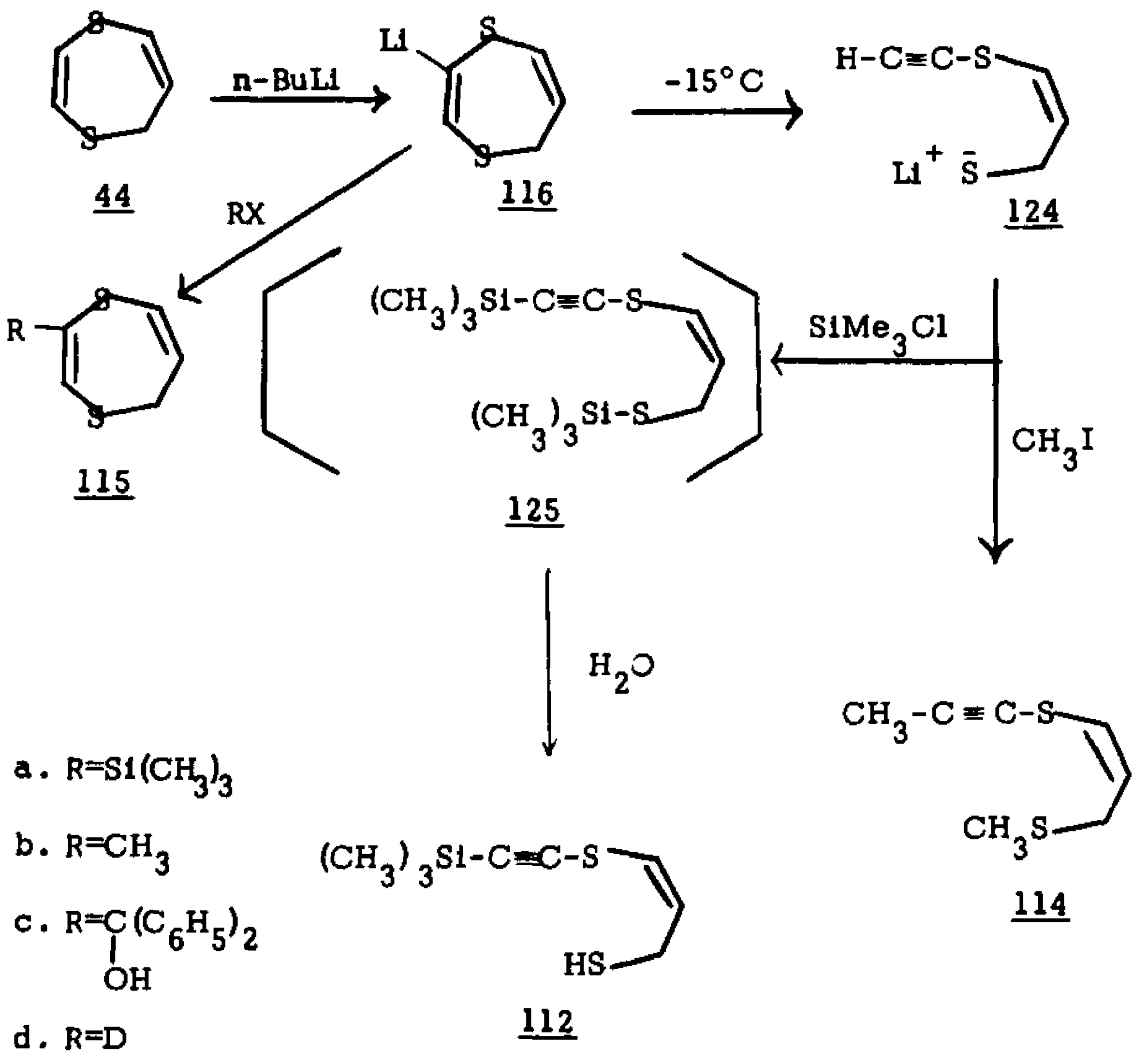


About the same time, Gronowitz[82] who also observed the ring-opening of a selenienyllithium compound. 2,5-Dimethyl-3-selenienyl iodide 122 reacted with ethyllithium in ether at -70°C to produce the corresponding lithio derivative which rapidly ring-opened. After quenching the solution with alkylating reagent, the alkylated product 123 was obtained in 85% yield.



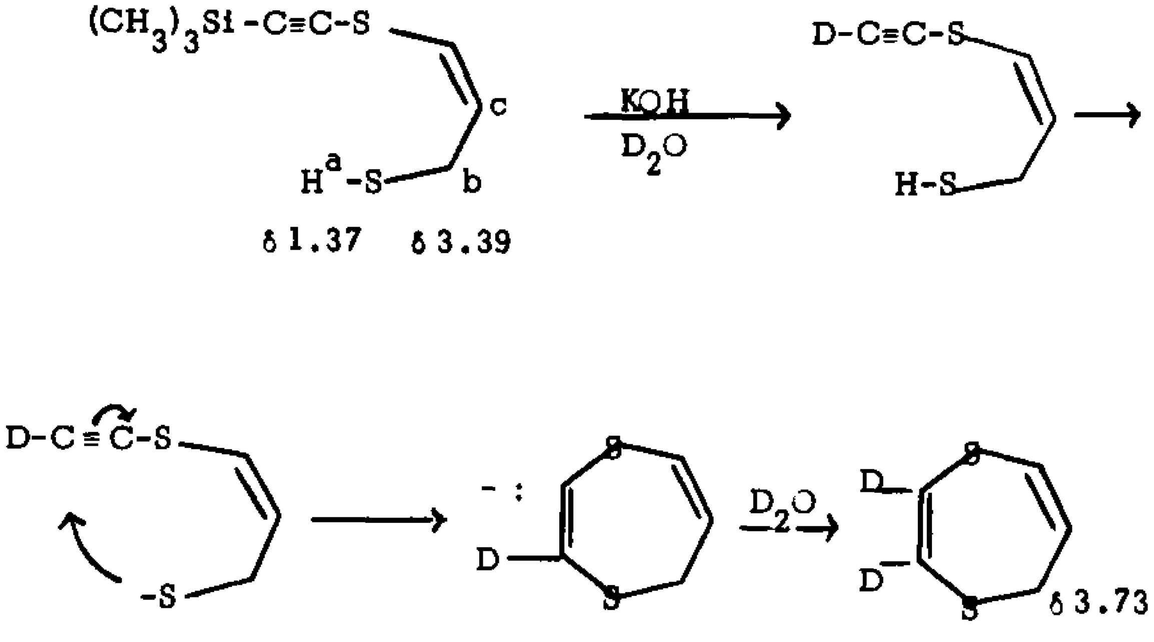
122 123

Our results can therefore be best explained as follows: 1,4-dithia-2,5-cycloheptadiene reacted with n-butyllithium at -70°C to afford 3-lithio-derivative 116 which was ring-opened to form 124 at ca. -15°C, followed by reaction with methyl iodide or trimethylsilyl chloride to give di-methyl product 114 (this is in good agreement with the works reported by Parham) or (the unisolated) ditrimethylsilyl compound 125. The S-trimethylsilyl function of 125 was readily broken under neutral hydrolytic condition associated with the subsequent workup procedure[83] and consequently the monotrimethylsilyl compound 112 was actually obtained. The summarized are shown in Scheme X, on the following page.



SCHEME X

The results obtained in an attempt to deuterate the S-H bond of 112 with D_2O in the presence of basic catalyst were very interesting. We observed, in the nmr tube, the fast H/D exchange followed by desilylation (with singlet of $SiMe_3$ split) and ring reclosure. The triplet of H_b at δ 3.39 in compound 112 broadened and disappeared, and a new doublet at δ 3.73, attributed to H_7 of compound 44, appeared and increased. After 8 minutes, 44-d_2 was obtained in essentially quantitative yield, as shown in Scheme XI.

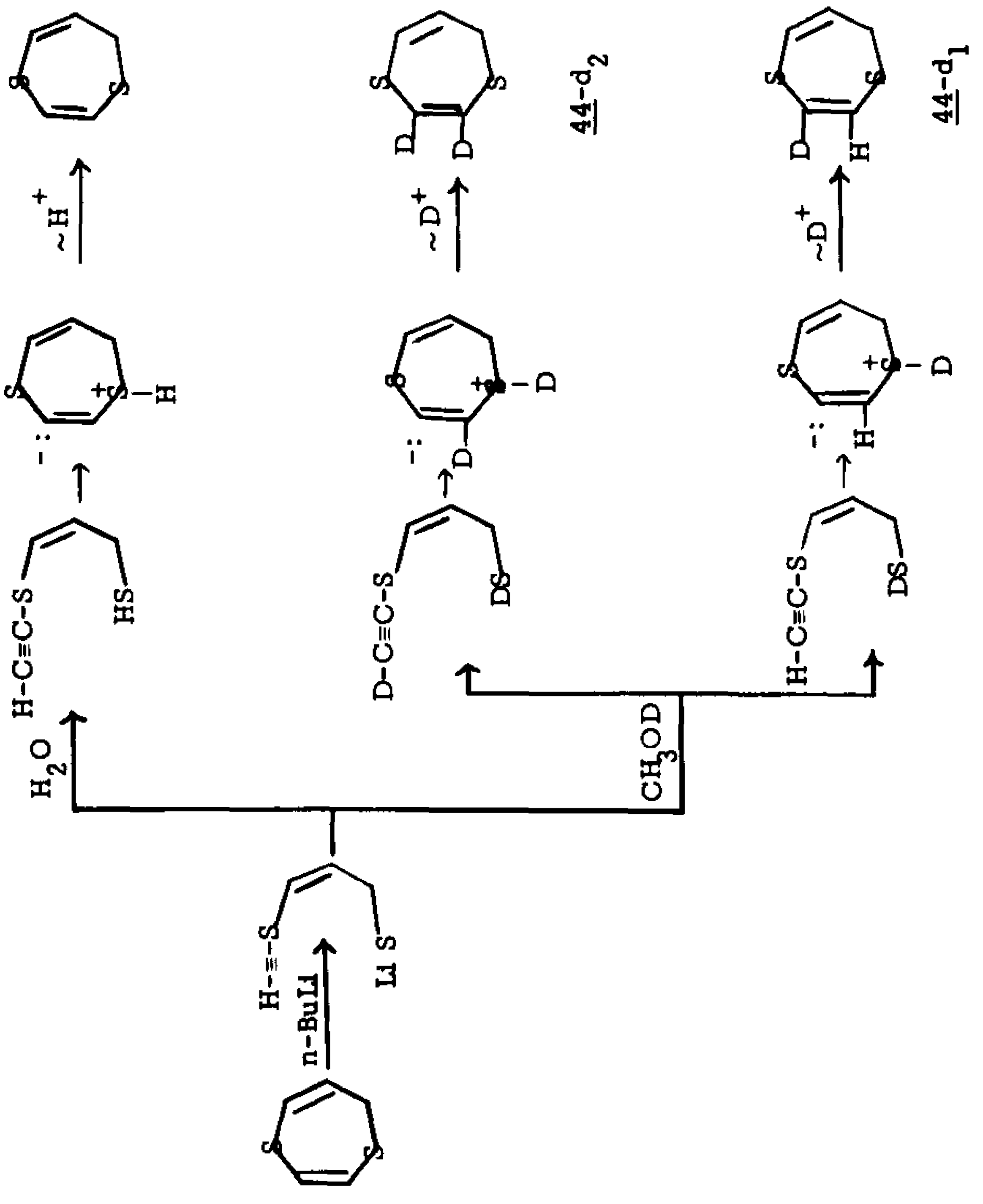


44-d$_2$

SCHEME XI

Compound 44-d$_2$ was characterized by ^1H and ^{13}C nmr, ir and mass spectrum; ir (CCl_4): 3058 cm^{-1} (alkane), 2890 cm^{-1} (C-D) and 1618 cm^{-1} (C=C); ^1H nmr (CCl_4, TMS): δ 3.73 (d,2H) δ 6.07 (d, H_5, $J_{5,6}$ = 10Hz), δ 6.50 (t,d, H_6, $J_{5,6}$ = 9 Hz); ^{13}C nmr ($CDCl_3$, TMS): δ 135.7 (100%, C_6), δ 125.6 (24%, C_2-D) 123.8 (77%, C_5) δ 118.4 (24%, C_3-D) and δ 33.4 (94%, C_7); mass spectrum: M^+ at m/e 132 (60%), 131 (M^+-1, 31.6%), 105 (, 100%) and 99 (38.8%,) ... etc. (the mechanism see page 113).

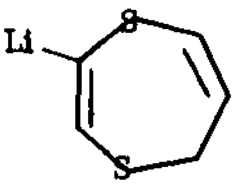
The same sequence has been observed in the case of treatment of diene 44 with n-butyllithium at -70°C and quenched with water or methanol-OD. With the former, starting material 44 was recovered and with the latter, an nmr spectrum with peaks at δ 3.75 (d), 1 H (or 4H) and δ 6.08-δ 6.73 (m), 1.25 H (or 5H) was observed, consistent with a mixture containing 44-d_1 and 44-d_2. The mechanism is proposed as shown in Scheme XII.



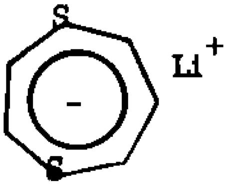
SCHEME XII

III. THE BEHAVIOR OF 1,4-DITHIA-2-CYCLOHEPTENE AND 1,4-DITHIACYCLOHEXADIENE TOWARDS N-BUTYLLITHIUM IN TETRAHYDROFURAN.

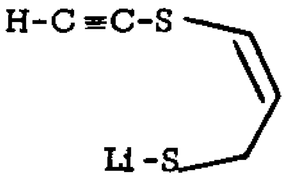
The reaction of 1,4-dithia-2,5-cycloheptadiene 44 with n-butyllithium in tetrahydrofuran at -70°C did not give the expected potentially aromatic 10π anion 25. Instead, vinylic metallation of 44 to form 116 followed by ring-opening at -15°C to give the S-lithium salt 124 was observed.



116



25

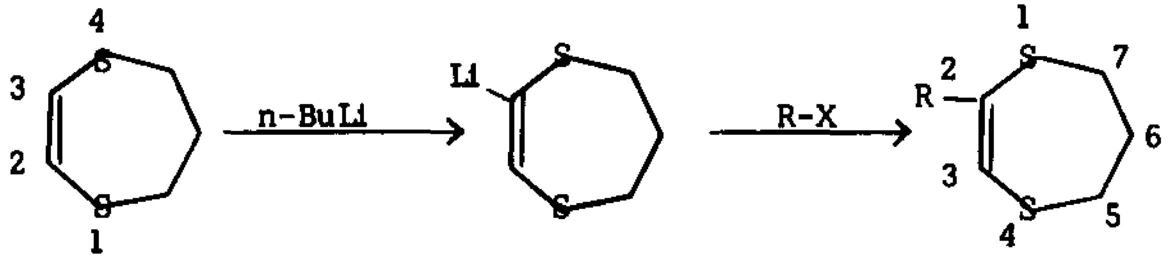


124

For a more detailed study of this vinylic metallation, we therefore investigated the behavior of 1,4-dithia-2-cycloheptene 102 and 1,4-dithiacyclohexadiene 133, close analogues of the diene 44, toward lithiation with n-BuLi in tetrahydrofuran.

A) 1,4-Dithia-2-cycloheptene.

Compound 102 was treated with n-butyllithium in tetrahydrofuran under nitrogen at -70°C to afford the lithioderivative 126 which has been fully characterized through its reactions with trimethylsilyl chloride, benzophenone, methyl iodide and D_2O to give 2-trimethylsilyl-1,4-dithia-2-cycloheptene 127a, diphenyl carbinol 127b, 2-methyl-1,4-dithia-2-cycloheptene 127c[86] and 2-deutero-1,4-dithia-2-cycloheptene 127d, respectively.



102 126 127

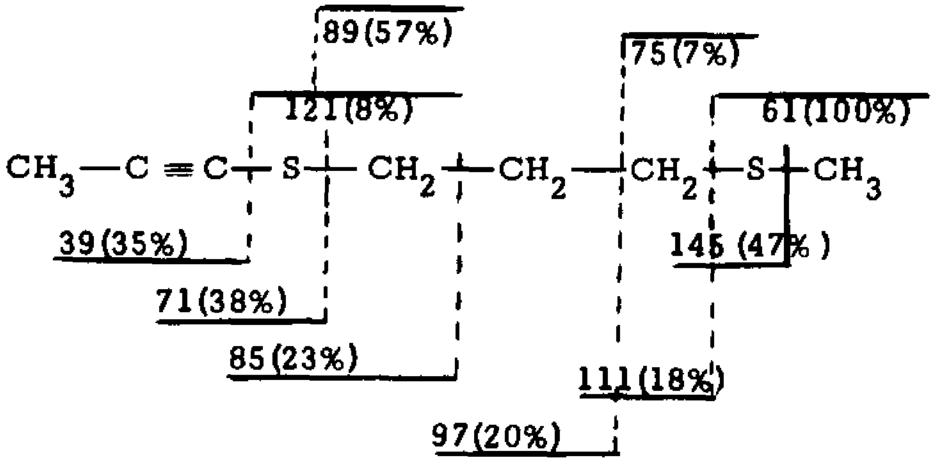
Their structures were established by nmr, and their nmr spectra are summarised in Table XIV.

Compound	δ H_3	δ H_5/H_7	δ H_6	δ R
R = $Si(CH_3)_3$ 127a	5.12 (s)	3.50 and 3.53 (superimposed t)	2.17 (quin.)	0.1 (s)
R = $C(C_6H_5)_2$ OH 127b	5.68 (s)	3.25 and 3.35 (superimposed t)	2.14 (quin.)	7.31 (sharp m, 10 H) 3.72 (exchanged with D_2O)
R = CH_3 127c	5.75 (q)	3.40 and 3.45 (superimposed t)	2.15 (m)	1.85 (d)
R = D 127d	5.75 (br.s)	3.50 (t)	2.17 (quin)	---

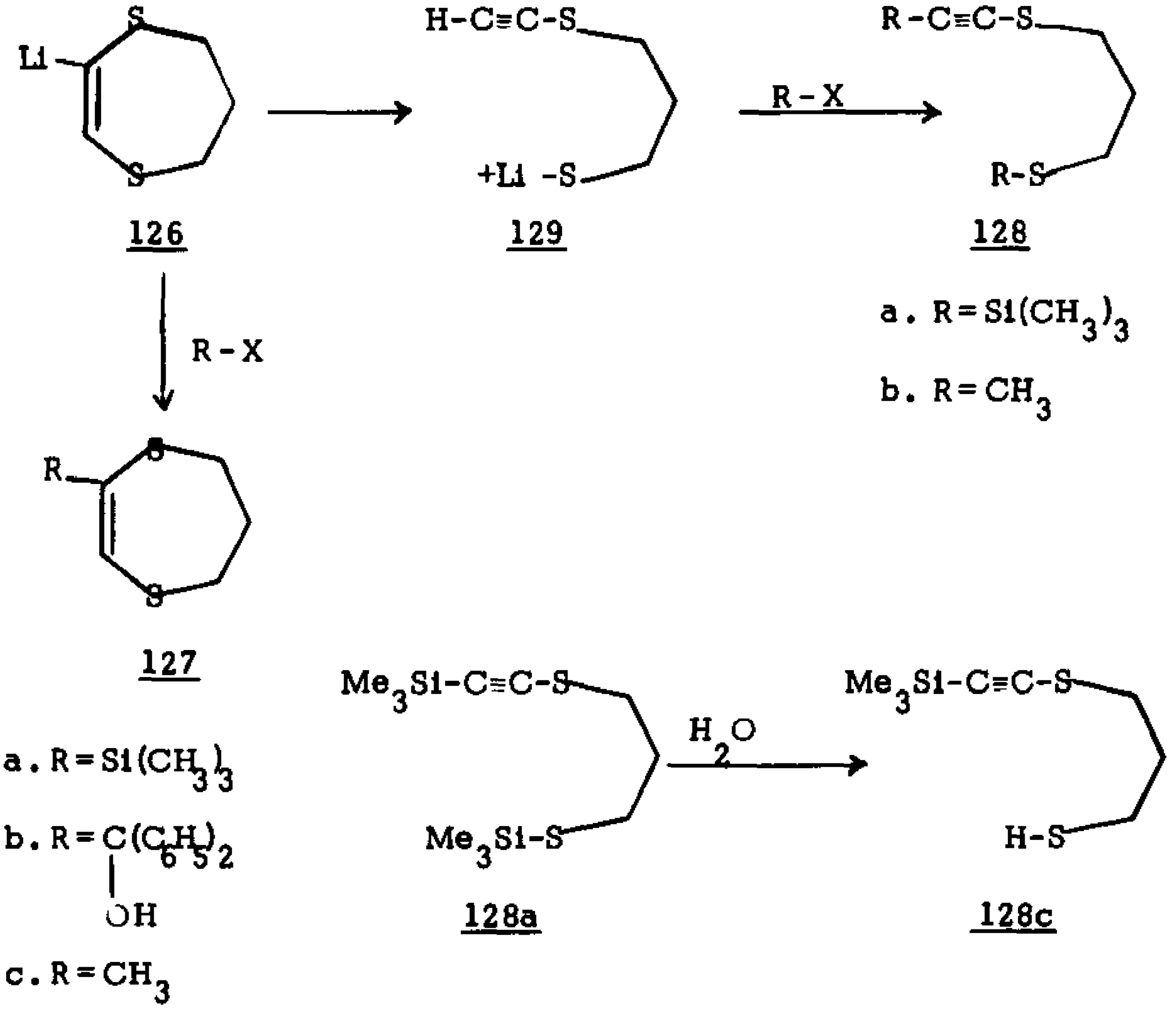
Table XIV: The ^1H nmr Chemical Shifts of 2-Substituted-1,4-Dithia-2-Cycloheptenes.

However, if a solution of the resulting lithio derivative 126 prepared at -70° C was warmed up to -40° C followed by quenching it with trimethylsilyl chloride or methyl iodide, the ring-opened acetylenic trimethylsilane 128c or the ring-opened dimethyl compound 128b (see Scheme XIII) were obtained.

Compound 128c was formed in 58% yield (together with 7.4% of the cyclic 127a) as a pale yellow liquid, bp 53.5° (0.02mm). IR showed that it has a characteristic peak of a terminal mercaptan at 2564 cm^{-1} and an acetylene group at 2105 cm^{-1}; nmr ($CDCl_3$, TMS): δ 0.17 (s,9H), δ 1.40 (t,1H,SH), δ 2.11 (center of symmetric m., 2H) and δ 2.77 (center of symmetric m., 4H). The ring-opened dimethyl compound 128b could be characterized by nmr and mass spectrum, although its ir spectrum did not positively show an acetylene group at 2119 cm^{-1} (very weak). Its nmr spectrum consists of a singlet at δ 1.78 (CH_3), a singlet at δ 2.08 (CH_3) and a multiplet at δ 2.48-3.12 (6H); the mass spectrum conformed the assigned structure is correct: M^+ at m/e 160 (46%) and the other important fragmentations are outlined in the diagram.

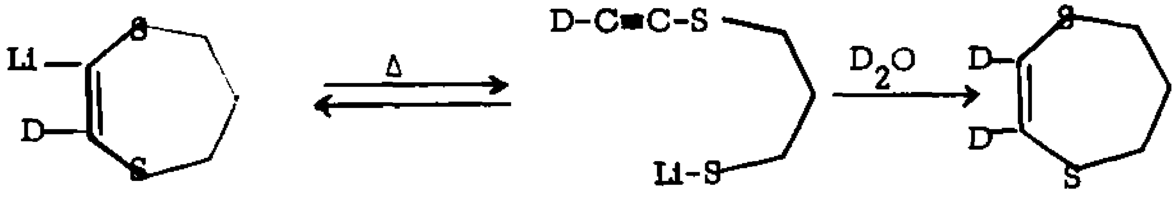


One can see that 44 and 102 exhibit very similar behavior toward lithiation in tetrahydrofuran. Thus, we concluded that 1,4-dithia-2-cycloheptene 102 metallated with n-butyllithium to form 126, which underwent ring-opening at -40° C giving the S-lithium salt 129. The S-lithium salt was then alkylated to afford di-alkylated product 128. The intermediate di-trimethylsilyl product 128a was hydrolyzed during the subsequent aqueous workup to give the mono-trimethylsilyl compound 128c.



SCHEME XIII

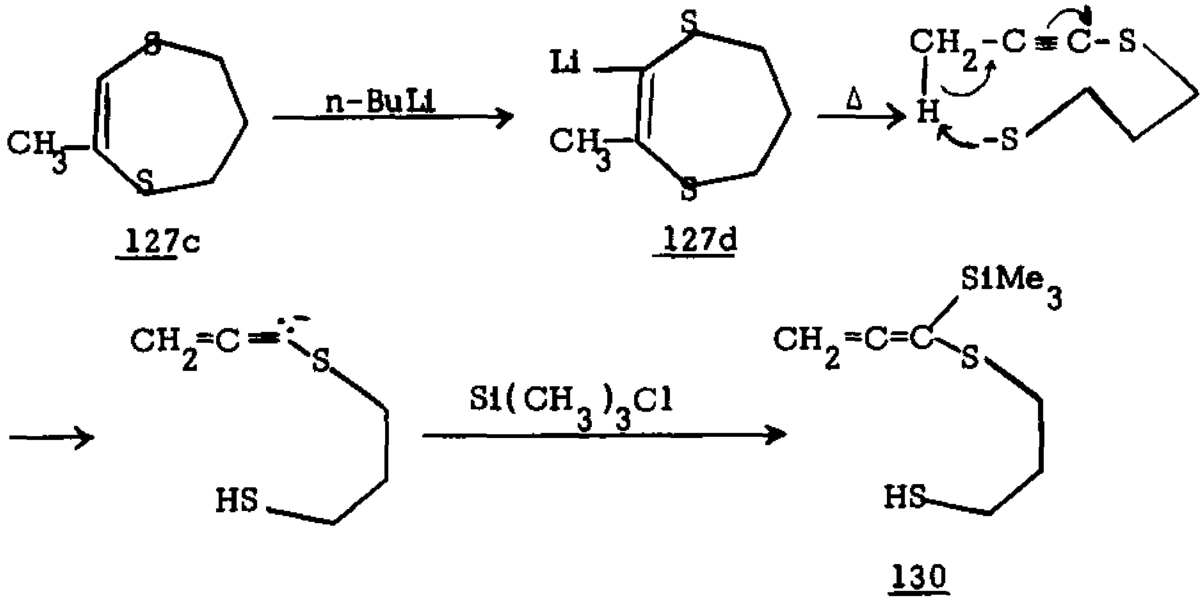
Treatment of compound 127d with n-butyllithium in tetrahydrofuran at -70°C, followed by warming to room temperature, gave the chain-opened lithio derivative 129-d_1. When the resulting anion solution was cooled again to -70°C and quenched with an excess of D_2O the ring reclosed compound, 102-d_2, was obtained. IR (neat): 2174 cm^{-1} (C-D), 1613 cm^{-1} (C=C); NMR ($CDCl_3$, TMS): δ 2.18 (quintet, 2H), δ 3.52 (t, 4H) and a trace of olefinic proton at δ 5.75 .



129-d_1 102-d_2

However, following the same sequence but trapping the resulting anion with trimethylsilyl chloride, 2-methyl-1,4-dithia-2-cycloheptene 127c was converted to an unexpected silane 130 which showed in the IR a terminal mercaptan at 2564 cm^{-1} and a peak characteristic of an allene at 1923 cm^{-1}; the upfield patterns of its nmr spectrum are very similar to that of 128c; nmr ($CDCl_3$, TMS): δ 0.10 (s), δ 1.37 (t, exchanged with D_2O), δ 1.97 (center of m.,) δ 2.70 (center of m.) and δ 4.72 (s, allene protons). These spectral data seem compatible with the structure 130 .

One explanation for this reaction leading to the allene derivative 130 is that a new path is possible in which the anionic sulfur attacks the methyl proton which is activated by the methyl group and the anionic sulfur attacked the closer methyl proton which is activated by the adjacent carbon-carbon triple bond as shown below:

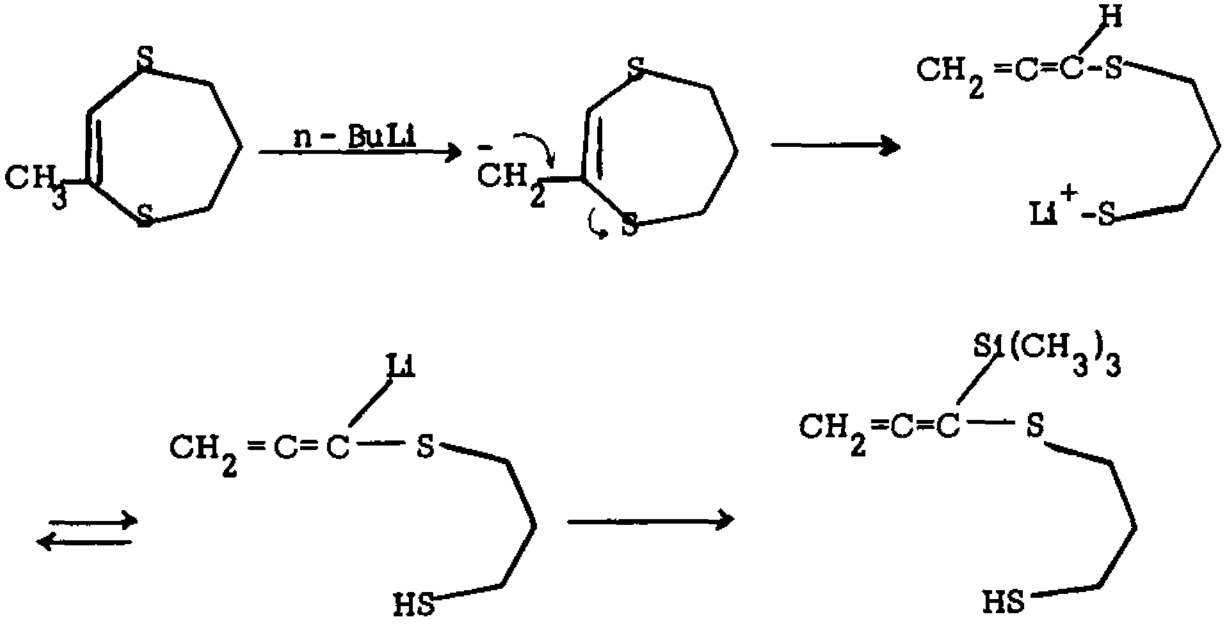


127c

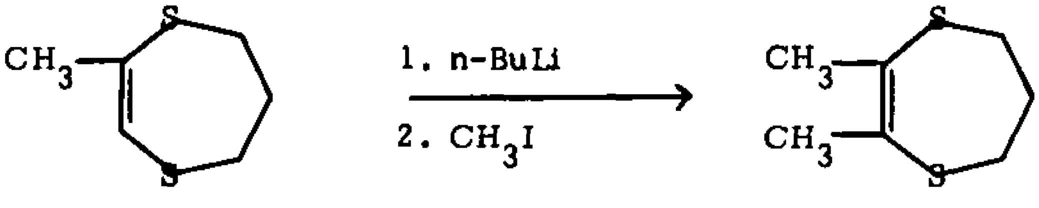
127d

130

An alternative mechanism may be proposed: n-butyllithium attack of the methyl group followed by ring-opening to form an allene S-lithium derivative, as shown below:



The anion solution of 127c produced at -90° C was quenched with methyl iodide. A trace of dimethyl product having an identical nmr with the compound 87 (see page 65, Scheme IX) has been obtained in less than 1% yield.

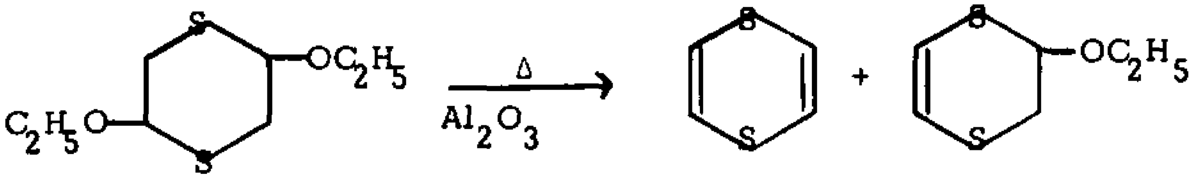


127c 87

B. 1,4-Dithiacyclohexadiene.

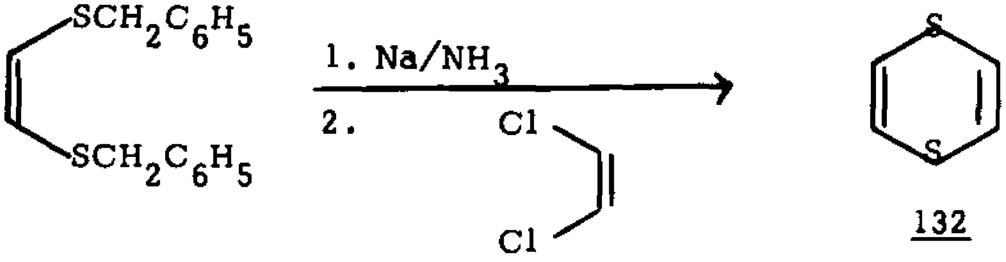
The preparation of 1,4-dithiacyclohexadiene 132 was first reported by W.E. Parham and coworkers[87] by vapor phase dealkoxylation of the cyclic acetal 131 over alumina.

$$\mathrm{Br\,CH_2CH(OC_2H_5)_2} \xrightarrow[2.\,\mathrm{Na/NH_3}]{1.\,\mathrm{Na_2S_3}} \mathrm{HSCH_2CH(OC_2H_5)_2} \xrightarrow[80\%]{\mathrm{H^+}}$$



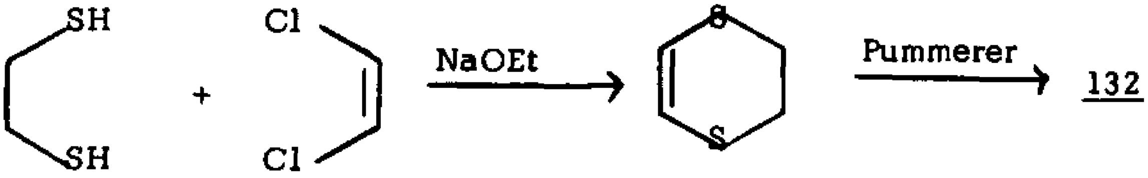
131 132

Later, W. Schroth[88] reported the independent synthesis of 132 by using the debenzylation of cis-dibenzylmercaptoethylene[89] followed by treatment with cis-dichloroethene.



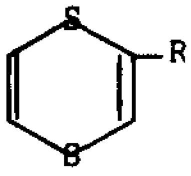
132

In principle, the following approach could be considered as the most ecconomic and convenient pathway to 132.



1,4-Dithiadiene, obtained by the Schroth's method in ca 50% yield, is a yellow liquid, bp 63-67° (9 mm), having a pleasant olefinic odor. nmr ($CDCl_3$,TMS): a singlet at δ 6.19.

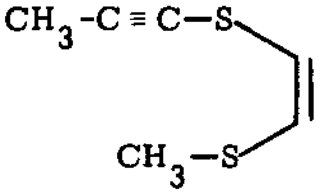
1,4-Dithiacyclohexadiene was treated with n-butyllithium in tetrahydrofuran under nitrogen at -70° C, and the resulting solution was kept at this temperature for one hour. The anion was quenched with chlorotrimethylsilane to afford 2-trimethylsilyl-1,4-dithiacyclohexadiene 133b which formed as yellow liquid, bp 42° (0.06 mm), nmr ($CDCl_3$, TMS): δ 0.19 (S,9H), δ 6.28-6.50 (m, 3H). Undoubtedly, based upon this result, lithio derivative 133a existed in the solution. A solution of lithio derivative 133a formed at -70°C was



133

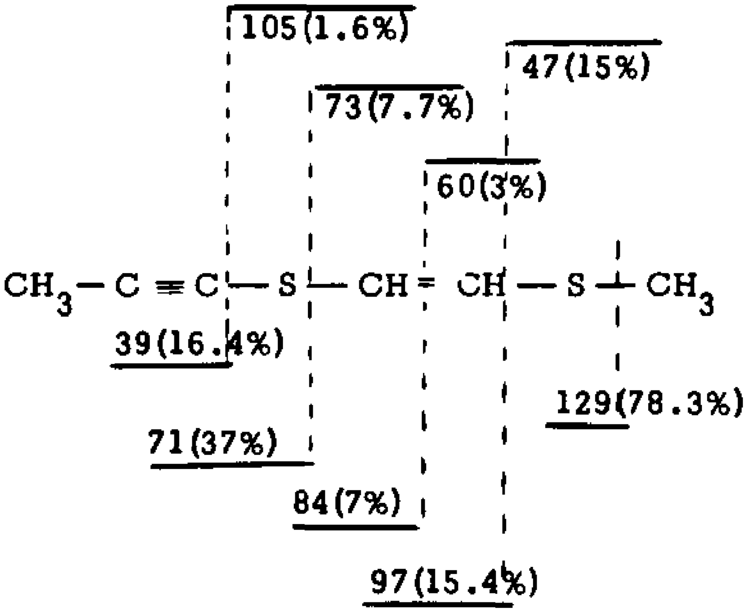
a. R = Li

b. $R = Si(CH_3)_3$



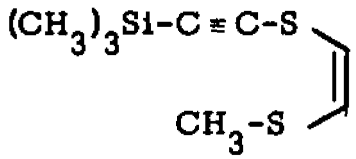
134

held at 0°C, followed by treatment with iodomethane at -70°C, giving dimethyl compound 134 (56%) together with the starting substance 132 (35%). After fractional distillation in vacuuo, 134 was isolated as pale yellow in color, bp 50° (0.06 mm). Its structure was characterized by ir, nmr and mass spectra: ir (neat): 3049 cm^{-1} (alkene), 2941 cm^{-1} and 2899 cm^{-1} (alkane), 2188 cm^{-1} (C≡C), 1439 cm^{-1} and 1282 cm^{-1} ($S-CH_3$); nmr ($CDCl_3$, TMS): δ 1.92 (s, 3H) δ 2.27 (S, 3H) and AB type at δ 5.95 and δ 6.15, $J_{AB} = 9$ Hz. The mass spectrum conformed to the assigned structure: M^+ at m/e 144 (base peak), the fragmentation pattern is outlined below.



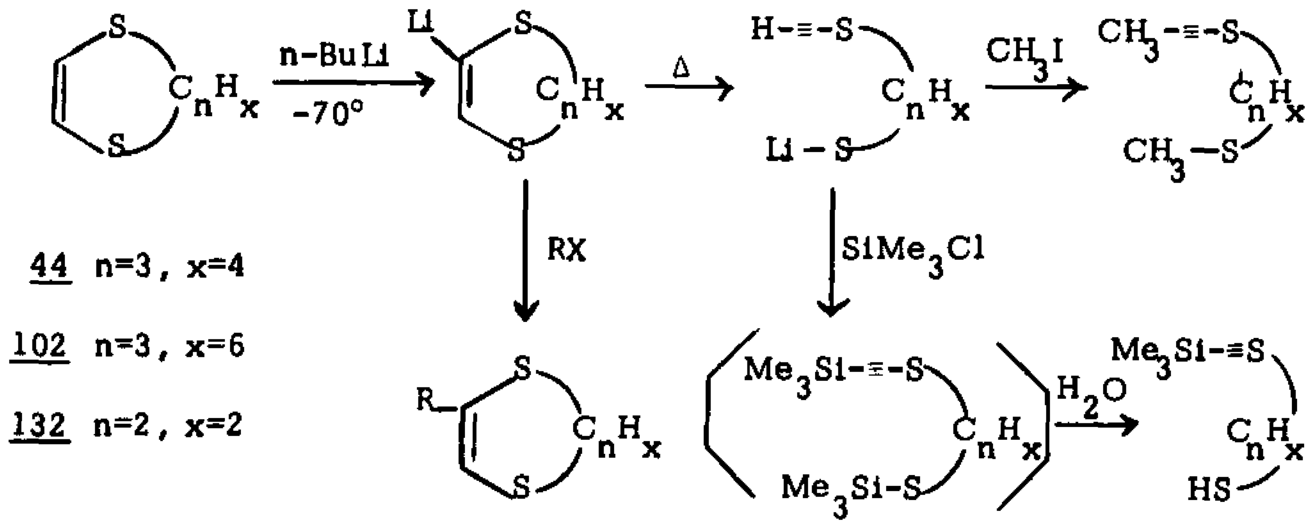
The same result was observed when a solution of 133a was warmed up to -40° C. This suggested that the lithio derivative 133a was only stable at a temperature somewhere below -40° C.

A solution of lithio derivative 133a was stirred at 0° C and quenched with chlorotrimethylsilane. Without isolating the product, the resulting reaction mixture was further treated with n-butyllithium at -70° C, followed by iodomethane to afford 135 in 50% yield. Compound 135 formed as yellow liquid, bp 64° C (0.06 mm); ir (neat): 3049 cm^{-1} (alkene), 2128 cm^{-1} (alkane), 1439 cm^{-1} and 1290 cm^{-1} ($S\text{-}CH_3$) and 1266 cm^{-1} ($Si\text{-}CH_3$); nmr ($CDCl_3$, TMS): δ 0.17 (s, 9H), δ 2.35 (s, 3H) and AB type at δ 6.11 and δ 6.45. J_{AB} = 9 Hz.



135

These results indicate the very similar behavior of 1,4-dithia-2,5-cycloheptadiene 44, 1,4-dithia-2-cycloheptene 102 and 1,4-dithiacyclohexadiene 132 toward lithiation in tetrahydrofuran. Therefore, one can write a general equation to represent these analgous compounds towards n-butyllithium in tetrahydrofuran, followed by alkylation, as shown in Scheme XIV on the following page.



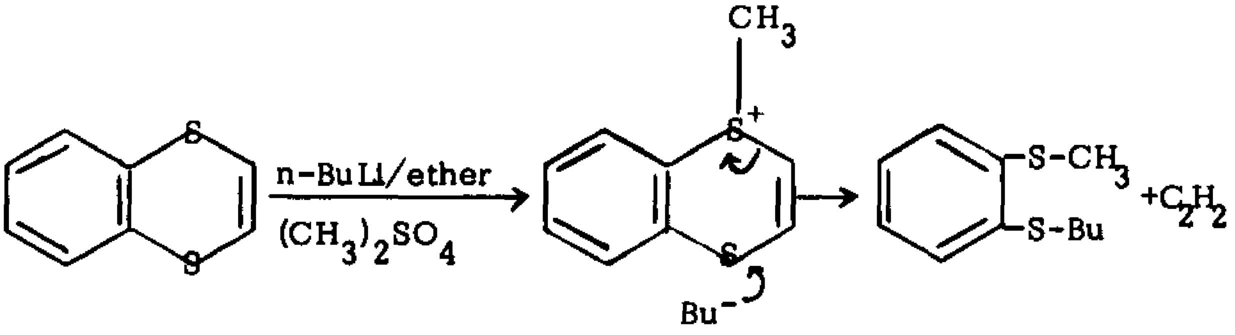
44 n=3, x=4

102 n=3, x=6

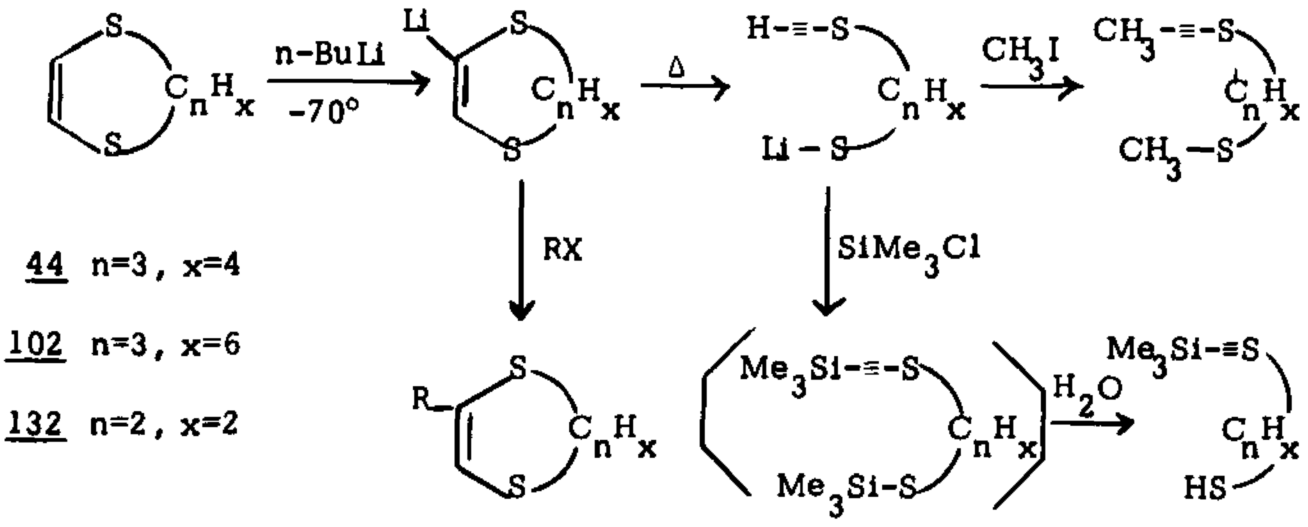
132 n=2, x=2

SCHEME XIV

However, it is interesting to note, as reported by Parham[79,90] benzo-1,4-dithiacyclohexadiene 136 and 2,5-diphenyl-1,4-dithiacyclohexadiene 137 did not undergo appreciable metalation with n-butyllithium in ether at 0° C. With n-butyllithium in the presence of dimethylsulfate a substitution-elimination reaction occurred giving acetylene and the open-chain sulfide.



136



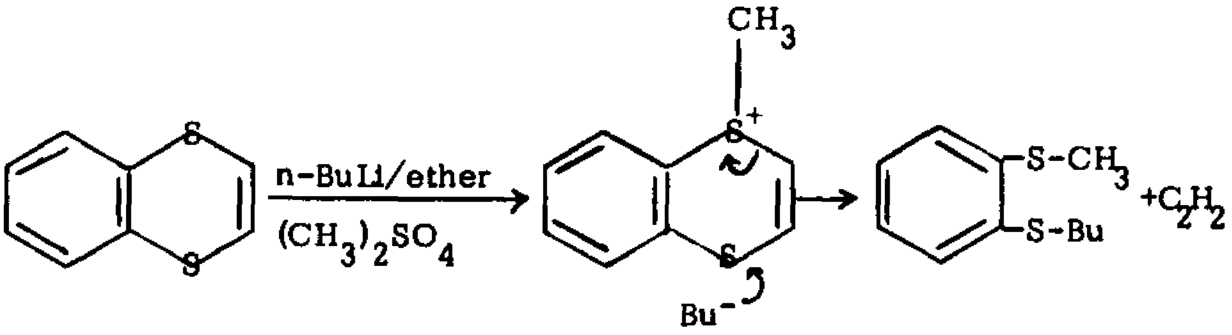
44 n=3, x=4

102 n=3, x=6

132 n=2, x=2

SCHEME XIV

However, it is interesting to note, as reported by Parham[79,90] benzo-1,4-dithiacyclohexadiene 136 and 2,5-diphenyl-1,4-dithiacyclohexadiene 137 did not undergo appreciable metalation with n-butyllithium in ether at 0° C. With n-butyllithium in the presence of dimethylsulfate a substitution-elimination reaction occurred giving acetylene and the open-chain sulfide.



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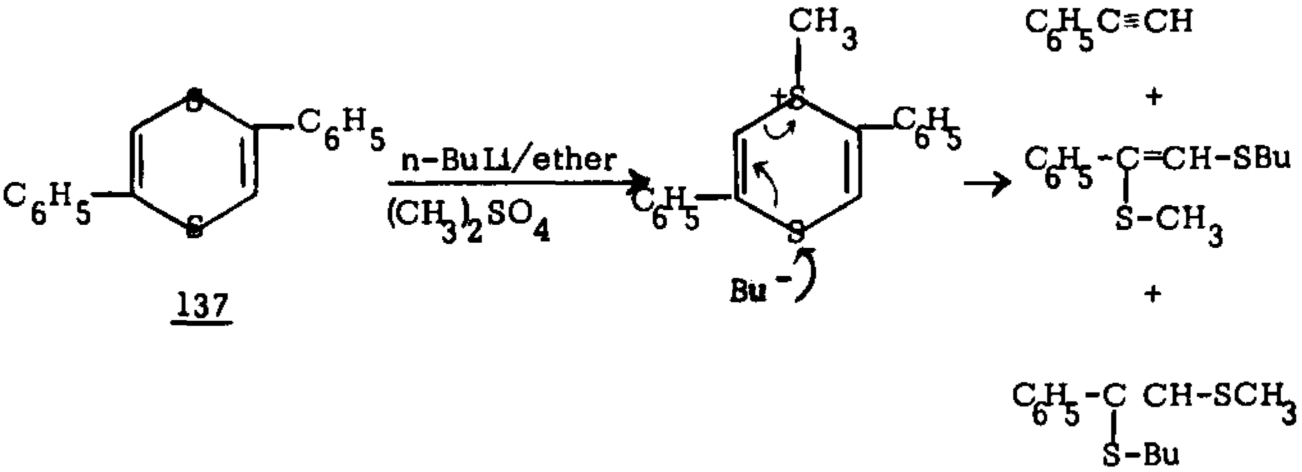
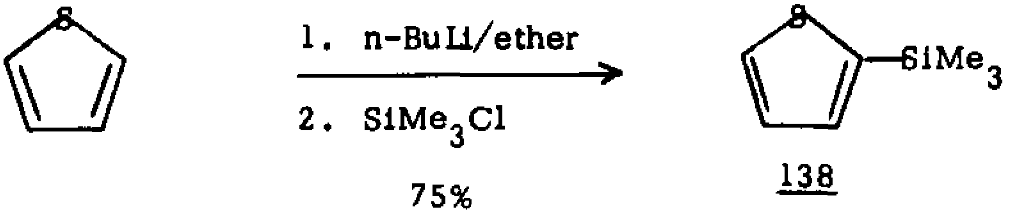


137

Under the same conditions, the aromatic thiophene and furan react with n-butyllithium in ether, followed by addition of trimethylsilyl chloride to produce 2-thienyltrimethylsilane 138 and 2-furyltrimethylsilane 139, respectively.[97]



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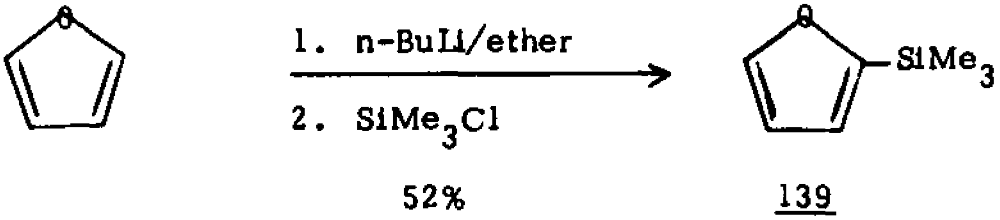
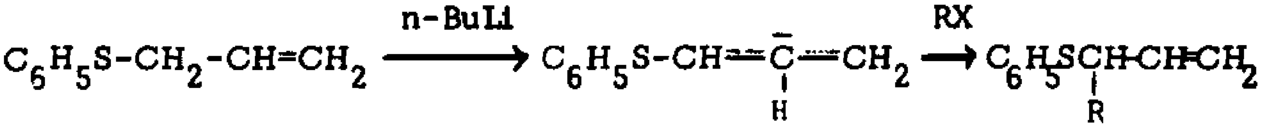


139

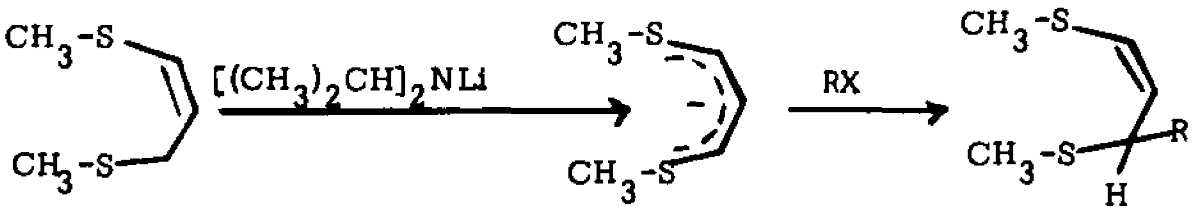
IV. THE BEHAVIOR OF 1,4-DITHIA-5-CYCLOHEPTENE AND 3-METHYL-1,4-DITHIA-2,5-CYCLOHEPTADIENE TOWARDS N-BUTYLLITHIUM IN TETRAHYDROFURAN.

The allylic proton is easily removed by base, because the resulting anion can be stabilized by resonance in which the unshared pair of electrons overlaps with the π-electrons of the double bond. In the chain-opened allyl sulfur compounds, such as 3-phenylthiopropene 140[91] and 1,3-bis(methylthio)-propene 141,[78] the expected allyl anions are afforded upon reaction of these compounds with organolithium; formation of these anions has been verified by their characteristic behavior toward alkyl halides and carbonyl compounds.[78,91]



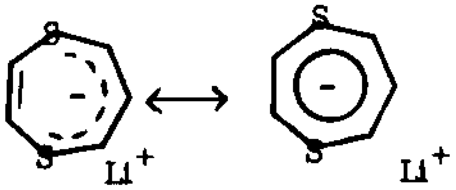
$$C_6H_5S\text{-}CH_2\text{-}CH{=}CH_2 \xrightarrow{n\text{-}BuLi} C_6H_5S\text{-}CH{=}\underset{H}{\overset{-}{C}}{=}CH_2 \xrightarrow{RX} C_6H_5S\underset{R}{CH}\text{-}CH{=}CH_2$$

140



141

However, as mentioned before, treatment of 1,4-dithia-2,5-cycloheptadiene 44 with n-butyllithium in THF did not give the expected allylic lithio derivative 25 (which should be aromatic), but instead, the vinylic lithio derivative 116 . In order to check the very unusual behavior of 1,4-dithia-2,5-cycloheptadiene towards lithiation, the cyclic sulfur compounds 1,4-dithia-5-cycloheptene 142 and 3-methyl-1,4-dithia-2,5-cycloheptadiene 115b , both containing an allylic sulfide, were selected to investigate their allylic metallation, since 142 lacks a double bond between C-2 and C-3, and 115b is blocked at C-3 by a methyl group.



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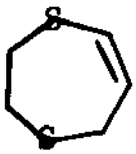

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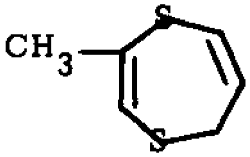
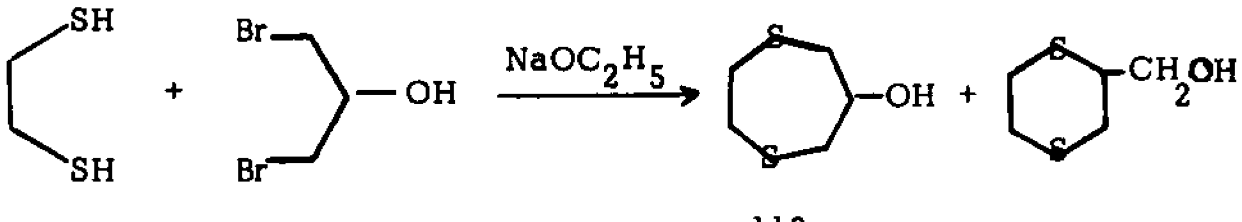


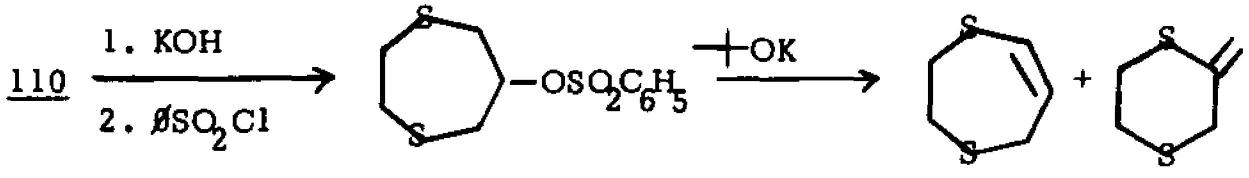
115b

A. 1,4-Dithia-5-cycloheptene

1,4-Dithia-5-cycloheptene (142) has been prepared from the known 6-hydroxy-1,4-dithiacycloheptane 110,[76] which was obtained from reaction of 1,2-ethandithiol with 1,3-dibromo-2-propanol in base solution, by the same procedure used for the synthesis of 44 .



110

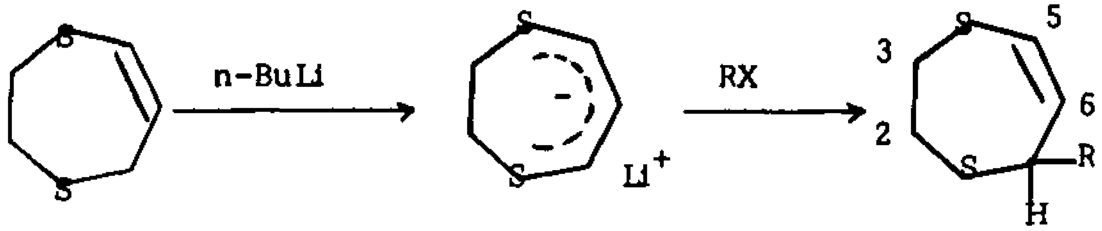


142 143

After elimination of the corresponding benzenesulfonate with potassium tert-butoxide, followed by work-up in usual manner, the residue was distilled under reduced pressure to give a colorless liquid boiling at 35° C (0.23 mm) which contained 90-93% of 142 and 7-10% of the ring contracted product 143 (based on GC analysis). This mixture was separated by column chromatography (silica gel, pet. ether). The structures were determined by nmr. The nmr spectrum of 142 consists of an AA'BB' system centered at δ 2.93, 4H; a doublet at δ 3.33, 2H, J=6.7 Hz and a multiplet between δ 6.19-δ 6.47, 2H; the nmr spectrum of 143 consists of a singlet at δ 2.94, 4H; singlet at δ 3.4, 2H and two signals at δ 5.14 and δ 5.22, 2H (could be of an AB type).

In a recent report by I. Murata,[92] 142 has been obtained independently together with the ring contracted compound 143.

Reaction of 142 with n-butyllithium in tetrahydrofuran under nitrogen at -70° C to 0° C furnished a deep pink solution of lithio derivative 144. Quenching with iodomethane, chlorotrimethylsilane or methanol-d at -70° C gave 7-methyl-1,4-dithia-5-cycloheptene 145a,[92] 7-trimethylsilyl-1,4-dithia-5-cycloheptene 145b and 7-deutero-1,4-dithia-5-cycloheptene 145c, respectively. The nmr spectra are summarized in Table XV.

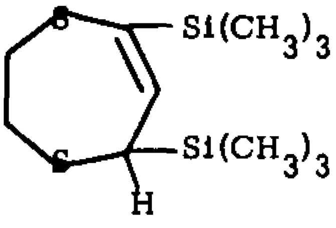


142 144 145

Compound	$\delta H_2/H_3$ (AA'BB')	δH_7	$\delta H_5/H_6$ (m)	δR
145a, R=CH_3	3.15	3.85-4.12 (m)	6.18-6.38	1.32(d,J's 7 Hz)
145b, R=$SiMe_3$	3.08	3.35 (br.d)	6.08-6.29	0.13 (s)
145c, R=D	2.93	3.36 (d)	6.20-6.47	---

Table XV: The NMR Chemical Shifts of 7-Substituent-1,4-dithia-5-Cycloheptene.

Compound 142 has been treated with 2 equivalents of n-butyllithium at -70° C to 0° C, followed by quenching with an excess of chlorotrimethylsilane to give 5,7-bis(trimethylsilyl)-1,4-dithia-5-cycloheptene 146. 7,7-Bis(trimethylsilyl)-1,4-dithia-5-cycloheptene 147 was not observed.



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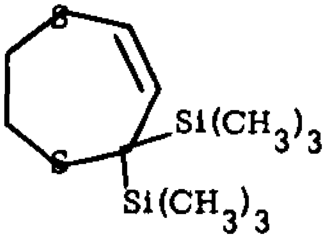
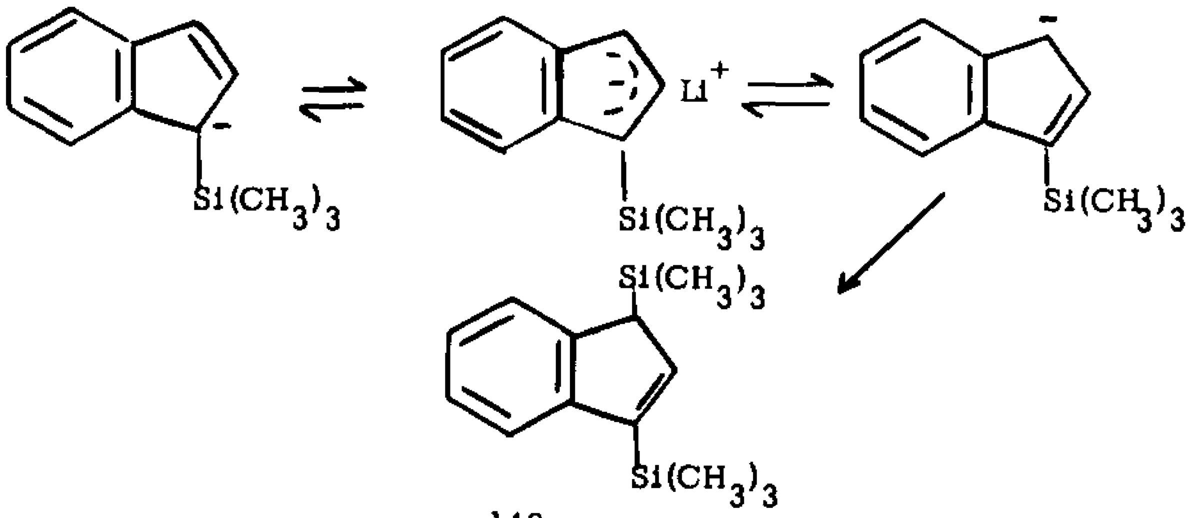


147

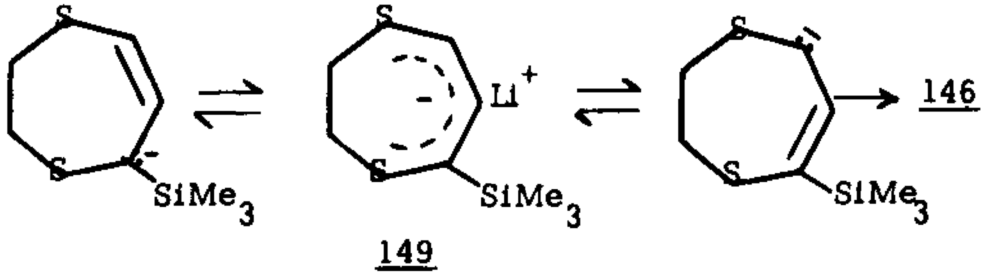
The nmr spectrum of 146 consists of two singlets at δ 0.13 and δ 0.16 corresponding to two trimethylsilyl groups; AA'BB' system centered at δ 3.01 4H; a doublet at δ 3.48, 1H, $J_{6,7}$= 8 Hz and a doublet at δ 6.33, 1H, $J_{6,7}$= 8 Hz clearly confirming the assigned structure.

As reported by Taylor and Rakita,[93] the results of the quenching experiments for the trimethylsilyl anion 148 may reflect a balance of opposing steric and electronic effects. The attachments of the $Si(CH_3)_3$ group is controlled by steric effects and not by unfavorable thermodynamic or electronic considerations. Therefore, 1,3-ditrimethylsilyl indene 148 was exclusively obtained.



148

From our experience in the laboratory, chlorotrimethylsilane does not react with n-butyllithium at low temperature. Thus 146 reacts with one equiv. of n-Buli, followed by silyation to form the intermediate 145b, which further reacted with a second equivalent of n-butyllithium to afford anion 149, and the final reaction with trimethylsilyl chloride gives 146. This result is in good agreement with the result observed by Rakita.



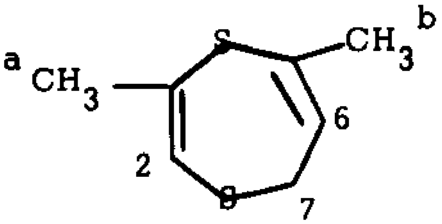
B) 3-Methyl-1,4-dithia-2,5-cycloheptadiene.

3-Methyl-1,4-dithia-2,5-cycloheptadiene 115b obtained from the lithiation of 44 followed by the methylation (see page 86).

The reaction of 115b with n-butyllithium in tetrahydrofuran under nitrogen at -70° C afforded a red anion solution. Trapping the resulting anion solution with methyl iodide, followed by workup in the usual manner, gave a dimethyl derivative of 44.

The 100 MHz 'H nmr spectrum[92] of this dimethyl derivative in $CDCl_3$ has been carefully analyzed and the outline shows as indicated on the following page.

This nmr spectrum is in agreement with structure 150 or 151. In view of the reaction mechanism, 150 and 151 are both



150

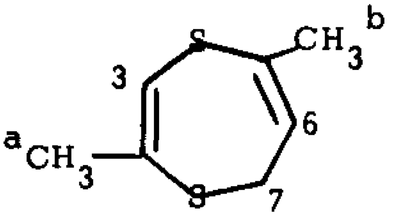
δ 1.86 (d, $^{a}CH_3$, $J_{CH_3,H_2 (or\ H_3)} = 1.0$ Hz)

δ 1.92 (d, t, $^{b}CH_3$, $J_{CH_3,H_6} = 1.5$ Hz, J_{CH_3,H_7} = 0.8 Hz)

δ 3.69 (br d, 2 H_7, $J_{H_6,H_7} = 7.5$ Hz)

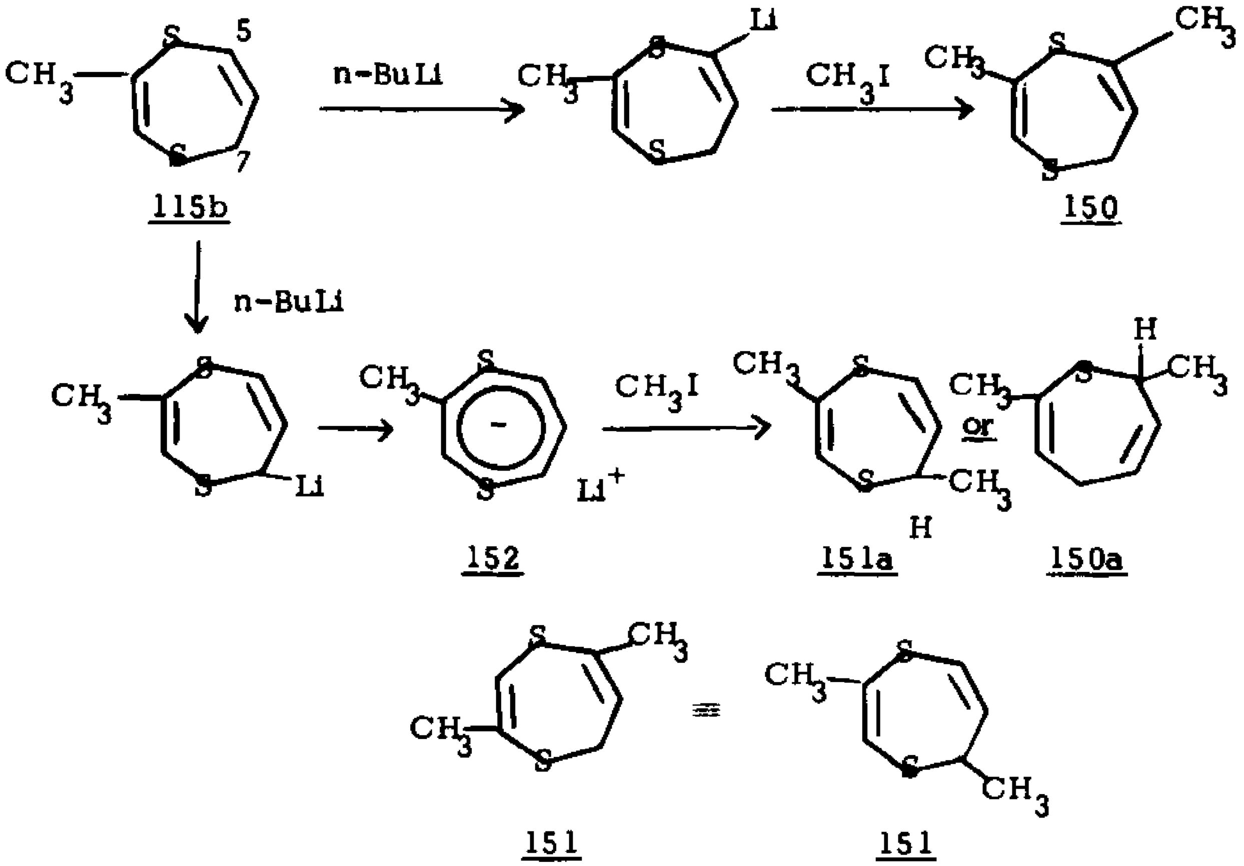
δ 5.89 (q, H_2 or H_3, $J_{CH_3,H_2 (or\ H_3)} = 1.0$ Hz)

δ 6.14 (t, q, H_6, $J_{H_6,H_7} = 7.5$ Hz, J_{H_6,CH_3} = 1.5 Hz).



151

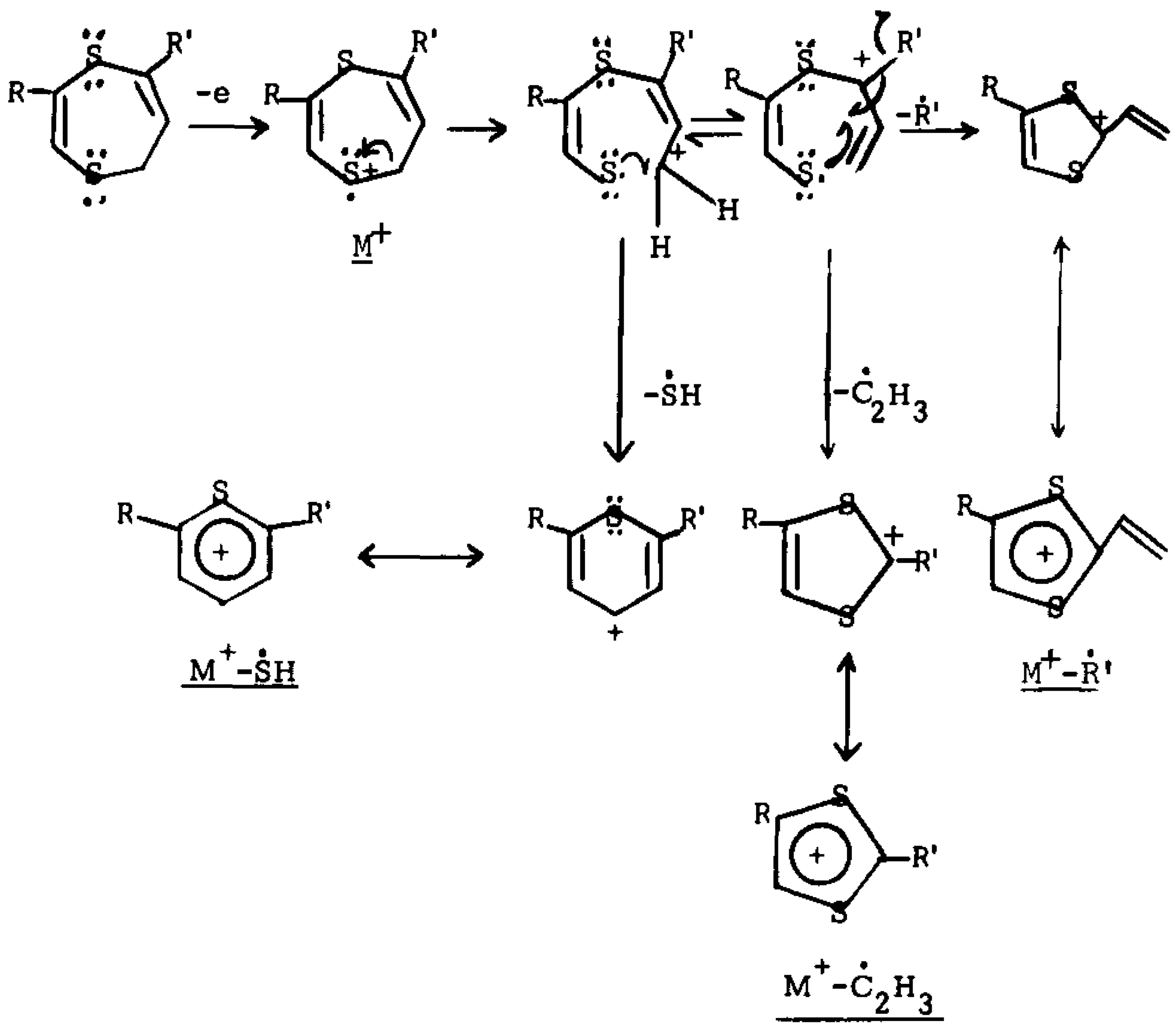
possible formed by the different pathways. In compound 115b, if H_5 is more acidic than H_7, vinylic metallation on C-5 could be occurred, and 150 would be formed. On the other hand, if H_7 is more acidic than H_5, the allylic position is normally metallated, and forms 152 which could react with methyl iodide to afford either 151a or its isomer 150a, and their thermodynamically controlled product 151 and 150, respectively. (See the diagram on the following page.)



The fragmentations of this dimethyl derivative in mass spectrum are in good agreement with the fragmentation obtained from 44 and 115b. The route leading to the aromatic 1,3-dithiolium cation and thiapyrylium cation in mass spectrum could be recognized as below: (the fragmentations of 44, 115b and 150 are summarized in Table XVI).

Compound	M^+		M^+-R'		$M^+-C_2H_2$		M^+-SH	
	m/e	intensity	m/e	intensity	m/e	intensity	m/e	intensity
44, R=R'=H	130	60%	129	28%	103	100%	97	33%
R=CH$_3$ 115b, R'=H	144	70.7%	143	29.1%	117	100%	111	66.8%
150, R=R'=CH$_3$	158	86.8%	143	100%	131	52.9%	125	23.0%

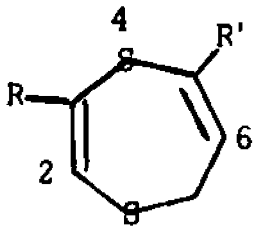
Table XVI: The Mass Spectral Data of 1,4-Dithia-2,5-cycloheptadiene and Its Methyl Derivatives.



Unfortunately, this proposed fragmentation of the dimethyl compound in mass spectrum will not distinguish between 150 and 151, because 151 will lead to isomeric fragments.

From a review of the chemical shifts of 1,4-dithia-2,5-cycloheptadiene 44 and 3-methyl-1,4-dithia-2,5-cycloheptadiene 115b, one notices that all olefinic protons of 115b are shifted 0.19 ppm upfield relative to 44 due to the electron-donating methyl group (see table XVII). Based upon the common olefinic proton H_6

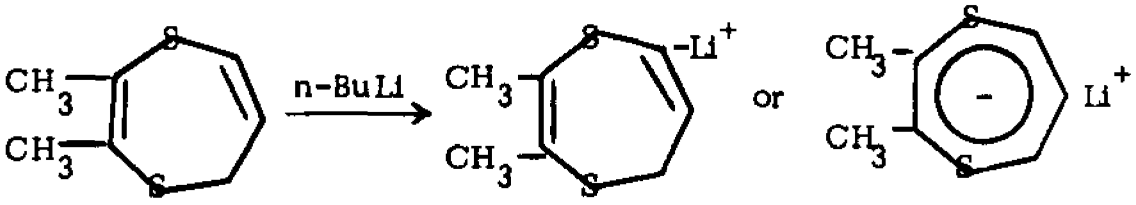
in 150 and 151 being shifted ca 0.33 ppm upfield relative to 44, the chemical shift at δ 5.89 should be assigned as H_2 instead of H_3. Furthermore, the chemical shift at position 2 is more downfield than that of position 5, but the chemical shifts of methyl groups in 151 are contrary to this rule. Thus, the previous nmr is much more compatible with the structure of 150 than the structure of 151.



Compounds	δ H_2	δ H_3	δ H_5	δ H_6
44, R=R'=H	6.29	5.83	6.03	6.47
115b, R=CH_3 R'=H	6.10	--	5.84	6.27
150, R=R'=CH_3	5.89	--	--	6.14

Table XVII: The NMR Chemical Shifts of Olefinic Protons of Compound 44, 115b and 150.

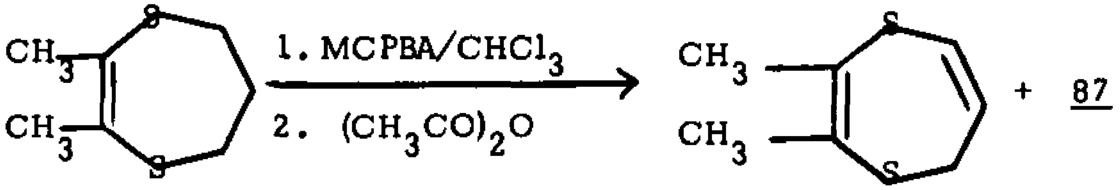
In order to establish more accurately as to whether 115b is metalated in the vinylic position, followed by alkylation leading to 150 or if it is metalated in the allylic position followed by alkylation and then transformation into the thermodynamically more stable product 151 (or 150). It is proposed to metallate the 2,3-dimethyl-1, 4-dithia-2,5-cycloheptadiene 166 with n-butyllithium in THF-d_8 and investigate the nmr spectrum of the resulting anion. This should clearly distinguish between the symmetrical 2,3-dimethyl-1, 4-dithia-2,5-cycloheptadienyl anion 167 or the unsymmetrical vinyl-anion 168.



166 168 167

The dimethyl diene 166 has been obtained from 2,3-dimethyl-1,4-dithia-2-cycloheptene 87 by a Pummerer reaction. Compound 87 was oxidized with m-chloroperbenzoic acid in chloroform. Without isolation of the monosulfoxide, the residue was refluxed in acetic anhydride at 120°-130° for 2 hours. After workup, the reaction products were chromatographed to give a less polar mixture (one spot on tlc) containing the desired dimethyl diene 166 and the starting material 87 in a ratio of 6 : 4 (based on GC analysis).

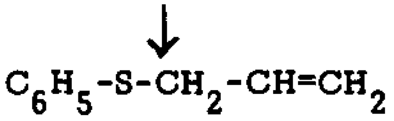
The formation of 166 in the reaction products was confirmed by GC and nmr spectrum, which consists of a broad singlet at δ 1.95; a doublet at δ 3.41 and a multiplet at δ 5.81- δ 6.31.



87 166

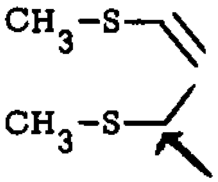
Unfortunately, we were unable to separate the dimethyl diene 166 from this mixture either by the fractional distillation or the preparative tlc. Another route to 166 is under way in this laboratory.

Allylic metallation occurred in the opened-chain compounds, such as 140 and 141 (see page 105), and was also observed in the heterocyclic compound 142 (see page 108). But, this allylic metallation is never observed in 1,4-dithia-2,5-cycloheptadiene 43 and the question as to whether its derivative 115b is being metallated at the allylic position can not be answered at this time. Based upon this abnormal behavior towards lithiation, one could state that 1,4-dithia-2,5-cycloheptadienyl anion 25 is a nonaromatic system. In other words, it is not characterized by a special stabilization. However, no clear conclusion concerning the aromatic character of 25 can be made at this moment and further work will have to be carried out.



$C_6H_5\text{-S-}\overset{\downarrow}{CH_2}\text{-CH=CH}_2$

140



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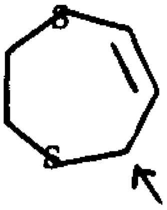

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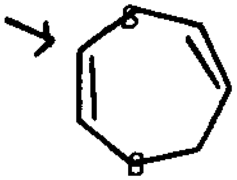
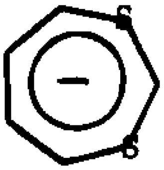


143

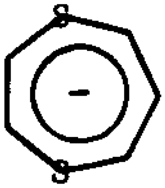
V. THE ATTEMPTS TO GENERATE 1,4-DITHIA-2,5-CYCLOHEPTADIENYL ANION

According to predictions based upon Huckel molecular orbital calculations by Zahradnik and Parkanyi,[28] 1,4-dithia-2,5-cycloheptadiene 44, should be unstable and difficult to prepare. However, in view of the stability of the 10π-electron heteroaromatic 1,3-dithia-4,6-cycloheptadienyl anion 52, one could predict that 25 is an aromatic system as well, because 52 and 25 are close analogs, and the only difference between them is the position of one of the sulfurs in the ring.

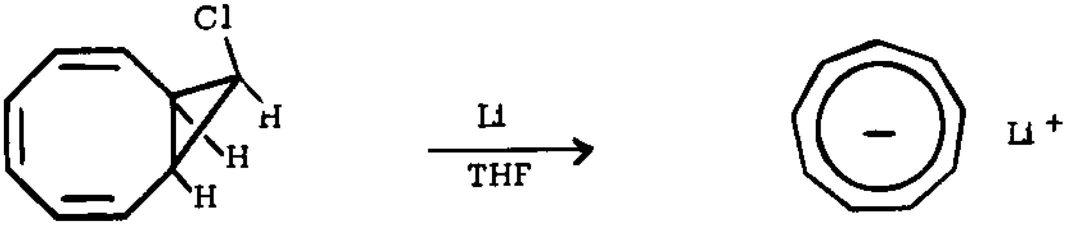
As mentioned in the previous section, we have attempted to generate 25 by reaction of 44 with n-butyllithium, but the vinylic metallation on C-3 was observed and 25 was not formed. Therefore, we have tried a different approach to generate 25.



52

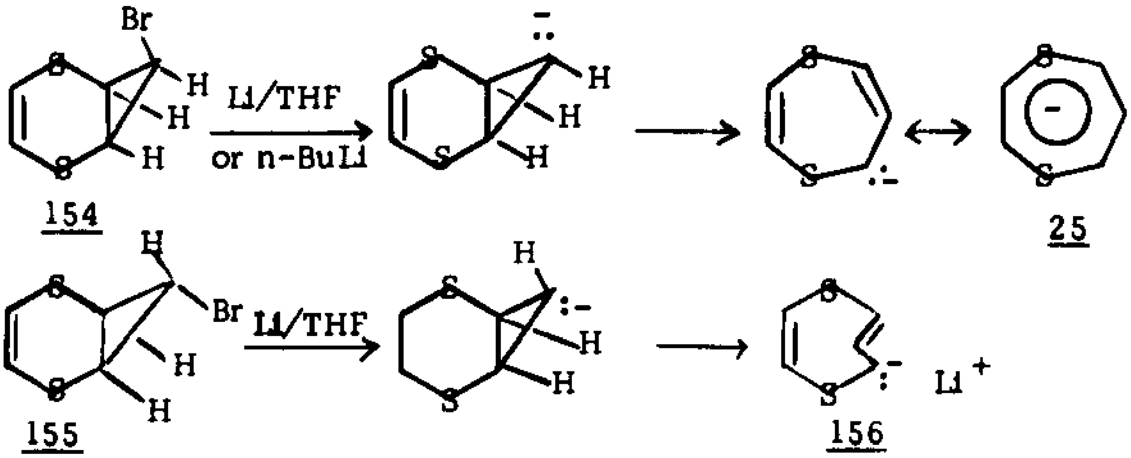


25



153

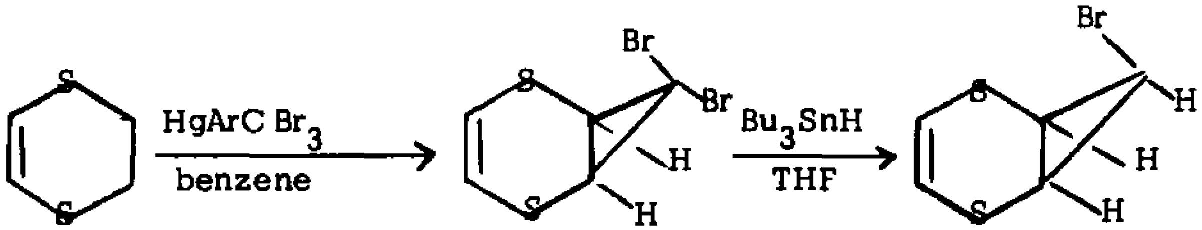
T. Katz and P.J. Garratt,[8] Lalancette and Benson[9] and G. Boche[98] have successfully generated the cyclononatetraenide ion by reaction of endo-9-cyclorobicyclo(6,1,0)nona-2,4,6-triene 153 or a mixture of endo and exo isomers with lithium in tetrahydrofuran. Hence, this reaction could be employed to generate 1,4-dithia-2,5-cycloheptadienyl anion 25 by treatment of endo-7-bromobicyclo (4,1,0)-1,4-dithiacyclohept-2-ene 154 with lithium (or potassium) or n-butyllithium in tetrahydrofuran. While the exo isomer 155 will form the anion 156.



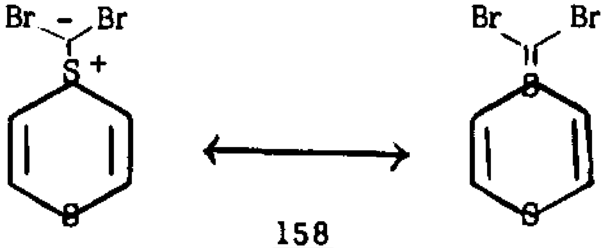
Compound 154 was synthsized by the addition of dibromocarbene to 1,4-dithiacyclohexadiene 132, followed by reduction with tributyltin hydride. The dichlorocarbene or dibromocarbene generated from chloroform or bromoform with base will react with sulfurs leading to undesired sulfur ylids. However, using phenyl tribromomethylmercury[94] as the carbene source, the addition adduct can be obtained (described below).

A solution of 1,4-dithiacyclohexadiene 132 in benzene was added to a solution of phenyltribromomethylmercury in benzene at reflux. Twenty minutes later, phenylmercuric bromide was deposited. After the removal of mercury salt and workup in a usual manner, the residue was chromatographed to give 7,7-dibromobicyclo(4,1,0)-1,4-dithiacyclohept-2-ene(157), as a white needle crystal, mp. 73-74°C, in 8-10% yield. Its nmr spectrum consists of a singlet at δ 2.82, 2H and a singlet at δ 6.18, 2H. A yield of about 70% of a white lachrymatory crystal having mp 110° (decomposed at 120°) was obtained in this reaction as a major product. Its nmr/spectrum consists of a broad singlet at δ 7.35. This compound may be the undesired dibromosulfur ylid 158 which was not studied further.

The dibromoderivative 157 was reduced by tributyltin hydride[95] in benzene under nitrogen at 0° to 50° to give exclusively endo-7-bromobicyclo(4,1,0)-1,4-dithiacyclohept-2-ene 154 which formed as a white crystal, mp 86-88°C, in quantitative yield. Its structure



132 157 154



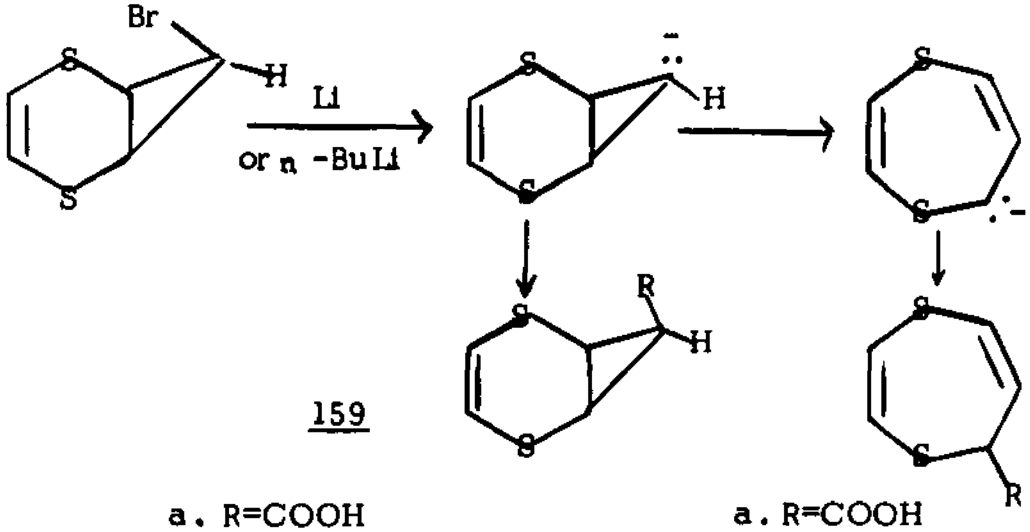
158

was characterized by nmr and mass spectrum, and the geometry was determined on the basis of the observed coupling constants.

nmr ($CDCl_3$,TMS): δ 2.45 (d,2H,J's ca. 7 Hz), δ 3.86 (t,1H,J's ca. 7 Hz), δ 6.34 (s,2H).

A triplet with a coupling constant ca. 7 Hz at δ 3.86 suggests that H_7 is coupled with two cis-cyclopropyl protons, according to the report by C.B. Reese.[96] Mass spectrum: M^+ at m/e 208 (p., 20.6%), m/e 210 (p+2, 22.8%) 129 (M^+- Br, 65.8%), 103 ( , 66.5%), 97 ( , 28.1%), 85 (38.6%) and 45 (S=CH^+, 100%).

Compound 154 was treated with lithium in dry tetrahydrofuran under nitrogen at -70° C to room temperature, followed by the addition of dry ice (CO_2). A dilute potassium hydroxide solution was added to the reaction mixture. The organic layer contained the starting material . The aqueous layer was acidified with dilute hydrochloric acid then extracted with ether. After the removal of ether solvent, some starting material was recovered again. No trace of the corresponding carboxylic acid 159a or 160a was observed.



159

160

a. R=COOH

b. $R=SiMe_3$

a. R=COOH

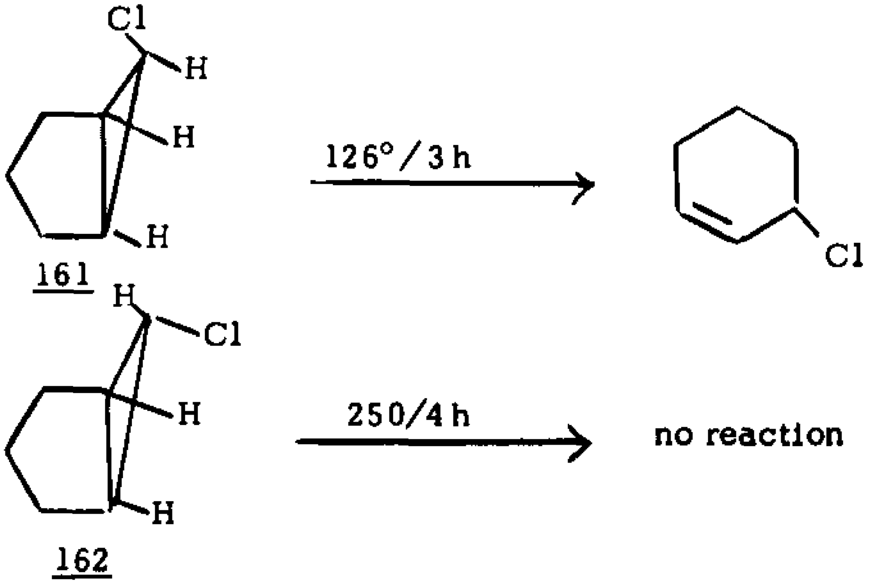
b. $R=SiMe_3$

The same result was obtained when 154 was treated with potassium.

Reaction of 154 with n-butyllithium in tetrahydrofuran under nitrogen at -70°C, followed by chlorotrimethylsilane has been carried out. TLC analysis of the crude product showed no starting material, and a new, green spot, with R_f value ca. 0.57 (solvent; 1/2 benzene in pet. ether) was observed. It suggested that 154 did react with n-butyllithium. The reaction was worked up in the usual manner. The residue after the removal of solvent was a green resin from which none of the expected 160b or 159b was obtained. Instead, a trace of an unknown compound with a nmr spectrum consisting of a singlet at δ 0.25, AB system at δ 2.4, J's ca. 7 Hz and a singlet at δ 6.8 was isolated. The triplet of H_7 at δ 3.86

in the starting material had completely disappeared.

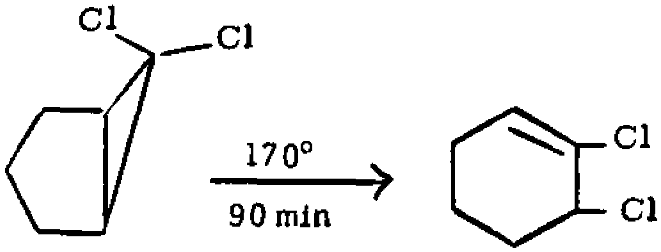
Ring opening of bicyclic cyclopropanes which have an _endo_ leaving group takes place smoothly while the _exo_ isomer generally opens with difficulty. One example is provided, as reported by C.B. Reese,[96] by the isomeric-6-chlorobicyclo-(3,1,0)-hexanes; the _endo_-isomer _161_ is converted into 3-chlorocyclohexene by heating for three hours at 126° C, but the _exo_-isomer _162_ was found to be unchanged, even under more vigorous conditions.



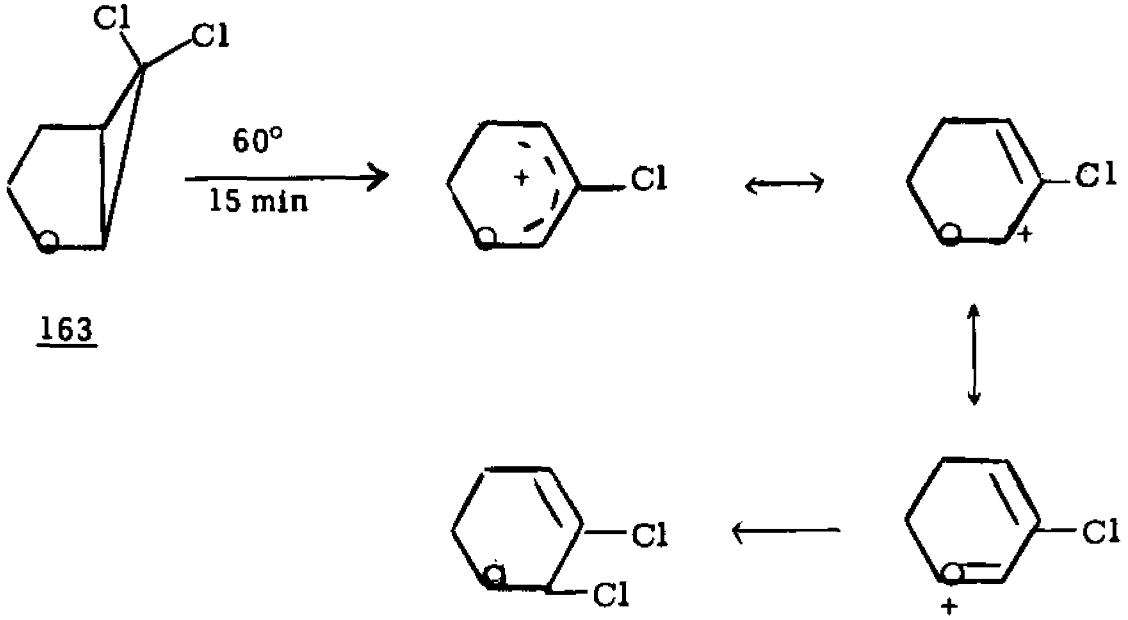
_161_

_162_

The author also reported that a factor which affects the ease of electrocyclic ring opening is the nature of the substituents, which can stabilize the developing positive charge. Thus, the adjacent oxygen may assist the opening of the ether _163_, which reacts smoothly at 60° C; while _163a_ opens with less facility.



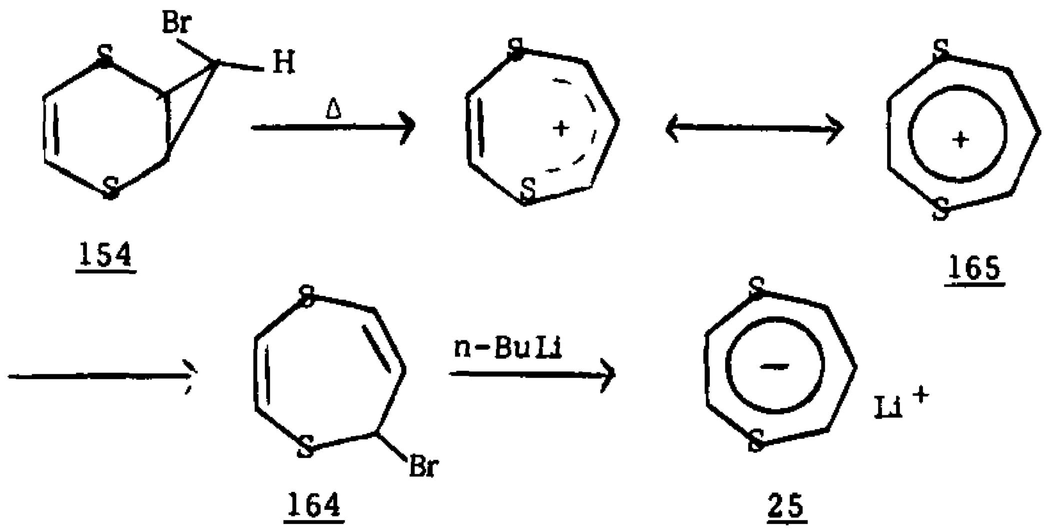
163a



163

In the endo bromocyclopropane 154, there are two adjacent sulfurs which should stabilize the carbonium ion. Thus, 154 is expected to ring enlarge easily to give 7-bromo-1,4-dithia-2,5-cycloheptadiene 164 whose reaction with n-butyllithium may afford 25.

The thermal rearrangement of 154 was performed without solvent at 90°C (above its melting point) under nitrogen for 20 minutes. The material became a brown liquid and its color darkened.



After cooling to room temperature, carbon tetrachloride was added and the black powder was filtered off. The clean substance in carbon tetrachloride has an nmr spectrum identical with the starting material.

The solvolysis of 154 in acetic acid has been carried out in the presence of a catalytic amount of sodium acetate under nitrogen at 65°C. After heating for two days, the reaction material was checked by tlc which showed that the starting material was still present. The temperature was then raised to 84°C and the mixture was heated further for another two days. After workup the starting material was recovered.

Using silver acetate as catalyst, a solution of 154 in acetic acid was heated at 65°C for one day, but no reaction was observed. However, heating the mixture at 84°C under nitrogen for another two days caused the substance to decompose.

In view of the ring-opening studies, 154 is very stable towards thermolysis and solvolysis. As we can see, the ring-opening of cyclopropane derivative 154 should afford the carbonium ion 165, however, it represents an antiaromatic 8π-electron system, and therefore, it might not be formed. Perhaps, this is the reason why 154 is so stable towards thermolysis and solvolysis, although there are two adjacent sulfurs in 154 which could stabilize the intermediate carbonium ion.

EXPERIMENTAL

General

Melting points were determined on a Buchi apparatus in a sealed capillaries, and are uncorrected. Boiling points were uncorrected. Unless otherwise stated, ^{1}H nmr and ^{13}C nmr spectra were determined in $CDCl_3$ solution (TMS internal standards), on Varian A-60 or R-24 spectrometers for 60 MHz spectra; on Varian HA 100 spectrometers for 100 MHz spectra; the 220-MHz nmr spectra were taken on a Varian instrument at Rockefeller University, New York; ^{13}C nmr spectra were determined on JEOL JNM-PS 100 spectrometer. UV spectra were recorded on a Cary 14 recording spectrometer; infrared spectra were recorded on Perkin-Elmer 521 or 137. Vapor phase chromatography was done in 6 feet OV 17 1/4 inch glass column. GC/mass spectroscopy were obtained on a Finnegan 3300 instrument at Cornell University under the direction of Dr. J. Henion.

PART ONE

Preparation of cis-1,4-dichloro-2-butene

Thionyl chloride (309.2 ml., 551.9 g., 4.3 moles) was dropped through the dropping funnel over 2 hours at 0-5° C into a solution of cis-2-butene-1,4-dithiol (164.8 ml., 176.3 g, 2 moles) and pyridine (10 ml) in a 1000 ml three-necked flask equipped with a dropping funnel and a water condenser.

The reaction mixture was immersed into a large ice-bath and stirred overnight in order to complete the evolution of hydrogen chloride.

The reaction mixture was transferred into a 500 ml round bottomed flask and distilled, with a Widmer column, under reduced pressure to give 194.8 g (87% yield) of cis-1,4-dichloro-2-butene, bp. 50-54°C; nmr (CCl_4): δ 4.1 (d,2H), δ 5.40 (t,1H).

Preparation of 1,3-dithia-5-cycloheptene(46)

Thioacetic acid (70.8 ml, 76.1 g, 1 mole) was slowly added into a stirring solution of sodium methoxide (64.8 g, 1.2 moles) in 1000 ml of methanol at 10-20° C. The reaction mixture was stirred for 1 hour before freshly distilled cis-1,4-dichloro-2-butene (62.5 g, 0.5 mole) was added dropwise. After finishing addition the reaction mixture was refluxed for 2 hours. A small portion of reaction solution was distilled under vacuum after the removal of solvent to give dithiolacetate, bp. 135-140° C (9 mm), nmr : δ 2.30 (s,3H), δ 3.6 (d,2H) and δ 5.51 (t,1H).

Without isolation of dithiolacetate, a concentrated aqueous potassium hydroxide solution (112 g, 2 moles) in 30 ml water was added into the cold reaction mixture and the reaction mixture was refluxed for 2 hours. Dibromomethane (79 ml, 121.7 g, 0.7 mole) was dropped in at reflux and the reaction mixture was refluxed for a further 5 hours. The mixture was cooled to room temperature and the precipitate was filtered off. After the solvent was removed under reduced pressure, the residue was chromatographed (silica gel, 10% benzene in pet. ether) to give 16.23 g (24.6% yield) of the title compound 46. The compound formed as white crystal, mp. 53-54°C after recrystallization from pet. ether; nmr: δ 3.50 (d,d,4H), δ 4.03 (s,2H), δ 5.87-6.08 (m,2H).

Anal Calcd for $C_5H_8S_2$: C, 45.41; H, 6.09; S, 48.49.

Found: C, 45.38; H, 6.00; S, 48.42.

Preparation of 1,3-dithia-4,6-cycloheptadiene (43)

Method A: N-Chlorosuccinimide (4 g, 30 mmol) was suspended into a stirring solution of 1,3-dithia-5-cycloheptene 46 (4 g, 30 mmol) in 50 ml of carbon tetrachloride (dried over P_2O_5) at 0-5°C under nitrogen. Fifteen minutes later, the solution turned a pink color and was continued to stir for 1 hour. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The dark oily residue was dissolved in 50 ml benzene (dried over P_2O_5), and potassium t-butoxide (4.48 g, 40 mmol) was added at 0-5°C. After stirring for four hours at room temperature, the reaction mixture was poured into 200 ml of ice water and extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum pressure to give 1.25 g (32% yield) of the title compound 43.

Method B: The diene 43 can also be prepared, without changing solvent, by the following straightforward procedure.

N-Chlorosuccinimide was suspended into a stirring solution of 1,3-dithia-5-cycloheptene in dry CCl_4 at 0-5°C under nitrogen. The reaction mixture was stirred for 1 hour and an excess of triethylamine was then added. The reaction mixture was stirred for 4 hours at room temperature, followed by workup and distillation to give 20-25% of desired diene 43. Bp: 28-35° (0.05 mm), a pale yellow liquid. Mp: 29°C after recrystallization from pentane. UV: λ_{max}^{EtOH} 257 nm (ϵ 4010) and 340 nm (ϵ 3310). ^{1}H nmr: δ 4.13 (s,2H), δ 6.28 (center of AA'BB', 4H). ^{13}C nmr: 39.7 ppm (C_2), 124.7 ppm (C_5/C_6) and 128.3 ppm (C_4/C_7). Mass spectrum: M^+ at m/e 130 (40%), base peak at m/e 84 (M^+- 46, loss of CH_2=S).

High resolution mass spectrum: Calcd $C_6H_6S_2$ 129.9911
Found: 129.9903

Anal calcd $C_5H_6S_2$: C, 46.12; H, 4.64; S, 49.24
Found: C, 46.05; H, 4.63; S, 49.21

Attempted synthesis of 1,3-dithia-4,6-cycloheptadiene 43.

cis, cis-1,4-Bis(benzylthio)butadiene (49) and the dithiolacetate (50) were prepared in ca. 40% and ca. 25%, respectively, by the reported methods of W. Schroth and coworkers.[42]

a) Via cis,cis-1,4-bis(benzylthio)butadiene (49)

Sodium (0.96 g, 40 mmol) was added piece by piece into a stirring suspension of cis,cis-1,4-bis(benzylthio)butadiene 49 (5.96 g, 20 mmol) in ca. 200 ml liquid ammonia at -70° C. The resulting deep red solution was stirred for 4 hours, dibromomethane (3.6 g, 21 mmol) was removed and the reaction mixture was allowed to stir overnight. The reaction mixture was poured into 100 ml of 15% NH_4Cl and extracted repeatedly with ether. The desired diene 43 was not observed on a tlc plate. After the solvent was removed, a lot of polymers were observed. However, 1,2-diphenylethane (2.56 g, 70%) was isolated from the reaction mixture by chromatography.

b) Via dithiolacetate (50)

To a stirring solution of potassium hydroxide (0.3 g, 5.4 mmole) in 50 ml methanol, was added at room temperature under N_2, a solution of dithiolacetate 50 (0.53 g, 2.6 mmol) in 5 ml methanol. After stirring for 1 hour, the starting material disappeared (based upon tlc). An excess of dibromomethane (0.7 g, 4 mmol) was added and the reaction mixture was stirred overnight at room temperature. The desired diene 43 was not observed in the reaction mixture (based on tlc). After workup polymers were observed.

2-Deutero-1,3-dithia-4,6-cycloheptadiene (53a)

To a stirring solution of 1,3-dithia-4,6-cycloheptadiene 43 (0.25 g, 2 mmol) in 40 ml of dry tetrahydrofuran was added, under nitrogen at -70° C, a solution of 2.45 M n-butyllithium (0.9 ml, 2 mmol) in n-hexane. The reaction mixture was allowed to stir at room temperature for 1 hour. An excess deuterium oxide (0.1 g, 5 mmol) was added to the resulting deep red anion solution (52). The reaction mixture was stirred at room temperature for a further 1 hour, then was poured into 40 ml of cold water and extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum to give 2-deutero-1,3-dithia-4,6-cycloheptadiene 53a (0.21 g, 84% yield). Mass spectrum: M^+ at m/e 131; base peak at M^+-47 = m/e 84 (loss of CHD=S); nmr: δ 4.12 (1H, 1:1:1 triplet); δ 6.28 (narrow AA'BB' system, 4H).

2-Trimethylsilyl-1,3-dithia-4,6-cycloheptadiene (53b)

To a stirring solution of 1,3-dithia-4,6-cycloheptadiene 43 (0.25 g, 2 mmol) in 40 ml of dry tetrahydrofuran was added, under nitrogen at -70° C, a solution of 2.45 M n-butyllithium (0.9 ml, 2 mmol) in n-hexane. The reaction mixture was allowed to warm to room temperature for 1 hour. To the resulting deep red anion solution (52), an excess of freshly distilled trimethylsilyl chloride was added (0.5 g, 4.6 mmol). The reaction mixture was stirred at room temperature for a further 1 hour, then was poured into 40 ml of cold water and extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum to give 0.31 g (81% yield) of 2-trimethylsilyl-1,3-dithia-4,6-

cycloheptadiene 53b, as a yellow liquid, bp. 40-45°C(0.05 mm), mass spectrum: M^+ m/e 202, base peak at m/e 97; nmr: δ 0.25 (s,9H) δ 3.11 (s,1H), δ 6.25 (AA'BB' system, 4H).

Anal calcd for $C_8H_{14}S_2Si$: C, 47.46; H, 6.97; S, 31.67;
Si, 13.76

Found: C, 47.38; H, 6.91; S, 31.57; Si, 13.76.

Diphenyl (1,3-dithiepin-2-yl)carbinol (53c)

To a stirring solution of 1,3-dithia-4,6-cycloheptadiene 43 (0.25 g, 2 mmol) in 40 ml of dry tetrahydrofuran was added, under nitrogen at -70° C, a solution of 2.45 M n-butyllithium (0.9 ml, 2 mmol) in n-hexane. The reaction mixture was allowed to stir at room temperature for 1 hour. To the resulting deep red anion solution (52), a solution of benzophenone (0.36 g, 2 mmol) in 5 ml of dry tetrahydrofuran was added. The reaction mixture was stirred at room temperature for 1 hour and was then poured into 100 ml of cold water. The reaction mixture was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was chromatographed (alumina II, benzene) to give 0.27 g (43% yield) of diphenyl(1,3-dithiepin-2-yl)carbinol 53c. nmr : δ 4.97 (s,H_2), δ 6.26 (s,4H), δ 3.53 (s, exchanged with D_2O), δ 7.2-7.7 (m,10H).

Anal calcd for $C_{18}H_{14}OS_2$: C, 69.64; H, 4.55; O, 5.15;
S, 20.66.

Found: C, 69.48; H, 4.50; S, 20.49.

2-Methyl-1,3-dithia-4,6-cycloheptadiene (53d)

To a stirring solution of 1,3-dithia-4,6-cycloheptadiene 43 (0.25 g, 2 mmol) in 40 ml of dry tetrahydrofuran was added, under nitrogen at -70° C, a solution of 2.45 M n-butyllithium (0.9 ml, 2 mmol) in n-hexane. The reaction mixture was allowed to warm to room temperature for 1 hour. To the resulting deep red anion solution (52), an excess of methyl iodide (0.56 g, 4 mmol) was added. The reaction mixture was stirred at room temperature for 1 hour and was then poured into 50 ml cold water. The reaction mixture was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum to give 1.26 g (88% yield) of 2-methyl-1,3-dithia-4,6-cycloheptadiene 53d, as a yellow liquid, bp. 35° C (0.05 mm), nmr: δ 1.73 (d,3H), δ 4.42 (quartet, 1H), δ 6.21 (broad s, 4H).

Anal calcd: $C_6H_8S_2$: C, 49.96; H, 5.59; S, 44.45.

Found: C, 49.87; H, 5.49; S, 44.22.

Reaction of 1,3-dithia-4,6-cycloheptadiene (43) with N-phenylmaleimide

The mixture solution of diene 1,3-dithia-4,6-cycloheptadiene 43 (0.65 g, 5 mmol) and N-phenylmaleimide (1,55 g, 5.1 mmol) was stirred and heated at 140° C under nitrogen for 19 hours. After workup in the usual way, the residue was chromatographed (silica gel, pet. ether) to give the Diel-Alder adduct 48 (0.87 g, 40% yield) mp. 196-

198° C after recrystallization from methanol. nmr : AB system centered at δ 3.5 (2H), δ 6.2 (2H) and δ 7.3 (5H), multiplet.

Anal. calcd for $C_{15}H_{13}NO_2S_2$: C, 59.38; H, 4.32; N, 4.62;
O, 10.56; S, 21.13

Found: C, 59.27; H, 4.24; N, 4.49; S, 21.06 .

Preparation of diphenyl ketenethioacetal (58a)

a) To a stirring solution of 2-trimethylsilyl-1,3-dithia-4,6-cycloheptadiene 53b (0.1 g, 5 mmol) in 20 ml dry tetrahydrofuran was added, under nitrogen at -70° C, a solution of 2.45 M n-butyllithium (2.9 ml, 7 mmol) in n-hexane. The reaction mixture was allowed to stir at room temperature for 1 hour. To the resulting anion solution was added, at -70° C, a solution of benzophenone (0.91 g, 5 mmol) in 5 ml dry tetrahydrofuran. After stirring at room temperature for 1 hour, the solution was poured into 100 ml cold water and extracted repeatedly with ether. The combined ether layers were dried over anhydrous $MgSO_4$, and evaporated off. The residue was chromatographed on neutral alumina II and eluted with a solution of 10% benzene in pet. ether. The crystal was recrystallized from ethanol to give 40% of the title compound 58a, as a yellow crystal, mp 88-89° C. ^{1}H nmr : δ 7.26 (broad s, 10H); δ 6.35 (AA'BB', 4H); ^{13}C nmr: eight signals; 148.24 ppm, 142.4 ppm, 130.66 ppm, 129.48 ppm, 129.22 ppm, 128.3 ppm, 128.04 ppm, and 127.84 ppm. UV: no definite maximum, but a broad tailing absorption into the region of visible.

Anal. calcd for $C_{18}H_{14}S_2$: C, 77.16; H, 5.03; S, 22.87

Found: C, 77.02; H, 4.79; S, 22.53.

b) To a stirring solution of 1,3-dithia-4,6-cycloheptadiene (43) (0.39 g, 3 mmol) in 50 ml of dry THF was added, under nitrogen at -70° C, a solution of 2.45 M n-BuLi (1.27 ml, 3.1 mmol) in n-hexane. The reaction mixture was allowed to stir at room temperature for one hour. An equivalent of trimethylsilyl chloride (0.33 g, 3 mmol) was added to the solution, and the reaction mixture was stirred at room temperature for one hour. The resulting solution was again cooled to -70° C then a solution of 2.45 M n-BuLi (1.27 ml, 3.1 mmol) in n-hexane was added. The reaction mixture was allowed to warm at room temperature and stirred for a further one hour. An equiv. of benzophenone (0.55 g, 3 mmol) in 3 ml dry THF was added, at -70° C, quickly to the resulting anion solution. The solution was stirred at room temperature for one hour again, before pouring into ice water. The organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhyd. $MgSO_4$ and evaporated off. The residue was chromatographed (alumina II, 10% benzene in pet. ether) to give ca. 37% yield of the title compound 58a.

Preparation of dimethyl ketenethioacetal (58b)

A) To a stirring solution of 2-trimethylsilyl-1,3-dithia-4,6-cycloheptadiene 53b (0.1 g, 0.5 mmol) in 20 ml dry tetrahydrofuran was added, under nitrogen at -70° C, a solution of 2.45 M n-butyllithium (2.9 ml, 7 mmol) in n-hexane. The reaction mixture was allowed to warm up to room temperature and stirred for a further 1 hour.

To the resulting anion solution was added, at -70° C, an excess of A.C.S. grade acetone. After stirring to room temperature, the reaction mixture was poured into cold water and extracted repeatedly with ether. The residue after the removal of ether was distilled under vacuum to give the compound 58b in quantitative yield; 58b is a yellow liquid of good smell, bp. 72° C (0.16 mm), nmr: δ 2.03 (s, 6H), δ 6.27 (s, 4H), UV: λ_{max}^{EtOH} 342 nm (ϵ 1181), 270 nm (shoulder, ϵ 1104), 255 nm (shoulder, ϵ 2053), 240 nm (shoulder, ϵ 3312) and 220 nm (shoulder, ϵ 11,039); mass spectrum: M^+ at m/e 170 (34.8%), m/e 155 (14.7%) 103 (21.2%), 97 (26.2%), 86 (91.5%), 71 (100%) and 45 (51.1%).

Anal. calcd. for $C_6H_{10}S_2$: C, 56.43; H, 5.92; S, 37.65.
Found: C, 56.37; H, 5.79; S, 37.52.

B) To a stirring solution of 1,3-dithia-4,6-cycloheptadiene 43 (0.39 g, 3 mmol) was added under nitrogen at -70° C, a solution of 2.45 M n-BuLi (1.27 ml, 3.1 mmol) in n-hexane. The mixture was allowed to stir at room temperature for 1 hour. Trimethylsilyl chloride

(0.35 g, 3.2 mmol) was added into the resulting anion solution at -70° C and the reaction mixture was stirred at room temperature for 1 hour.

To the reaction mixture was added at -70° C, a solution of 2.45 M n-butyllithium (2 ml, 5 mmol) in n-hexane. The mixture was allowed to warm to room temperature and stirred for a further 1 hour. The mixture was again cooled to -70° C, and an excess of ACS grade acetone was added. After stirring at room temperature for 1 hour, the reaction mixture was poured into 100 ml cold water and extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum to give compound 58b in quantitative yield.

Reaction of diphenyl ketenethioacetal 58a with methyllithium

a) Quenching with water

To a stirring solution of diphenyl ketenethioacetal 58a (85 mg, 0.28 mmol) in 10 ml of dry tetrahydrofuran was added, under nitrogen at -70° C, a solution of 1.56 M methyllithium (0.2 ml, 0.3 mmol) in ether. The reaction mixture was allowed to stir at room temperature for 2 hours, before poured into 20 ml cold water. The mixture was extracted repeatedly with ether. The ether layers were dried over anhydrous $MgSO_4$.

The residue after removal of solvent remained a yellow solid (83 mg). Without purification, the yellow solid has an identical nmr spectrum with the starting material.

b) Quenching with Trimethylsilyl Chloride

To a stirring solution of diphenyl ketenethioacetal 58a (70 mg, 0.24 mmol) in 10 ml of dry THF was added, under nitrogen at -70° C, a solution of 1.56 M methyllithium (0.2 ml, 0.31 mmol) in ether. The reaction mixture was allowed to stir to room temperature for 1 hour. An excess of freshly distilled trimethylsilyl chloride (ca. 0.2 g) was added into the resulting anion solution at -70° C. The reaction mixture was stirred at room temperature for 1 hour, and then poured into 20 ml cold water. The mixture was extracted repeatedly with ether. The combined ether layers were dried over anhydrous $MgSO_4$, and evaporated off. The residue was recrystallized from pet. ether to give trimethylsilyl compound 64, in quantitative yield, as a yellow crystal mp 96-98° C, after recrystallization from pet. ether. nmr (no TMS): δ 0.00 (s, 9H), δ 6.46-6.95, split into two areas 1:2 (3H), δ 7.38 (broad s, 10H).

Anal calcd for $C_{21}H_{22}S_2Si$: C, 68.80; H, 6.05; S, 17.49; Si, 7.66.

Found: C, 68.75; H, 6.07; S, 17.31; Si, 7.60.

Reaction of dimethyl ketenethioacetal 58b with methyllithium

a) Quenching with water

To a stirring solution of dimethyl ketenethioacetal 58b (0.2 g, 1.2 mmol) in 10 ml dry tetrahydrofuran was added, under nitrogen at -70° C, a solution of 1.56 M methyllithium (1 ml, 1.56 mmol) in ether. The reaction mixture was allowed to stir to room temperature for 2 hours, before poured into 20 ml cold water. The reaction mixture was extracted repeatedly with ether. The combined ether layers were dried over anhydrous $MgSO_4$. The residue after the removal of the ether was distilled under vacuum to recover the starting material in ca. 85% yield.

b) Quenching with trimethylsilyl chloride.

To a stirring solution of dimethyl ketenethioacetal 58b (0.15 g, 0.8 mmol) in 5 ml dry tetrahydrofuran was added, under nitrogen at -70° C, a solution of 1.56 M methyllithium (0.7 ml, 1.1 mmol) in ether. The reaction mixture was allowed to stir to room temperature for 1 hour. An excess of freshly distilled trimethylsilyl chloride was added to the resulting anion solution at -70° C. The reaction mixture was stirred at room temperature for 2 hours, before poured into 20 ml ice water. The mixture was extracted repeatedly with ether, dried over anhydrous $MgSO_4$ and evaporated off the solvent. The residue was distilled under vacuum to give the trimethylsilyl compound 64b in quantitative yield. As a yellow liquid, nmr ($CDCl_3$, TMS): δ 0.18 (s,9H) singlet at δ 2.05 and δ 2.09 (6H), δ 6.24-6.70 split into two area 1 : 2 (3H).

Anal. calcd for $C_{11}H_{18}S_2Si$: C, 54.49; H, 7.48; S, 26.44;

Si, 11.58 .

Found: C, 54.52; H, 7.43; S, 26.40; Si, 11.46 .

The Measurement of ^1H and ^{13}C NMR spectrum of 1,3-dithia-4,6-cycloheptadienyl anion 52 .

The 1,3-dithia-4,6-cycloheptadienyl anion 52 was generated in a NMR tube equipped with a three way stopcork, one for nitrogen, and one for pump.

To make sure the tube had no air and moisture, the nmr tube was inlet with nitrogen for about 15 minutes and then heated gentely with a Benson burner.

Using 1 cc thringe, 0.17 ml (0.4 mmol) of 2.4 M n-butyl lithium in n-hexane was injected into above cold nmr tube. The solvent was removed slowly by the vacuum pump. A solution of 1,3-dithia-4,6-cycloheptadiene (52 mg., 0.4 mmol) in about 0.5 ml freshly distilled THF-d_8 (dried over $LiAlH_4$; containing TMS as reference) was added into the nmr tube at -70° under nitrogen. The resulting deep red anion solution was allowed to warm at 0° C for about ten minutes. While keeping an atmosphere of nitrogen in the tube, its contents were cooled in dry ice-acetone bath, and the tube was carefully sealed.

The sealed nmr tube was always kept in dry ice-acetone bath besides the spectrum was run.

The proton NMR spectrum of anion <u>52</u> showed that the sharp AA'BB' system in <u>43</u> was split into AA'XX' system. The lower part of the spectrum centered at δ 6.63, and the upper part of AA'XX' centered at δ 5.80. H_2 was a triplet at δ 1.48 with a coupling constant 0.8 Hz, (coupled with lower part of the spectrum).

The C-13 NMR spectrum of anion <u>52</u> showed three signals at 25.6 ppm (C_2), 146.7 ppm (C_4/C_7) and 121.6 ppm (C_5/C_6).

<u>Preparation of 1,3-dithiacycloheptane</u> <u>(70).</u>

Thioacetic acid (30 ml, 0.423 mole) was added to a solution of sodium (9.73 g, 0.423 mole) in 400 ml anhydrous methanol at 0-5° C. The mixture refluxed for 2 hours before 1,4-dibromobutane (45.79 g, 0.212 mole) was added dropwise at reflux. The reaction mixture was allowed to reflux overnight. Dithiolacetate was expected to form at this step. Without isolation of dithiolacetate, a concentrated aqueous solution of potassium hydroxide (47.5 g, 0.848 mole) in 30 ml of water was added slowly into the cold reaction mixture, and the reaction mixture was refluxed for 2 hours. Dibromomethane (34 ml, 0.3 mole) was dropped in at reflux and the reaction mixture was refluxed for a further 5 hours. The mixture was cooled to room temperature and the precipitate was filtered off. After the solvent was removed under reduced pressure, the concentrated solution was poured into cold brine water and extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum to give two fractions: 1,2-dithiane, bp 42-50°C (1.8 mm), colorless liquid was obtained in ca 7% (2.52 g); nmr: δ 1.98 (br. m, 4H) and δ 2.80 (br. m, 4H).

Anal calcd for $C_4H_8S_2$: C, 39.96; H, 6.71; S, 53.33.

Found: C, 40.01; H, 6.65; S, 53.28.

1,3-dithiocycloheptane, bp 58-65°C (1.8 mm), colorless liquid, was obtained in 31% yield (8.72 g); nmr: δ 2.00 (br. m, 4H), δ 2.80 (br. m, 4H) and δ 3.85 (s, 2H).

Anal calcd for $C_5H_{10}S_2$: C, 44.73; H, 7.51; S, 47.76.

Found: C, 44.70; H, 7.55; S, 47.71.

Reaction of 1,3-dithiacycloheptanyl anion with electrophiles.

A) The generation of 1,3-dithiacycloheptanyl anion.

To a stirring solution of 1,3-dithiacycloheptane (0.54 g, 4 mmol) in 40 ml of dry tetrahydrofuran was added, under nitrogen at -70°C, a solution of 2.45 M n-butyllithium (1.8 ml, 4 mmol) in n-hexane. The reaction mixture was allowed to warm at room temperature for one hour.

B) Reaction with iodomethane

To the above resulting colorless 1,3-dithiacycloheptanyl anion solution, an excess of iodomethane was added at -70°C. The reaction mixture was stirred at room temperature for a further one hour, then was poured into 50 ml of cold water and extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum pressure to give 0.54 g (92% yield) of 2-methyl-1,3-dithiacycloheptane <u>72a</u> as a colorless liquid, bp. 47°C (0.55 mm), nmr: δ 1.50 (d,3H), δ 1.98 (br. m, 4H), δ 2.79 (center of two brm m, 4H) and δ 4.23 (q, 1H).

Anal calcd for $C_6H_{12}S_2$: C, 48.60; H, 8.16; S, 43.24.
Found: C, 48.49; H, 8.11; S, 43.30.

C) <u>Reaction with benzophenone</u>

To the above resulting colorless 1,3-dithiacycloheptanyl anion solution was quickly added at -70°C, a solution of benzophenone (0.73 g, 4 mmol) in 4 ml THF. The reaction mixture was stirred at room temperature for one hour, then poured into about 50 ml of cold water and extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was chromatographed (Al_2O_3 II, benzene) to give 0.64 g (51% yield) of carbinol <u>72b</u>, mp. 91-93°C. After recrystallization from benzene-petrolem ether gave white crystal, mp. 93-94°C, nmr: δ 1.87 (center of br. m, 4H), δ 2.85 (center of two br. m, 4H), δ 3.65 (s, 1H, exchanged with D_2O), δ 5.56 (s, 1H) and δ 7.22-7.72 (m, 10H).

Anal calcd for $C_{18}H_{20}S_2$: C, 68.31; H, 6.37; S, 20.26.
Found: C, 68.28; H, 6.25; S, 20.07.

D) Reaction with trimethylsilyl chloride.

To the above 1,3-dithiacycloheptanyl anion solution, an excess of freshly distilled trimethylsilyl chloride was added at -70° C. The reaction mixture was stirred at room temperature for a further 1 hour, then was poured into about 50 ml of cold water and extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum pressure to give 2-trimethylsilyl-1,3-dithiacycloheptane 72c (0.77 g, 94% yield), as a colorless liquid, bp. 65-69°C (0.16 mm); nmr: δ 0.18 (s, 9H), δ 2.03 (center of br. m, 4H), δ 2.88 (center of two wide br. m, 4H) and δ 3.44 (s, 1H).

Anal. calcd for $C_8H_{18}S_2Si$: C, 46.55; H, 8.79; S, 31.06; Si, 13.61.

Found: C, 46.50; H, 8.71; S, 31.12; Si, 13.49.

Preparation of dimethyl keteneacetal of 1,3-dithiacycloheptane (73a).

To a stirring solution of 2-trimethylsilyl-1,3-dithiacycloheptane 72c (0.35 g, 1.7 mmol) in 25 ml dry THF, was added, under nitrogen at -70° C, s solution of 2.4 M n-butyllithium (0.7 ml, 1.7 mmol) in n-hexane. The reaction mixture was allowed to warm up to room temperature and stirred for one hour.

To the resulting anion solution was added, at -70° C, an excess of ACS grade acetone. After stirring to room temperature, the reaction mixture was poured into about 50 ml cold water and extracted repeatedly with ether. The ether layer was dried over anhydrous $MgSO_4$ and evaporated off ether. The residue was distilled under vacuum to give 0.25 g (85% yield) of title compound 73a, as a colorless liquid, bp. 57°C (0.16 mm), nmr: δ 1.98 (s, 3H), δ 1.93 (center of br. m, 2H) and δ 2.90 (center of brm m, 2H).

Anal. calcd for $C_8H_{14}S_2$: C, 55.12; H, 8.10; S, 36.78.
Found: C, 55.02; H, 8.15; S, 36.55.

Preparation of diphenyl keteneacetal of 1,3-dithiacycloheptane (73b).

To a stirring solution of 2-trimethylsilyl-1,3-dithiacycloheptane 72c (0.4 g., 0.98 mmol) in 20 ml of dry THF was added, under nitrogen at -70°C, a solution of 2.4 M n-butyllithium (0.8 ml, 0.98 mmol) in n-hexane. The reaction mixture was allowed to stir at room temperature for 1 hour. To the resulting anion solution was added, at -70°C, a solution of benzophenone (0.4 g, 2.2 mmol) in 3 ml dry THF. After stirring at room temperature for one hour, the solution was poured into 50 ml cold water and extracted repeatedly with ether. The combined ether layers were dried over $MgSO_4$ and evaporated off. The residue was chromatographed (Al_2O_3 II, benzene), and the obtained crystals were recrystallized from benzene-pet. ether to give 0.15 g (53% yield) of diphenyl keteneacetal of 1,3-dithiacycloheptane 73b, as a white crystal, mp. 162-163° C, nmr: δ 1.97 (center of br. m, 4H), δ 2.97 (center of br. m, 4H) and δ 7.22 (br. s, 10 H).

Anal. calcd for $C_{18}H_{18}S_2$: C, 72.44; H, 6.08; S, 21.48.
Found: C, 72.33; H, 6.01; S. 21.39.

Preparation of bis(vinylmercapto)methane (67).

To a stirring suspensed mixture of powdered sulfur (7.68 g, 0.24 mole) in 40 ml dry tetrahydrofuran was added, under nitrogen at -70° C, a solution of vinyllithium (100 ml, 0.24 mole) in ether. The mixture was allowed to rise to room temperature. After stirring for 1 hour, the mixture was cooled at -70° C. To the cold mixture dibromomethane (21.12 g, 0.12 mole) was added dropwise. The reaction mixture was then stirred at room temperature for 2 hours. The mixture was poured into ca 50 ml cold water and extracted repeatedly with ether. After dried and removed the solvent, the residue was distilled under vacuum to give 8.23 g (52.4% yield) of the title compound 67 as a colorless liquid, bp. 78-79° (11 mm). ^{1}H nmr (CCl_4): δ 3.92 (s, 2H), ABX type at δ 5.08-5.37 (m, 4H) and δ 6.19-6.63 (m, 2H). ^{13}C nmr (CCl_4): 131.48 ppm (α-C), 112.76 ppm (β-C) and 34.56 ppm. IR (CCl_4): 3100 cm^{-1}, 1580 cm^{-1}. UV: λ_{max}^{EtOH} 227 (ϵ 4759). Mass spectrum: m/e (M^+, 11.5%), 104 (21.5%), 73 (83.1%) 58 (24%), 45 (100%).

Anal. calcd for $C_5H_8S_2$: C, 45.41; H, 6.10; S, 48.49.
Found: C, 45.44; H, 6.21; S, 48.47.

Reaction of bis(vinylmercapto)methane with n-butyllithium.

a) Quenching with trimethylsilyl chloride.

To a stirring solution of bis(vinylmercapto)methane (0.264 g, 2 mmol) in 20 ml dry tetrahydrofuran was added, under nitrogen at -70°, a solution of n-butyllithium (9 ml, 2.1 mmol) in n-hexane. The reaction mixture was allowed to hold at room temperature for 1 hour. To the resulting straw-yellow anion was added at -70°, an excess of trimethylsilyl chloride. The mixture was then stirred at room temperature for 1 hour. After workup in the usual manner, the residue was distilled under reduced pressure to give bis(vinylmercapto)methyl trimethylsilane (75a) in quantitative yield; yellow liquid, bp. 68-70°C (11 mm); nmr (CCl_4, no reference): δ 0.00 (s, 9H), δ 3.17 (s, 1H). ABX type at δ 4.96-5.25 (m, 4H) and δ 6.11-6.55 (m, 2H).

Anal calcd for $C_8H_{16}S_2Si$: C, 47.00; H, 7.89;
S, 31.37; Si, 13.74.

Found: C, 46.92; H, 7.77; S, 31.40; Si, 13.68.

b) Quenching with benzophenone.

To a stirring solution of bis(vinylmercapto)methane (0.36 g, 2.8 mmol) in 20 ml dry tetrahydrofuran was added, under nitrogen at -70°C, a solution of 2.45 M n-butyllithium (1.5 ml, 2.9 mmol) in n-hexane. The reaction mixture was allowed to stir at room temperature for 1 hour. To the resulting anion solution was added at

-70° C, a solution of benzophenone (0.46 g, 2.5 mmol) in 3 ml dry tetrahydrofuran. The reaction mixture was held at room temperature for 1 hour. After workup in the usual way, the residue was chromatographed (alumina III, benzene) to give the carbinol 75b in 85% yield. nmr (CCl_4): δ 3.32 (s, 1H, exchanged with D_2O), δ 4.90 (s, 1H), δ 5.03-5.32 (m, 4H), δ 6.03-6.47 (m, 2H), δ 7.12-7.57 (m, 10H).

Anal. calcd for $C_{18}H_{18}OS_2$: C, 68.75; H. 5.77; O, 5.77; S, 20.40.

Found: C, 68.70; H, 5.69; S, 20.28.

Preparation of diphenyl keteneacetal of bis(vinylmercapto)methane (76).

To the stirring solution of bis(vinylmercapto)methyl trimethylsilane (75a) (0.15 g, 0.73 mmol) in 20 ml dry THF was added, under nitrogen at -70° C, a solution of 2.45 M of n-butyllithium (0.3 ml, 0.75 mmol) in n-hexane. The reaction mixture was allowed to rise to room temperature for one hour. The resulting blood-red anion solution was quenched with a solution of benzophenone (excess) in THF at -70° C. Before pouring into 50 ml of cold water, the reaction mixture was stirred at room temperature for a further one hour. The mixture was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was chromatographed (silica gel, pet. ether) to give 0.19 g (ca. 92% yield) of the title compound, as yellow oil, nmr: δ 5.09-5.37 (m,4H), δ 6.31-6.74 (m,2H) and δ 7.20 (s,10H).

Anal. calcd for $C_{18}H_{16}S_2$: C, 72.93; H, 5.44; S, 21.63.
Found: C, 72.85; H, 5.41; S, 21.54.

The measurement of ^1H and ^{13}C nmr spectrum of lithioderivative of bis(vinylmercapto)methane.

Following the same procedure as the measurement of ^1H and ^{13}C nmr spectrum of 1,3-dithia-4,6-cycloheptadienyl anion, we sealed the nmr tube which contained 53 mg (0.4 mmol) of bis(vinylmercapto)methane and one equivalent of n-butyllithium in dry THF-d_8. ^1H nmr spectrum showed ABX system at δ 4.61-5.50 and δ 6.38-6.81, and a singlet at δ 2.40. ^{13}C nmr spectrum showed three signals at δ 148.7 ppm (C_α), δ 102.9 (C_β) and δ 25.5 ppm (C_2).

H/D exchange with 1,3-dithia-4,6-cycloheptadiene (43) and 1,3-dithiacycloheptane (70).

To a solution of a small piece of clean potassium (ca. 0.01 g, 0.26 mmol) in 8 ml of t-butanol-OD was added, under nitrogen at 70° C, an equimolar mixture of 43 (0.205 g, 1.58 mmol) and 70 (0.211 g, 1.58 mmol) in 2 ml of t-butanol-OD.

After stirring at this temperature for 24 hours, the resulting deep red solution was poured into ca. 50 ml of cold 15% NH_4Cl

aqueous solution and the organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum. Tlc analysis of distilled product showed two spots corresponding to compound 43 and 70. nmr: δ 2.00 (center of m), δ 2.80 (center of m) and δ 6.28 (br. s).

The same procedure was repeated for several different temperatures and times.

Four hours/75°C, nmr: δ 2.00 (m), δ 2.80 (m), δ 3.85 (s) and δ 6.28 (m).

Two hours/75°C, nmr: δ 2.00 (m), δ 2.80 (m), δ 3.85 (s) and δ 6.28 (m).

Ten mins./85°C, nmr: δ 2.00 (m), δ 2.80 (m), δ 3.85 (m) and δ 6.28 (m).

30 mins./35°C, nmr: δ 2.00 (m), δ 2.80 (m), δ 3.85 (s) and δ 6.28 (m).

H/D Exchange with 1,3-dithia-4,6-cycloheptadiene (43) and bis(vinylmercapto)methane (67).

To a solution of a small piece of clean potassium (ca. 0.01 g, 0.26 mmol) in 8 ml of t-butanol-OD was added, under nitrogen at 50°C, an equimolar mixture of 43 (0.135 g, 1.03 mmol) and 67 (0.135 g, 1.02 mmol) in 2 ml of t-butanol-OD.

After stirring at this temperature for 30 minutes, the resulting deep red solution was poured into ca. 150 ml of cold 15% NH_4Cl aqueous solution and extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled by water pump (67 has a low boiling point) and then by oil pump. Tlc analysis of distilled product showed two spots corresponding to compound 43 and 67. nmr: δ 3.92 (s), δ 4.13 (t, trace), δ 5.08-5.37 (m), δ 6.19-6.63 (m).

Photolysis of 1,3-dithia-4,6-cycloheptadiene.

The solution of 1,3-dithia-4,6-cycloheptadiene (0.65 g, 5 mmol) in 100 ml of dry THF in a 150 ml Pyrex tube equipped with a drying tube was immersed into ice water. The solution was irridiated with a 450 W Hanovia mercury lamp for two hours. Tlc indicated only one spot. The residue was distilled under vacuum after the removal of solvent to give 0.60 g (92% yield) of 2,4-dithiabicyclo(3,2,0)heptene 77.

Compound 77 formed as a colorless liquid, bp. 30-33°C (0.05 mm). ^1H nmr: δ 5.77 (s, 2H), δ 5.00 (s, 2H), δ 3.8 (center of AB system, 2H, J's, 12 Hz). ^{13}C nmr: δ 134.6, δ 61, δ 35.8. Mass spectrum: m/e: 130 (M^+, 22%), 103 (17%), 84 (100%).

Anal. calcd for $C_6H_6S_2$: C, 46.12; H, 4.64; S, 49.25.

Found: C, 46.01; H, 4.59; S. 49.13.

Photolysis of tetradeuteroderivative of 1,3-dithia-4,6-cycloheptadiene.

Following the preceeding procedure, a solution of tetradeuteroderivative of 1,3-dithia-4,6-cycloheptadiene (0.402 g, 3 mmol) in THF was irridiated for 2 hours. The residue was distilled after the removal of solvent to give 0.37 g of 1,3,3,5-tetradeutero-2,4-dithiabicyclo(3,2,0)heptene, its nmr spectrum only consists of one singlet at δ 5.75.

4,7- Dideutero - 1,3-dithia-4,6-cycloheptadiene.

A small piece of clean potassium (ca. 0.01 g) was dissolved in 10 ml of t-butanol. A solution of tetradeutero (0.29 g, 2.16 mmol) in 5 ml t-butanol was added into the above t-butanol solution under nitrogen at 75°C (oil bath temperature). The resulting red solution was stirred for 30 minutes at 75°C before pouring into 40 ml of cold 15% of NH_4Cl solution, and the organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$. The residue was distilled after the removal of solvent to give 0.17g (59.6%) of H/D exchanged product. ^1H nmr: δ 4.13 (s, 2H), δ 6.30 (br. s, 2H). ^{13}C nmr: 127.9 ppm (peak height 12%), 124.2 ppm (peak height 58%), 39.3 ppm (peak height 37%).

Equilibrium Acidity

a) 1,3-dithiacycloheptanyl anion with 1,3-dithia-4,6-cycloheptadiene.

To a stirring solution of 1,3-dithiacycloheptane (0.27 g, 2 mmol) in 40 ml of dry tetrahydrofuran was added, at -70° C under nitrogen, a solution of 2.45 M n-BuLi (0.9 ml, 2 mmol) in n-hexane. The resulting colorless anion solution was allowed to warm at room temperature for one hour, and a solution of 43 (0.26 g, 2 mmol) in 4 ml dry THF was then added at -70° C. The reaction mixture was stirred at room temperature for about 10 minutes, the resulting red solution was held at ice bath temperature for 2 hours. An excess of freshly distilled trimethylsilyl chloride was added quickly at -70° C. Before poured into 100 ml of cold water, the reaction mixture was stirred at room temperature for one hour. The mixture was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum to give 0.3338 g of yellow oil. nmr: δ 0.25 (s), δ 2.00 (m), δ 2.80 (m), δ 3.13 (s), δ 3.82 (s), δ 4.13 (s) and δ 6.23-6.77 (m). The relative areas of singlets at δ 3.13 (compound 53b), 2.5, 6, 7, 4; at δ 3.82 (compound 70), 14, 30, 44, 22: at δ 4.13 (compound 43), 5, 12, 17, 8.1. Based upon this analysis, the product contained 22% of 1,3-dithia-4,6-cycloheptadiene, 57.5% of 1,3-dithiacycloheptane and 20.4% of 2-trimethylsilyl-1,3-dithia-4,6-cycloheptadiene.

b) Bis(vinylmercapto)methyl anion with 1,3-dithia-4,6-cycloheptadiene.

To a stirring solution of bis(vinylmercapto)methane (0.264 g, 2 mmol) in 40 ml of dry THF was added, under nitrogen at -70°C, a solution of 2.45 M n-BuLi (0.82 ml, 2 mmol) in n-hexane. The resulting anion solution was allowed to stir at room temperature for one hour, and a solution of 1,3-dithia-4,6-cycloheptadiene (0.26 g, 2 mmol) in 4 ml of dry THF was then added at -70°C. The reaction mixture was allowed to warm to room temperature for 10 minutes and then held at ice bath temperature for 2 hours.

To the resulting solution was added at -70°C, an excess of freshly distilled trimethylsilyl chloride. Before pouring into 40 ml of cold water, the reaction mixture was stirred at room temperature for one hour. The mixture was extracted with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled by water pump (to distill out bis(vinylmercarpto) methane first), followed by oil pump. nmr: δ 0.25 (s), δ 3.18 (s, 9.1H), δ 3.97 (s, 35H), δ 4.15 (s, 21H), δ 5.11-5.40 (m) and δ 6.19-6.63 (m).

Based on nmr analysis, the product contained 28.3% of <u>43</u>, 47.2% of <u>67</u> and 24.5% of <u>53b</u>.

H/D exchange reaction with 2-methyl-1,3-dithia-4,6-cycloheptadiene and 1,3-dithiacycloheptane.

To a solution of a small piece of clean potassium (ca. 0.01 g, 0.26 mmol) in 8 ml of t-butanol-OD was added, under nitrogen at 75° C, an equimolar mixture of 2-methyl-1,3-dithia-4,6-cycloheptadiene (0.4 g, 2.78 mmol) and 1,3-dithiacycloheptane (0.38 g, 2.8 mmol) in 3 ml of t-butanol-OD.

After stirring at 75° C for three and a half hours, the resulting red solution was poured into ca. 150 ml of cold 15% NH_4Cl aqueous solution, and the organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$. The residue was distilled under vacuum after the removal of the solvent. Tlc indicated two spots corresponding to compound 53d and compound 70. nmr (CCl_4): δ 1.71 (m, CH_3, 5.8 H), δ 4.30 (q, H_2, 0.45 H), δ 6.08 (A_4 system, vinyl, 5.4 H) for compound 53d. Another integration showed that at δ 6.08 (vinyl) is 145 H and 149 H, at δ 4.30 (H_2) is 16 H and 14 H.

δ 3.73 (m, H_2, 19 H and 17 H), δ 2.05 (m, CH_2, 155 H and 155 H), δ 2.75 (m, CH_2, 155 H and 155 H) for compound 70.

Calculations:	Actual	Theoretical
a. H_2 in 53d	16; 14	1 (36.3; 37)
vinyl	145; 149	4 (145; 149)

Calculations:

	Actual	Theoretical
b. H_2 in <u>53d</u>	0.45	1(1.933)
vinyl	5.4	4(7.73)
methyl	5.8	3(5.8)

Data obtained from integration b, using the CH_3 signal, indicate certain degree of vinylic deuteration.

$C_{\underline{53d}}$ based on vinyl integration: a. 16/36.3 = 44.1%

14/37.3 = 37.5%

b. <u>0.45/1.35 = 33.3%</u>

average = 38.3%

based on methyl integration b. 0.45/1.933 = 23.3%

	Actual	Theoretical
H_2 in <u>70</u>	19 ; 17	1(77.5 ; 77.5)
$(CH_2)_2$	155 ; 155	2 (155 ; 155)

19/77.5 24.5%

<u>17/77.5 21.9%</u>

average = 23.2% with 2H,

or 76.8% deuterium exchange for 2 H, that means 38.4% deuterium exchange for 1 H, therefore the Conc. of unexchanged material (corrected value) 61.6%

$$k = 1/t \times 2.303 \times \log C_0/C$$

where C_0 100%, $C_{\underline{53d}}$ 38.3% (based on vinyl), $C_{\underline{70}}$ 61.6%

$C_{\underline{53d}}$ 23.3% (based on methyl)

$$k_{\text{relative}} = \frac{k_{\underline{53d}}\ \text{(faster)}}{k_{\underline{70}}\ \text{(slower)}} = \frac{1/t\ 2.303\ \log 100/38.3}{1/t\ 2.303\ \log 100/61.6} = \frac{0.41681}{0.21031} = 2$$

$$k_{\text{relative}} = \frac{k_{\underline{53d}}\ \text{(faster)}}{k_{\underline{70}}\ \text{(slower)}} = \frac{\log 100/23.3}{\log 100/61.6} = \frac{0.63174}{0.21031} = 3$$

mass spectrum of 2-methyl-1,4-dithia-2,5-cycloheptadiene: m/e 144 (1.3%), 145 (7.7%, D_1), 146 (16.4%, D_2), 147 (13.0%, D_3). Mass spectrum of 1,3-dithiacycloheptane: m/e 134 (6.7%), 135 (35.1%, D_1), 136 (56.6%, D_2).

H/D Exchange reaction with 2-methyl-1,3-dithia-4,6-cycloheptadiene and bis(vinylmercapto)methane.

To a solution of a small piece of clean potassium (ca. 0.01 g) in 8 ml of t-butanol-OD was added, under nitrogen at 50° C, an equimolar mixture of 2-methyl-1,3-dithia-4,6-cycloheptadiene (0.14 g, 1 mmol) and bis(vinylmercapto)methane (0.13 g, 1 mmol) in 2 ml of t-butanol-OD.

After stirring at 50° C for one hour, the resulting solution was poured into 100 ml of cold 15% NH_4Cl aqeuos solution, and the organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$. Tlc indicated two spots corresponding to compound 67 and compound 53d. The residue was distilled under water pump after the removal of solvent, and followed distillation by oil pump. Nmr (CCl_4): δ 1.71 (d, CH_3, 55 H; 56 H), δ 4.33 (q. H_2, 17 H ; 17 H) for compound 53d and δ 3.88 (m, H_2, 11 H ; 11 H), δ 5.08-5.28 (m, CH_2, 51 H ; 50 H) for compound 67, a multiplet at δ 5.98-6.44 is for 53d and 67.

Calculation:

53d	actual	theoretical
H_2	17 ; 17	1 (18.33 ; 18.67)
CH_3	55 ; 56	3 (55 ; 56)

Hence: C_{53d} 17/18.33 = 92.74%

17/18.67 = 91.06%

average 91.9%

67	actual	theoretical
H_2	11; 11	1 (25.5 ; 25)
CH_2	51 ; 50	2 (51 ; 50)

11/25.5 = 43.2%

11/25 = 44%

average 43.6% unexchanged material left.

That means, 56.4% exchanged for 2 hydrogens or corrected per hydrogen 28.2% exchanged. Therefore, corrected C_{67} is 71.8% .

$$k_{relative} = \frac{k(faster)}{k(slower)} = \frac{1/t\ 2.303\ \log 100/71.8}{1/t\ 2.303\ \log 100/91.9} = \frac{0.14395}{0.03663} = 3.93$$

Mass spectrum of 2-methyl-1,4-dithia-2,5-cycloheptadiene (<u>53d</u>): m/e 144 (19.8%), 145 (5.5%, D), 146 (2.2%, D_2), mass spectrum of <u>67</u>: 132 (1.8%), 133 (1.8%), 133 (6.0%, D), 134 (4.5%, D_2).

<u>H/D exchange reaction with 1,3-dithiacycloheptane and bis(vinylmercapto)methane.</u>

To a solution of a small piece of clean potassium (ca. 0.01 g) in 8 ml of t-butanol-OD was added, under nitrogen at 50° C, an equimolar mixture of 1,3-dithiacycloheptane (0.13 g, 1 mmol) and bis(vinylmercapto)methane (0.13 g, 1 mmol) in 3 ml of t-butanol-OD.

After stirring at 50° C for 2 hours and 40 minutes, the resulting solution was poured into 100 ml of 15% cold NH_4Cl aqueous solution, and the organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. Tlc indicated two spot corresponding to compound <u>67</u> and compound <u>70</u>. The residue was distilled under water pump to remove the lower bp of bis(vinylmercapto)methane first, then followed by oil pump.

Nmr (CCl_4): δ 2.04 (center of m, 146 H; 145 H), δ 2.72 (center of m, 146 H; 145 H) and δ 3.70 (s, H_2, 54 H; 55 H) for compound <u>70</u>; δ 3.84 (m, H_2, 20 H), δ 5.04-5.24 (m, CH_2, 194 H) and δ 6.14-6.40 (m) for compound <u>67</u>.

Calculations:

67	actual	theoretical
H_2	20	1 (97)
CH_2	194	2 (194)

Hence: $C_{\underline{67}}$ 20/97 = 20.6%

70	actual	theoretical
H_2	54 ; 55	1 (73 ; 72.5)
CH_2	146 ; 145	2 (146 ; 145)

Hence: $C_{\underline{70}}$ 54/73 = 74%

55/72.5 = 76%

average 75%

$$k_{\text{relative}} = \frac{k_{\underline{67}}}{k_{\underline{70}}} = \frac{1/t \;\; 2.303 \;\; \log 100/20.6}{1/t \;\; 2.303 \;\; \log 100/75} = \frac{0.68607}{0.12483} = 5.5$$

Dehydration of diphenyl (1,3-dithiepin-2-yl) carbinol (53c)

The solution of carbinol 53c (0.93 g, 3 mmol) and a catalytic amount of p-toluenesulfonic acid (ca. 0.1 g) in 50 ml of distilled benzene was refluxed in a Dean-Stark Apparatus under nitrogen for three hours. The reaction mixture was poured into ice water and the organic material was extracted with ether. The ether layers were combined and dried over anhydrous $MgSO_4$ and evaporated off. The residue was chromatographed on silica gel and eluted with pet. ether to give 0.61 g of the ring enlarged product 80. After recrystallization from methanol to form a white crystal having mp. 101-102°C; nmr: δ 6.75 (s, 1H), δ 7.21 (br. s, 5H), δ 7.4 (br. s, 4H) and an underlying multiplet of about $H between δ 6.85 and δ 7.5; UV: λ_{max}^{EtOH} 229 nm (ε 21,700), 298 nm (ε 15,340); mass spectrum: M^+ at 294 (100%).

Anal. calcd for $C_{18}H_{14}S_2$: C, 73.43; H, 4.79;
S, 21.78.

Found: C, 73.21; H, 4.65; S, 21.64.

Dehydration of diphenyl (1,3-dithiacycloheptan-2-yl) carbinol (72b).

The solution of carbinol 72b (1.1 g, 3.5 mmol) and a catalytic amount of p-toluenesulfonic acid (ca. 0.15 g) in 50 ml distilled benzene was refluxed in Dean-Stark trap under nitrogen for 3 hours. After concentration under reduced pressure, the reaction mixture was worked up in the usual manner. The residue was chromatographed (silica gel, pet. ether) to give 0.6 g, of diphenyl ketenethioacetal (73b) and 0.41 g of ring enlarged product 87. Nmr: δ 1.75 (br. m, 4H), δ 2.68 (br. m, 4H), δ 6.57 (s, 1H), δ 7.23 and δ 7.35 (s and s, ca. 9H).

Anal Calcd for $C_{18}H_{18}S_2$: C, 72.44; H, 6.08;
S, 21.48.

Found: C, 72.37; H, 6.01; S, 21.32.

Preparation of 2-methyl-1,3-dithiane (89).

To a stirring solution of 1,3-dithiane (purity 97%, 5 g, 40 mmol) in 100 ml of dry THF was added, under nitrogen at -70° C, a solution of 2.45 M of n-BuLi (17 ml, 41 mmol) in n-hexane. The reaction mixture was allowed to stir at room temperature for one hour. To the resulting solution was added an excess of methyl iodide at -70° C. Before pouring into 100 ml of cold water, the reaction mixture was stirred at room temperature for another hour. The reaction mixture was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum to give 5.04 g (94% yield) of title compound, yellow liquid, bp. 45° C (0.05 mm), nmr (CCl_4): δ 1.40 (d, 3H), δ 1.61-2.23 (m), δ 2.72-2.94 (m), δ 4.08 (q, 4H).

Preparation of methyl (2-methyl-1,3-dithian-2-yl) carbinol (88).

To a stirring solution of 2-methyl-1,3-dithiane (1.32 g 9.6 mmol) in 100 ml dry THF was added, under nitrogen at -70° C, a solution of 2.45 M n-BuLi (3.9 ml, 9.6 mmol) in n-hexane. The reaction mixture was allowed to stir at room temperature for one hour. The resulting reaction solution was quenched with an excess of acetaldehyde, and was warmed to room temperature for another one hour. After pouring into 150 ml of cold water, the reaction mixture was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was chromatographed on alumina (grade II) and eluted with benzene to give 1.21 g (71% yield) of the title compound, white crystal, mp 59-60° C after recrystallization from pet. ether. Nmr (CCl_4): δ 1.27 (d,3H), δ 1.34 (s,3H), δ 4.16 (quintet, 1H). Ir (CCl_4): 3450 cm^{-1} (OH, weak).

Anal. calcd for $C_7H_{14}OS_2$: C, 47.15; H, 7.91; O, 8.97; S, 35.96.

Found: C, 46.98; H, 7.87; s, 35.92.

Dehydration of methyl (2-methyl-1,3-dithian-2-yl) carbinol (88).

The solution of carbinol 88 (3 g, 16.8 mmol) and a catalytic amount of p-toluenesulfonic acid (ca. 0.2 g, 1.16 mmol) in 200 ml of benzene was refluxed in a Dean-Stark apparatus under nitrogen for 4 hours. Before pouring into 200 ml of 15% aqueous $NaHCO_3$, the reaction solution was concentrated under reduced pressure. The reaction mixture was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was chromatographed (silica gel, pet. ether) to give 1.88 g (70% yield), as colorless liquid, bp. 52-53° C (0.05 mm) and 0.75 g (25%) of starting material. Nmr: δ 3.30 (t, 4H, J's 7 Hz), δ 2.06

(quintet, 2H, J's 7 Hz) and δ 1.78 (s, 6H). Ir (neat): 1613 cm^{-1} (C=C).

Anal calcd for $C_7H_{12}S_2$: C, 52.45; H, 7.55;
S, 40.00.

Found: C, 52.48; H, 7.39; S, 39.87.

Preparation of methyl (2-methyl-1,3-dithiepin-2-yl) carbinol (95).

To a stirring solution of 2-methyl-1,3-dithiepin (0.886 g, 6.15 mmol) in 25 ml dry THF was added, under nitrogen at -70° C, a solution of 2.45 M n-BuLi (2.54 ml, 6.15 mmol). The reaction mixture was allowed to stir at room temperature for one hour.

To the resulting solution was added an excess of acetaldehyde at -70° C. After stirring at room temperature for one hour, the reaction mixture was poured into 150 ml of cold water and extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum to give 0.95 g (82.5% yield) of the title compound, as yellow oil, bp. 83° C (0.05 mm), nmr: δ 6.20 (br s, 4H), δ 4.06 (q, 1H), δ 2.72 (br s, exchanged with D_2O), δ 1.61 (s, 3H) and δ 1.31 (d, 3H). Ir (neat): 3448 cm^{-1}, 3145 cm^{-1}, 1615 cm^{-1}.

Anal. calcd for $C_8H_{12}OS_2$: C, 51.03; H, 6.42;
O, 8.50; S, 34.05.

Found: C, 50.84; H, 6.39; S, 33.98.

Dehydration of methyl-(2-methyl-1,3-dithiepin-2-yl) carbinol (95).

The solution of carbinol 95 (0.31 g, 1.65 mmol) and a catalytic amount of p-toluenesulfonic acid (ca. 0.1 g) in 50 ml of distilled benzene was refluxed in a Dean-Stark Apparatus under nitrogen for three hours. The reaction mixture was checked by GC and tlc. No o-xylene appeared on GC, and the tlc showed a series of spots. The material seemed decomposed, no further study was done.

Preparation of methyl (2-methyl-1,3-dithiepin-2-yl) methanol (95a).

To the stirring solution of 2-methyl-1,3-dithiacycloheptane (72a) (1 g, 6.8 mmol) in 100 ml dry THF was added, under nitrogen at -70° C, a solution of 2.45 M n-BuLi (2.8 ml, 6.8 mmol) in n-hexane. The reaction mixture was allowed to warm at room temperature for one hour. To the resulting solution was added an excess of acetaldehyde at -70° C. After stirring to room temperature for one hour, the reaction mixture was worked up in the usual manner. The residue was chromatographed (Al_2O_3, benzene) to give 1.1 g (85% yield) of the title compound, as a pale yellow liquid, bp. 103° C (1.5 mm). Nmr: δ 1.21 (d,3H), δ 1.46 (s,3H), δ 1.9 (br. m, 4H), δ 2.86 (br. m, ca 5H) and δ 3.74 (q,1H). Ir (neat): 3480 cm^{-1} (OH).

Anal. calcd for $C_8H_{16}OS_2$: C, 49.96; H, 8.39;
O, 8.32; S, 33.34.

Found: C, 49.87; H, 8.28; S, 33.26.

Dehydration of methyl (2-methyl-1,3-dithiepin-2-yl) methanol (95 a).

The mixture of carbinol 98 (0.8 g, 4.2 mmol) and a catalytic amount of p-toluenesulfonic acid (ca 0.01 g) in 100 ml of benzene was refluxed under nitrogen in a Dean-Stark Apparatus for 4 hours. After concentrated under reduced pressure, the reaction mixture was poured into 150 ml of cold 15% of aqueous $NaHCO_3$, and worked up in the usual manner. The residue was chromatographed (silica gel, pet. ether) to give ca 0.3 g of colorless liquid which has identical R_f on tlc, retension time on GC and nmr spectrum with 1,2-dithiane (71). Nmr: δ 1.98 (m,4H) and δ 2.80 (m, 4H).

PART II

Preparation of 1,4-dithia-2-cycloheptene (102).

To a stirring solution of 23 g sodium (1 mole) in 500 ml absolute ethanol was added 54 g (0.5 mole) of propane-1,3-dithiol under nitrogen. The reaction mixture was heated to reflux and 50 g (0.515 mole) of cis-1,2-dichloroethylene was added slowly over a period of five hours. The reaction mixture was refluxed overnight. After cooling to room temperature, the reaction mixture was poured into 2 liters of cold brine water and the organic material was extracted repeatedly with ether. Some polymeric material did not dissolve in ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The oily residue was distilled under vacuum to give 63.4 g (48% yield) of the title compound, as colorless liquid, bp. 91-93° C (15 mm). Nmr: δ 2.17 (q,2H), δ 3.50 (t,4H) and δ 5.95 (s,2H); ir (neat): 3018 cm^{-1}, 1530 cm^{-1}; UV: λ 294 nm (shoulder, ϵ 4326), λ_{max}^{EtOH} 287 nm (ϵ 4805) and λ 235 nm (shoulder, ϵ 1473); mass spectrum: m/e: 132 (M^+), 103, 99, 73, 45.

Anal calcd for $C_5H_8S_2$: C, 45.41; H, 6.10; S, 48.49.
Found: C, 45.32; H, 5.99; S, 48.40.

Preparation of 1,4-dithia-2-cyclohepene-6-ol (106).

In a three 1,3-necked flask equipped with a mechanic stirrer, reflux condenser and dropping funnel are placed two 1 absolute ethanol. Sodium (166 g, 7.22 moles) was added in portions and after sodium went into solution, 1,3-dimercapto-2-propanol (202 g, 1.63 moles) was added slowly under nitrogen at room temperature. The solution was heated to reflux. One hour later, cis-1,2-dichloroethylene (160 g, 1.65 moles) was added through the dropping funnel over a period of 8 hours to the solution. After refluxing overnight, ethanol was distilled out (ca. 1800 ml) and the concentrated reaction mixture was poured into 2 liters of cold brine water. The organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The oily residue was distilled under vacuum to give 146 g (60.5% yield) of the title compound; bp. 85-100°C (1 mm). After recrystallization from benzene-pet. ether to give white crystal, mp. 53-54°C; ^{1}H nmr: δ 3.06 (s, 1H), δ 3.35 - 3.351 (m, 5H), δ 6.03 (2H); ^{13}C nmr: δ 121, δ 69.5, δ 38.4; ir: 1613 cm^{-1} (C=C), 3509 cm^{-1} (OH).

Anal. calcd for $C_5H_8OS_2$: C, 40.51; H, 5.44;
O, 10.79; S, 43.25.

Found: C, 40.44; H, 5.28; S, 43.19.

Preparation of 1,4-dithia-2,5-cycloheptadiene (44).

A) Pummerer Reaction.

To a stirring solution of 1,4-dithia-2-cycloheptene (102) (7 g, 53 mmol) in glacial acetic acid (65 ml) was added slowly at 5°C, a solution of 30% H_2O_2 (6.5 ml). After stirring for one and one half hours (the starting material disappeared on tlc), the solvent was removed under reduced pressure and the oily residue was dissolved in 50 ml acetic anhydride. The solution was heated to reflux under nitrogen. The solution turned dark and some brown tar was formed. Tlc indicated the formation of a less polar compound (solvent system: pet. ether/benzene 2 : 1). After refluxing for 3 hours, the dark mixture was poured on 500 ml cold water and left overnight in order to hydrolyze the acetic anhydride. The acetic acid was neutralized with Na_2CO_3 and the organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum to give 3.85 g (ca. 55% yield) of a constant boiling oil, 90-92° C, (15 mm), which contained 65% of the title compound, 22% of the starting material and 12% of other product (based on GC analysis).

B. Elimination of Benzenesulfonate

A mixture of dry powdered potassium hydroxide (2.27 g, 50.6 mmol) and 300 ml anhydrous ether was placed in a 500 ml, three necked flask. To the above ethereal mixture was added, under nitrogen at 0-5° C, 6 g of 1,4-dithia-2-cyclohepten-6-ol (40.5 mmol) which was dried under high vacuum before using. After stirring for one hour (the alcohol disappeared on tlc), a solution of benzenesulfonyl chloride (4.75 g, 40.6 mmol) in 50 ml anhydrous ether was then added dropwise. After stirring for 2 hours, potassium t-butoxide (9.10g, 81.2mmol) was quickly suspended to the ethereal solution. The reaction mixture was allowed to rise gradually to room temperature and was stirred for a further three hours. (Tlc indicated a less polar spot). The reaction mixture was poured into 500ml cold aqueous NH_4Cl, and the organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was contained ca. 90% of desired product (based upon GC analysis). The residue was distilled under vacuum to give 4.38g (83.1% yield) of 1,4-dithia-2,5-cycloheptadiene as a yellow oil, bp. 31°C (0.12mm). ^{1}H nmr (60MHz): δ 3.70 (d,2H), δ 5.80-6.75 (m,4H): ^{13}C nmr: δ 135.3, δ 125.1, δ 123.2, δ 117.8, δ 33.1: ir ($CDCl_3$): 3020cm^{-1}, 2960cm^{-1}, 2920cm^{-1}, 1608cm^{-1}: UV; 310nm (sh, ϵ1393) λ_{max}^{EtOH} 285nm (ϵ3366): mass spectrum, m/e; 130 (M^+ 60%), 129 (32%), 103 (100%), 97 (39%).

^{1}H nmr (220MHz): δ 5.83 (d,d, H_3, $J_{2,3}$ = 10.2Hz, $J_{3,5}$ = 1.74Hz)
δ 6.03 (d,d, H_5, $J_{5,6}$ = 9.2Hz, $J_{3,5}$ = 1.74Hz)
δ 6.29 (d, H_2, $J_{2,3}$ = 10.2Hz)
δ 6.47 (c. of t,d, H_6, $J_{5,6}$ = 9.2Hz, $J_{6,7}$ = 7Hz).

Anal. calcd for $C_5H_6S_2$: C, 46.12; H, 4.64; S, 49.24
Found: C, 45.97; H, 4.62; S, 49.04.

Reaction of 1,4-dithia-2,5-cycloheptadienyl anion with electrophiles.

A. Trimethylsilyl chloride.

To a stirring solution of 1,4-dithia-2,5-cycloheptadiene (1.3 g, 10 mmol) in 100 ml of dry THF was added, under nitrogen at -70° C, a solution of 2.45 M n-BuLi (5 ml, 12 mmol). The resulting deep red anion solution was slowly raised to room temperature and stirred for 20 minutes. The red solution changed to brown-green and a muddy-like solid was developed when the solution was warmed at -15° C.

To the resulting solution was added at -70° C, an excess of trimethylsilyl chloride. The reaction mixture was allowed to stir at room temperature for one hour before pouring into 200 ml of cold water. After work up in the usual manner, the residue contained 60.1 - 66% of trimethylsilylacetyl 3-mercapto-2-propenyl sulfide (112) (based on GC analysis), and was distilled under vacuum to give 1.03 g (51% yield) of compound 112, as a yellow-golden liquid, bp. 55° C (0.12 mm). Nmr: δ 0.20 (s, 9H), δ 1.72 (t, 1H), δ 3.39 (br. t., 2H), δ 5.98-6.54 (m, 2H). Ir (neat): 3077 cm^{-1} (C=C), 3941 cm^{-1} (alkane), 2577 cm^{-1} (SH), 2128 cm^{-1} (C≡C), 1613 cm^{-1} (C=C). ^{1}H nmr (220 M Hz): δ 1.22 (t, H_a, $J_{a,b}$ 7.8Hz) δ 2.97 (d.t., 2 H_b, $J_{b,c}$ 7.8Hz, $J_{b,d}$ 1Hz) δ 5.61 - 5.75 (m, H_c, $J_{c,d}$ 9 Hz, $J_{c,b}$ 7.8 Hz)

δ 5.81 (d.t., H_d, $J_{c,d}$ 9Hz, $J_{b,d}$ 1 Hz): ^{13}C nmr: 0.2 ppm (-SiMe$_3$) 22.4 ppm (-CH$_2$-SH), 91.3 ppm, 101.9 ppm (C≡C) 123.5 ppm, 131.5 ppm (olefin). Mass spectrum, m/e : 202 (M^+ 10.3%), 169 (M^+-SH, 7.3%), 115 (55.6%), 97 (100%), 83 (-SiM$_3$, 8.8%).

Anal. calcd for $C_8H_{14}S_2Si$: C, 47.47; H, 6.97;
S, 31.68; Si, 13.88.

Found: C, 47.25; H, 6.79; S, 31.59; Si, 13.56.

B. Methyl iodide.

To a stirring solution of 1,4-dithia-2,5-cycloheptadiene (0.65 g, 5 mmol) in 25 ml of dry THF was added, under nitrogen at -70° C, a solution of 2.45 M n-BuLi (2.3 ml, 5 mmol) in n-hexane. The reaction mixture was stirred at room temperature for about 20 minutes. The deep red solution changed to brown-green and a muddy-like solid was observed when the temperature was raised to -15° C. To the reaction solution was added, at -70° C, one equivalent of methyl iodide (0.71 g, 5 mmol). The reaction mixture was allowed to stir at room temperature for one hour before pouring into 150 ml of cold water. After work up in the usual manner, the residue was distilled under vacuum to give 0.32 g (ca. 40% yield) of dimethyl compound 114, a red liquid, bp. 51° C (0.04 mm). Nmr: δ 1.92 (s, 3H, -CH$_3{}^b$), δ 2.03 (s, 3H, -CH$_3{}^a$), δ 3.13 (d, 2H, H_c, J = 8 Hz), δ 5.67 (d, t, ^{1}H, H_d, J = 8 Hz and 9 Hz) and δ 6.17 (d, 1H, J = 9 Hz).

Ir: 3077 cm^{-1} (C=C), 2940 cm^{-1} (alkane), 2130 cm^{-1} (C≡C, very weak), 1613 cm^{-1} (C=C). Mass spectrum: m/e = 158 (M$^+$, 27%), 143 (M$^+$, CH$_3$, 30%), 111 (100%), 85 (34%), 71 (41%), 47 (18%), 39 (37%).

Anal. calcd for $C_7H_{10}S_2$: C, 53.12; H, 6.37; S, 40.51.
Found: C, 53.04; H, 6.28; S, 40.43.

C. Water.

To a stirring solution of 1,4-dithia-cycloheptadiene (1.3 g, 10 mmol) in 100 ml of dry THF was added, under nitrogen at -70° C, a solution of 2.45 M n-BuLi (5 ml, 12 mmol) in n-hexane. The resulting deep red solution was warmed gradually to room temperature for one hour. The red solution changed to brown-green and a muddy-like solid was observed in the reaction mixture.

The reaction mixture was poured into 200 ml of cold water. After workup in the usual manner, the residue showed the same R_f value and retention time on tlc and GC as the starting material. After distillation 87% of the starting material was recovered. The nmr spectrum was identical with 1,4-dithia-2,5-cycloheptadiene.

D. Methanol-OD.

To a stirring solution of 1,4-dithia-2,5-cycloheptadiene (1.3 g, 10 mmol) in 100 ml of dry THF, was added, under nitrogen at -70°C, a solution of 2.45 M n-BuLi (5 ml, 12 mmol) in n-hexane. The resulting deep red solution was stirred at room temperature for one hour. The brown-green solution was cooled at -70°C and an excess of methanol-OD was added. The reaction mixture was stirred at room temperature for a further hour before pouring into 200 ml of cold water. After workup in the usual manner, the residue was distilled under vacuum to give 1.05 g of yellow liquid, nmr: δ 3.75 (d, 4H) and multiplet at δ 6.08 - 6.73 (5H).

Deuteration of trimethylsilylacetyl 3-mercapto-2-propenyl sulfide (112).

A small piece of potassium hydroxide (ca. 0.01 g) was dropped in a solution of ca. 50 mg of sulfide 112 in 0.4 ml CCl_4 and four drops of D_2O. The mixture was shaken a few minutes and after eight minutes the solution was poured into ice water and extracted with ether. The ether layers were combined, dried over anhydrous $MgSO_4$. The residue was distilled under vacuum after the removal of solvent to give 2,3-dideutero-1,4-dithia-2,5-cycloheptadiene in quantitative yield. ^{1}H nmr (CCl_4): δ 3.73 (d, 2H), δ 6.07 (d, H_5, $J_{5,6}$ = 10 Hz), δ 6.50 (t, d, H_6, $J_{5,6}$ = 9 Hz, $J_{6,7}$ = 7 Hz). ^{13}C nmr: δ 135.7 (100%, C_6), δ 125.6 (24%, C_2), δ 123.8 (77%, C_5), δ 118.4 (24%, C_3) and δ 33.4 (94%, C_7). Mass spectrum: M^+ at m/e 132 (60%), 131 (M^+-1, 31.6%), 105 (100%) and 99 (38.8%). Ir (neat): 3049 cm^{-1} (alkene), 2941 cm^{-1} (alkane), 2890 cm^{-1} (C-D) and 1618 cm^{-1} (C=C).

Methylation of trimethylsilylacetyl 3-mercapto-2-propenyl sulfide (112).

To a stirring solution of compound 112 (0.39 g, 1.9 mmol) in 20 ml of dry THF was added, under nitrogen at -70° C, a solution of 2.25 M n-BuLi (0.61 ml, 2.0 mmol) in n-hexane. The reaction mixture was allowed to stir at 0° C for one hour, and methyl iodide (0.29 g, 2.0 mmol) was then added quickly. The reaction mixture was stirred at room temperature for one hour before workup. Tlc indicated only one spot. The residue was distilled by simple distillation under vacuum to give 3.89 g (94% yield) of the corresponding methylated product 113, bp. 61-63° C (0.12 mm). Nmr: δ 0.18 (s,9H), δ 2.08 (s,3H), δ 3.19 (d,2H) and δ 5.58 - 6.33 (m,2H).

Anal. calcd for $C_9H_{16}S_2Si$: C, 49.95; H, 7.45;
S, 29.63; Si, 12.98.

Found: C, 49.81; H, 7.33; S, 29.49; Si, 12.91.

3-Trimethylsilyl-1,4-dithia-2,5-cycloheptadiene (115a).

To the stirring solution of 1,4-dithia-2,5-cycloheptadiene (1.3 g, 10 mmol) in 100 ml of dry THF was added, under nitrogen at

-70°, a solution of 2.45 M n-BuLi (5 ml, 10 mmol) in n-hexane. The resulting deep red anion solution was allowed to warm at -35°C for one half hour. An excess of freshly distilled trimethylsilyl chloride was added quickly to the solution at -70°C, and the reaction mixture was allowed to rise gradually to room temperature. After stirring for a further hour, the mixture was worked up in the usual manner. The residue contained 55.4 - 69% of 3-trimethylsilyl-1,4-dithia-2,5-cycloheptadiene 115a and 14% of open-chained compound 112 (based on GC analysis). After distillation the residue gave 1.71 g (42% yield) of 3-trimethylsilyl-1,4-dithia-2,5-cycloheptadiene (115a), yellow liquid, bp. 61°C (0.18 mm). Nmr: δ 0.15 (s,9H,Si(CH$_3$)$_3$), δ 3.75 (d,2H,H$_7$,J$_{6,7}$=7 Hz), δ 6.00 (d,1H, H$_5$, J$_{5,6}$=9 Hz), δ 6.4 (s,1H, Hz) and δ 6.45 (center of d,t,1H,H$_6$, J$_{5,6}$=9 Hz, J$_{6,7}$= 7 Hz).

Anal. calcd for $C_8H_{14}S_2Si$: C, 47.46; H, 6.97;
S, 31.67; Si, 13.89.

Found: C, 47.33; H, 6.82; S, 31.54; Si, 13.68.

3-Methyl-1,4-dithia-2,5-cycloheptadiene (115b).

To the above deep red 1,4-dithia-2,5-cycloheptadienyl anion solution was added, under nitrogen at -70°C, an excess of methyl iodide. The reaction mixture was allowed to stir at room temperature for one hour before pouring into 200 ml of cold water. The organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum to give 0.9 g (ca. 66% yield) of 3-methyl-1,4-dithia-2,5-cycloheptadiene 115b, as red liquid, bp. 43°C (0.18 mm). Nmr: δ 1.94 (d, 3H, J = 2 Hz), δ 3.51 (d, 2H, H_7, J = 7 Hz), δ 5.84 (d, 1H, H_5, J = 9 Hz), δ 6.10 (s, 1H, H_2), δ 6.26 (center of d, t, 1H, H_6, J = 7 Hz and 9 Hz).

Anal. calcd for $C_6H_8S_2$: C, 49.96; H, 5.59; S, 44.45.
Found: C, 49.69; H, 5.47; S, 44.19.

Diphenyl (1,4-dithiepin-3-yl) carbinol (115 c).

To the above deep red 1,4-dithia-2,5-dithiacycloheptadienyl anion solution was added, under nitrogen at -70°C, a solution of benzophenone (1.82 g, 10 mmol) in 5 ml of dry THF. The reaction mixture was stirred at room temperature for one hour, followed by workup in the usual manner. The residue was chromatographed on alumina column (grade II) and eluted with 3 : 1 of pet. ether/benzene to give 0.97 g (31% yield) of diphenyl-(1,4-dithiepin-3-yl) carbinol 115c. After recrystallization from pet. ether-ether (3 : 1) gave white crystal, mp. 104.5 - 106°C. Nmr: δ 3.52 (s, 1H, exchanged with D_2O), δ 3.83 (d, 2H, H_7, J = 7 Hz), δ 5.81 (s, H_2), δ 6.11 (d, H_5, J = 8.5 Hz), δ 6.52 (center of m., H_6, J = 8.5 Hz and 7 Hz) and δ 7.33 (m, 10H).

Anal. calcd for $C_{18}H_{16}OS_2$: C, 69.20; H, 5.16; O, 5.12;
S, 20.52.

Found: C, 69.11; H, 5.04; S, 20.48.

3-Deutero-1,4-dithia-2,5-cycloheptadiene (115d).

To the above deep red 1,4-dithia-2,5-cycloheptadienyl anion was added, under nitrogen at -70°C, an excess of D_2O. The decolorized solution was allowed to stir at room temperature for one hour before pouring into 200 ml of cold water. The organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum to give 3-deutero-1,4-dithia-2,5-cycloheptadiene (115d) in 88% yield. Nmr: δ 3.75 (d, 2H), δ 6.03 (d, 1H), δ 6.29 (S, 1H) δ 6.47 (d,t,1H). Ir: 2890 cm^{-1}, 1620 cm^{-1}.

2-Trimethylsilyl-1,4-dithia-2-cycloheptene (127a).

To a stirring solution of 1,4-dithia-2-cycloheptene (0.66 g, 5 mmol) in 50 ml of dry THF was added, under nitrogen at -70°C, a solution of 2.4 M n-BuLi (2.1 ml, 5 mmol) in n-hexane. The resulting red solution was stirred for one hour at this temperature.

To the above anion solution was added at -70°C, an excess of trimethylsilyl chloride. The reaction mixture was allowed to stir at room temperature for another hour. After workup in the usual manner, the residue was distilled under vacuum to give 0.48 g (47.7%) of the title compound. Nmr: δ 0.10 (s, 9H), δ 2.17 (quintet, 2H, H_6, $J_{5,6}$, $J_{6,7}$ 6 Hz), δ 3.50 (t, 2H, $J_{6,7}$ 6 Hz), δ 3.53 (t, 2H, H_5, $J_{5,6}$ 6 Hz) and δ 6.12 (s, 1H, H_2).

Anal. calcd for $C_8H_{16}S_2Si$: C, 47.00; H, 7.89;
S, 31.37; Si, 13.74.

Found: C, 46.71; H, 7.80; S, 31.45; Si, 13.65.

However, the resulting anion solution was stirred at -40° - -70°C for half hour before an excess of trimethylsilyl chloride was added. After stirring at room temperature for one hour, the reaction mixture was worked up in the usual manner. Based on GC analysis, the products contained 33% of starting material and 61% of 2-trimethylsilyl-1,4-dithia-2-cycloheptene and 5.3% of ring-opened silylated compound.

Diphenyl (1,4-dithia-2-cyclohepten-2-yl) carbinol (127b).

To the above 1,4-dithia-2-cycloheptenyl anion solution was added, under nitrogen at -70°C, a solution of benzophenone (0.91 g 5 mmol) in 2 ml of dry THF. The reaction mixture was allowed to stir at room temperature for one hour. After workup in the usual manner, the residue was chromatographed on alumina (grade II) and eluted with benzene to give 0.83 g (ca. 53%) of the title compound, mp. 96.5 -

98° after recrystallization from pet. ether. Nmr: δ 2.14 (quintet, 2H, J's 6 Hz), δ 3.25 and δ 3.35 (superimposed t., 4H, J's 6 Hz), δ 3.72 (s, 1H exchanged with D_2O), δ 5.68 (s, 1H) and δ 7.31 (sharp m., 10H).

Anal. Calcd for $C_{18}H_{18}OS_2$: C, 68.75; H, 5.77;
O, 5.09; S, 20.39.

Found: C, 68.41; H, 5.42; S, 20.46.

<u>2-Methyl-1,4-dithia-2-cycloheptene (127 c).</u>

To the above 1,4-dithia-2-cycloheptenyl anion solution was added, under nitrogen at -70° C, an excess of methyl iodide. The reaction was allowed to stir at room temperature for one hour before pouring into 100 ml of cold water. The organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum to give 0.58 g (79%) of the title compound, pale yellow liquid, bp. 55 - 57° C (0.3 mm). Nmr: δ 1.85 (d, 3H, J's 1 Hz), δ 2.15 (m, 2 H), δ 3.40 and δ 3.45 (superimposed t., 4H, J's 6 Hz) and δ 5.75 (quartet, 1 H).

Anal. calcd for $C_6H_{10}S_2$: C, 49.29; H, 6.89; S, 43.84.

Found: C, 49.47; H, 6.64; S, 44.05.

2-Deutero-1,4-dithia-2-cycloheptene (127d).

To the above 1,4-dithia-2-cycloheptenyl anion was added, under nitrogen at -70° C, an excess of deuterium oxide. The reaction mixture was allowed to stir at room temperature for one hour before pouring into 100 ml of cold water. The organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum to give 0.59 g (89% yield) of the title compound. Nmr: δ 2.17 (quintet, 2H, J's 6 Hz), δ 3.50 (t, 4H, J's 6 Hz) and δ 5.75 (br., S., ca. 0.9 H).

Reaction of 1,4-dithia-2-cycloheptenyl anion with trimethylsilyl chloride at 0° C.

To a stirring solution of 1,4-dithia-2-cycloheptene (1.32 g, 10 mmol) in 100 ml of dry THF was added, under nitrogen at -70° C, a solution of n-BuLi (4.6 ml, 11 mmol) in n-hexane. The resulting red solution was allowed to stir gradually to 0° C and held at this temperature for one hour. The reaction mixture was cooled at -70° C again, and an excess of trimethylsilyl chloride was added. The reaction mixture was allowed to stir at room temperature for a further hour, followed by workup in the usual manner. The residue was distilled under vacuum to give 1.24 g (59% yield) of the acetylenic trimethylsilane <u>128c</u> formed as pale yellow liquid, bp. 51 - 53.5° C

(0.02 mm). Nmr: δ 0.17 (s, 9H), δ 1.40 (t, 1H), δ 2.11 (center of sym m., 2H), δ 2.77 (center of sym. m., 4H). Ir ($CDCl_3$): 2564 cm^{-1} (S-H), 2105 cm^{-1} (C≡C).

Anal. calcd for $C_8H_{16}S_2Si$: C, 47.00; H, 7.89; S, 31.37;
Si, 13.74.

Found: C, 47.13; H, 7.56; S, 31.44; Si, 13.69.

Reaction of 1,4-dithia-2-cycloheptenyl anion with methyl iodide at 0° C.

To a stirring solution of 1,4-dithia-2-cycloheptene (2.64 g, 20 mmol) in 100 ml of dry THF was added, under nitrogen at -70° C, a solution of 2.45 M of n-BuLi (11 ml, 25 mmol) in n-hexane. The red resulting solution was allowed to warm gradually to 0° C and was held at this temperature for a further hour. To the reaction mixture was added at -70° C an excess of methyl iodide. The mixture was stirred at room temperature for another hour. After workup in the usual manner, the residue was distilled under vacuum to give 1.54 g (48%) of acetylenic dimethyl compound <u>128h</u>, formed a pale yellow liquid, bp. 70-73° C (0.3 mm). Nmr: δ 1.78 (s, CH_3), δ 2.08 (s, CH_3) and δ 2.48 - 3.12 (m, 6H). Ir (neat): 2120 cm^{-1} (C≡C, very weak). Mass spectrum: M^+ at m/e 160 (46%), m/e 145 (47%), 121 (8%), 111 (18%), 97 (20%), 89 (57%), 85 (23%), 75 (7%), 71 (38%), 61 (100%), 39 (35%).

Anal. calcd for $C_7H_{12}S_2$: C, 52.45; H, 7.55; S, 40.00.

Found: C, 52.16; H, 7.32; S, 39.64.

2,3-Dideutero-1,4-dithia-2-cycloheptene.

To a stirring solution of 2-deutero-1,4-dithia-2-cycloheptene (127d) (1.33 g, 10 mmol) in 100 ml of dry THF was added, under nitrogen at -70° C, a solution of 2.45 M n-BuLi (4.28 ml, 11 mmol) in n-hexane. The reaction mixture was allowed to stir at room temperature for one hour. An excess of D_2O was then added quickly into the anion solution at -70° C. The mixture was held for a few minutes at this temperature, and then was stirred at room temperature for another hour. After workup in the usual manner, the residue was distilled under vacuum to give ca. 1 g (ca. 75% yield) of 2,3-dideutero-1,4-dithia-2-cycloheptene. Ir (neat): 2174 cm^{-1} (C-D), 1615 cm^{-1} (C=C); nmr: δ 2.18 (quintet, 2H), δ 3.52 (t, 4H) and a trace of olefinic proton at δ 5.75.

The reaction of 2-methyl-1,4-dithia-2-cycloheptene with n-BuLi at higher temperature.

To a stirring solution of 2-methyl-1,4-dithia-2-cycloheptene 127c (1.2 g, 7.7 mmol) in 50 ml dry THF was added, under nitrogen at -70° C, a solution of 2.45 M n-BuLi (3.16 ml, 7.75 mmol) in n-hexane. The reaction mixture was allowed to stir at room temperature for about 1 hour. An excess of trimethylsilyl chloride was added quickly into the reaction mixture at -70° C. The reaction solution was warmed at room temperature and stirred for a further hour before pouring into ice water. After workup in the usual manner, the residue was distilled to give 1.14 g (65% yield) of allene trimethylsilane 130, Ir: 2564 cm^{-1} (S-H), 1925 cm^{-1} (allene); Nmr: δ 0.10 (s), δ 1.37 (t, exchanged with D_2O, S-H), δ 1.97 (center of m), δ 2.70 (center of m) and δ 4.72 (s, allene).

Anal. calcd for $C_9H_{18}S_2Si$: C, 49.48; H, 8.31;
S, 29.35; Si, 12.86.

Found: C, 49.17; H, 8.54; S, 29.08; Si, 12.59.

The reaction of 2-methyl-1,4-dithia-2-cycloheptene with n-BuLi at lower temperature.

To a stirring solution of 2-methyl-1,4-dithia-2-cycloheptene (1.4 g, 8.9 mmol) in 50 ml of dry THF was added, under nitrogen at -90° C (acetone/liquid nitrogen) a solution of 2.45 M n-BuLi (3.65 ml, 8.95 mmol) in n-hexane. The reaction mixture was stirred between -70° C and -90° C for one hour, then was cooled in acetone-liquid nitrogen bath again. An excess of methyl iodide was added into the solution. After stirring for ca. 30 minutes at -90° C, the reaction solution was allowed to warm at room temperature. After stirring for another hour, the reaction mixture was worked up in the usual manner. The residue was chromatographed on silica gel to give 2,3-dimethyl-1,4-dithia-2-cycloheptene (91) in 1-2% yield. 91 Formed as colorless liquid and had an identical ir and nmr spectra with the dehydration product of carbinol 88. The more polar products (two spots on tlc plate) were eluted out together and were not further studied.

Preparation of 1,4-dithiacyclohexadiene.

In a 500 ml three necked round bottomed flask equipped with a dry-ice/acetone condenser, was condensed 250 ml of liquid ammonia. A solution of cis-(bisbenzylmercapto)ethene (13.6 g, 0.05 mmol) in 50 ml of dry THF was added slowly. To the cloudy ammonia solution, sodium (3 g, 0.13 mole) was added in several portions under nitrogen. The solution changed from white to orange and finally turned a brown-blue. The resulting brown-blue ammonia solution was stirred for 2 hours and cis-1,2-dichloroethylene (6 g, 0.062 mole) was then added dropwise slowly over 1 hour (with shield). The reaction mixture was allowed to stir overnight before pouring into 500 ml of 15% NH_4Cl aqueous solution. The organic material was extracted, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under reduced pressure to give ca. 2.9 g (ca. 50%) of yellow liquid with pleasant smell, bp. 63-67°C (9 mm); nmr: only one singlet at δ 6.19.

2-Trimethylsilyl-1,4-dithiacyclohexadiene (133b).

To a stirring solution of 1,4-dithiacyclohexadiene (0.58 g, 5.0 mmol) in 30 ml of dry THF was added slowly, under nitrogen, at -70° C, a solution of 2.4 M n-BuLi (2.1 ml, 5.1 mmol) in n-hexane. The reaction mixture was stirred at -70° C for one hour before an excess of trimethylsilyl chloride was added. The reaction mixture was allowed to warm at room temperature. After stirring for a further hour, the reaction mixture was worked up in the usual manner. The residue was distilled in vacuum to give 0.37 g of the title compound (40% yield), as a pale yellow liquid, bp. 42° C (0.06 mm), nmr ($CDCl_3$): δ 0.19 (s,9H), δ 6.28-6.50 (m,3H); ir: 3030 cm^{-1} (C=C), 1260 cm^{-1} ($Si-CH_3$), 1615 cm^{-1} (C=C).

Anal. calcd for $C_7H_{12}S_2Si$: C, 44.63; H, 6.42;
S, 34.04; Si, 14.91.

Found: C, 44.47; H, 6.38; S, 34.42; Si, 14.76.

The reaction of 1,4-dithiacyclohexadienyl anion with methyl iodide at room temperature.

To a stirring solution of 1,4-dithiacyclohexadiene (0.58 g, 5 mmol) in 50 ml of dry THF was added, under nitrogen at -70° C, a solution of 2.4 M n-BuLi (2.1 ml, 5.1 mmol) in n-hexane. After stirring for half an hour, the reaction mixture was warmed at room temperature (the solution became white cloudy at -60° C), and sitrred for a further hour. An excess of methyl iodide was then added at -70° C. The reaction mixture was allowed to sitr at room temperature for one hour. After workup in the usual manner, the residue was distilled under vacuum to give 0.40 g (56% yield) of the acetylenic dimethyl compound 134, as a pale yellow liquid, bp. 50° C (0.06 mm). Nmr: δ 1.92 (s, 3H), δ 2.27 (s, 3H), AB type at δ 5.95 and δ 6.15 (2H, J=9 Hz), ir: 3049 cm^{-1} (C=C), 2105 cm^{-1} (C≡C, very weak), 1430 cm^{-1} and 1280 cm^{-1} (S-CH_3). Mass spectrum: m/e: 144 (M^+, 100%), 129 (78.3%), 105 (1.6%) 97 (15.4%), 84 (7%), 73 (7.7%), 71 (37%), 60 (3%), 47 (15%), 39 (16.4%)

Anal. calcd for $C_6H_8S_2$: C, 49.96; H, 5.59;
S, 44.45

Found: C, 50.13; H, 5.45; S, 44.12.

Following the same procedure, the 1,4-dithiacyclohexadienyl anion solution was stirred at -40° C for half hour and then quenched with methyl iodide at -70° C. After work-up in the usual manner, the reaction products showed on GC contained 40% of starting material 132 and 49.8% of acetylenic dimethyl 134.

The reaction of 1,4-dithiacyclohexadienyl anion with trimethylsilyl chloride and methyl iodide.

To a solution of 1,4-dithiacyclohexadiene (0.58 g, 5 mmol) in 30 ml of dry THF was added, under nitrogen at -70° C, a solution of

2.4 M n-BuLi (2.1 ml, 5.1 mmol) in n-hexane. The resulting white cloudy solution was allowed to stir at room temperature for one hour. To the solution was added quickly at -70°C an equivalent of trimethylsilyl chloride (0.55 g, 5 mmol), the reaction mixture was then stirred at room temperature for one hour. To the resulting reaction mixture was added at -70°C a solution of 2.4 M n-BuLi (2.1 ml, 5.1 mmol) in n-hexane. The reaction mixture was stirred for a few minutes and then was allowed to warm up to room temperature. The solution was cooled at -70°C again, and methyl iodide (0.71 g, 5 mmol) was added quickly. The reaction mixture was stirred at room temperature again for one hour. After workup in the usual manner, the residue was distilled under vacuum to give ca 50% of the expected acetylenic methylmercapto trimethylsilane derivative <u>135</u> which formed as yellow liquid, bp. 64° (0.06 mm). Nmr: δ 0.17 (s,9H), δ 2.35 (s,3H) and AB type at δ 6.11 and δ 6.48 (2H, J=9 Hz); Ir (neat): 3050 cm^{-1} (C=C), 2130 cm^{-1} (C≡C), , 1440 cm^{-1} and 1290 cm^{-1} ($S-CH_3$), 1266 cm^{-1} ($Si-CH_3$).

Anal. calcd for $C_8H_{14}S_2Si$: C, 47.46; H, 6.97;
S, 31.67; Si, 13.89.

Found: C, 47.38; H, 7.09; S, 31.54; Si, 13.96.

<u>The preparation of 1,4-dithia-5-cycloheptene (142).</u>

The method of Fuson[76] was adopted to prepare the 1,4-dithiacycloheptan-6-ol.

Powdered potassium hydroxide (3.42 g, 61 mmol) was suspended in a solution of 1,4-dithiacycloheptan-6-ol (9 g, 60 mmol) in 150 ml anhydrous ether. The mixture was stirred at 0° C under nitrogen for 2 hours. A solution of freshly distilled benzenesulfonyl chloride (12 g, 67 mmol) in 45 ml of dry ether was added dropwise into the ethereal solution. The reaction mixture was stirred at room temperature for one and a half hours before potassium t-butoxide (13.5 g, 120 mmol) was added. The resulting yellow-brown mixture solution was stirred for 2 hours and then was poured into 400 ml of cold water. The organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled under vacuum to give a constant boiling at 35° C (0.23 mm), as a colorless liquid, in 54-73% yield. Based on GC analysis this liquid contained 90-93% of the title compound (142) and 7 - 10% of the ring contracted by-product 143. The 1,4-dithia-5-cycloheptene 142 was separated by column chromatograph (silica gel, pet. ether) from this mixture. ^{1}H nmr: δ 2.93 (center of AA'BB', 4H), δ 3.33 (d, 2H, J=6.7 Hz) and δ 6.19 - δ 6.47 (m, 2H). ^{13}C nmr: 137.8 ppm, 126.3 ppm, 36.3 ppm, 34.6 llm 30.4 ppm.

Anal. calcd for $C_5H_8S_2$: C, 45.41; H, 6.10; S, 48.49.

Found: C, 45.41; H, 5.94; S, 48.22.

7-Methyl-1,4-dithia-5-cycloheptene (145d).

To a stirring solution of 1,4-dithia-5-cycloheptene (0.66 g, 5 mmol), in 50 ml of dry THF was added, under nitrogen at -70° C, a solution of 2.4 M n-BuLi (2.1 ml, 5 mmol) in n-hexene. The reaction mixture was allowed to stir at -10° C for 1 hour. An excess of methyl iodide was added quickly to the resulting anion at -70° C. After stirring at room temperature for one hour, the reaction mixture was poured into ice water and extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was distilled after the removal of solvent to give 0.3 g (42%) of the title compound, bp. 39-40° C (0.06 mm); nmr ($CDCl_3$, TMS): δ 3.15 (center of AA'BB', 4H), δ 3.85 - 4.12 (m, 1H), δ 6.18 - 6.38 (m, 2H) and δ 1.32 (d, 3H, J's 7 Hz).

Anal. calcd for $C_6H_{10}S_2$: C, 49.27; H, 6.89; S, 43.84.
Found: C, 49.07; H, 6.54; S, 43.66.

7-Trimethylsilyl-1,4-dithia-5-cycloheptene (145b).

To a solution of 1,4-dithia-5-cycloheptene (0.66 g, 5 mmol) in 50 ml of dry THF was added, under nitrogen at -70° C, a solution of 2.4 M n-BuLi (2.1 ml, 5 mmol) in n-hexane. The resulting brown-red solution was allowed to stir at -10° C for one hour.

An excess of freshly distilled trimethylsilyl chloride was added quickly to the anion solution at -70° C, and the mixture was stirred at room temperature for one hour. After workup in the usual manner, the residue was distilled under vacuum to give 0.34 g (33%) of the title compound, bp. 57°C (0.2 mm); nmr: δ 0.13 (s,9H), δ 3.08 (AA'BB', 4H), δ 3.35 (broad d, 1H) and δ 6.11 - 6.31 (m,2H).

Anal. calcd for $C_8H_{16}S_2Si$: C, 47.00; H, 7.89;
S, 31.37; Si, 13.74.

Found: C, 47.12; H, 7.75; S, 31.61; Si, 13.55.

7-Deutero-1,4-dithia-5-cycloheptene (145c).

To a stirring solution of 1,4-dithia-5-cycloheptene (0.78 g, 5.9 mmol) in 60 ml of dry THF was added, under nitrogen at -70° C a solution of 2.4 M n-BuLi (2.5 ml, 6 mmol) in n-hexane. The resulting brown-red solution was stirred at -10° C for one hour.

An excess of D_2O was added quickly to the anion solution at -70° C, and the solution was stirred at room temperature for one hour. After workup in the usual manner, the residue was distilled under vacuum to give 0.6 g (77%) of product, bp. 35° C (0.23 mm); nmr: δ 2.93 (AA'BB', 4H), δ 3.36 (d, 1H) and δ 6.20 - 6.47 (m,2H); ir (neat): 2890 cm^{-1} (C-D), 1620 cm^{-1} (C=C).

5,7-Bis(trimethylsilyl)-1,4-dithia-5-cycloheptene (146).

To a stirring solution of 1,4-dithia-5-cycloheptene (0.66 g, 5 mmol) in 50 ml of dry THF was added, under nitrogen at -70° C, a solution of 2.4 M n-BuLi (4.2 ml, 10 mmol) in n-hexane. The resulting brown-red solution was stirred at -10°C for one hour. An excess of freshly distilled trimethylsilyl chloride was added quickly to the anion solution and the reaction mixture was stirred at room temperature for one hour before pouring into ice water. The organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was chromatographed (silica gel, pet. ether) after the removal of solvent to give 0.4 g (29%) of the title compound; nmr : δ 0.13 (s, 9H), δ 0.16 (s, 9H), δ 3.01 (center of AA'BB', 4H), δ 3.48 (d, 1H, J=8 Hz), δ 6.33 (d, 1H, J=8 Hz).

Anal. calcd for $C_{11}H_{24}S_2Si$: C, 53.16; H, 9.73;
S, 25.80; Si, 11.30.

Found: C, 53.43; H, 9.69; S, 25.64; Si, 11.17.

<u>The reaction of 3-methyl-1,4-dithia-2,5-cycloheptadiene with n-butyllithium.</u>

To a stirring solution of 3-methyl-1,4-dithia-2,5-cycloheptadiene (0.79 g, 5.4 mmol) in 100 ml of dry THF was added, under nitrogen at -70°C, a solution of 2.4 M n-BuLi (2.3 ml, 5.4 mmol) in n-hexane. The resulting dark grape color solution was allowed to stir at 0°C for one hour.

An excess of methyl iodide was added quickly to the anion solution at -70° C, and the reaction mixture was stirred at room temperature for another hour before pouring into 50 ml ice water. The organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The residue was chromatographed on silica gel (eluted with pet. ether) to give ca. 0.41 g (ca. 48%) of dimethyl product. Nmr: δ 1.86 (d, 3H, J = 1.0 Hz), δ 1.92 (d, t, 3H, J = 1.5 Hz and 0.8 Hz), δ 3.69 (br, d, 2H, J = 7.5 Hz), δ 5.89 (br, d, 1H, J = 1.0 Hz) and δ 6.14 (t, q, 1H, J = 7.5 Hz and 1.5 Hz); mass spectrum: m/e 158 (M^+, 86.8%), 143 (100%), 131 (52.9%) and 125 (23.0%).

Anal. calcd for $C_7H_{10}S_2$: C, 53.12; H, 6.37; S, 40.51.
Found: C, 53.03; H, 6.14; S, 40.78.

Preparation of 7,7-dibromobicyclo(4,1,0)-1,4-dithiacyclohept-2-ene (157).

To the stirring solution of phenyl(tribromomethyl)mercury (2.65 g, 5 mmol) in 50 ml of dry benzene was added a solution of 1,4-dithiacyclohexadiene (0.58 g, 5 mmol) in 10 ml of dry benzene. The reaction mixture was refluxed under nitrogen for 20 minutes, the solution changed from yellow to red-brown and crystals were developed. After stirring for a further 15 minutes, the reaction mixture was cooled into ice bath and filtered off the crystals. The residue was chromatographed on silica gel after the removal of solvent to give 0.141 g (9.8% yield) of the title compound <u>157</u>, mp 74-76°C and ca. 1 g (ca. 70%) of a white lachrymatory crystal having mp. 110°C, (decomposed at 120°C), nmr: δ 7.35 (br, s).

Compound <u>157</u>, mp. 73-74°C after recrystallization from chloroform; nmr: δ 2.82 (s, 2H), δ 6.18 (s, 2H), ir ($CDCl_3$): 1615 cm^{-1}.

Anal. calcd for $C_5H_4Br_2S_2$: C, 20.85; H, 1.40;
Br, 55.49; S, 22.26.
Found: C, 20.51; H, 1.15; Br, 55.74; S, 22.42.

<u>Preparation of endo-7-bromobicyclo(4,1,0)-1,4-dithiacyclohept-2-ene (154).</u>

To a stirring solution of dibromoderivative <u>157</u> (0.29 g, 1 mmol) in 30 ml of dry benzene was added, under nitrogen at 0°C, 1 equiv. of tributyltin hydride (0.27 ml, 0.29 g). The reaction mixture was stirred at 50°C (oil bath temperature) for 2 hours and then evaporated off the solvent under reduced pressure. The residue formed as a mixture of solid and liquid (tributyltin bromide) which can be isolated either by recrystallization from carbon tetrachloride or chromatography on silica gel to give exclusively endo-7-bromobicyclo(4,1,0)-1,4-dithiacyclohept-2-ene <u>154</u> in quantitative yield. Mp: 86-88°C, white crystal. Nmr: δ 2.45 (d, 2H, J=7 Hz), δ 3.86 (t, 1H, J = 7 Hz) and δ 6.34 (s, 2H), ir ($CDCl_3$): 1615 cm^{-1} (C=C); mass spectrum: M^+ at m/e 208 (20.6%), m/e 210 (22.8%), 129 (M^+ - Br, 65.8%), 103 ( , 66.5%), 97 ( 28.1%), 85 (38.6%) and 45 ($S=\overset{+}{C}H$, 100%).

Anal. calcd for $C_5H_5S_2Br$: C, 28.72; H, 2.41; S, 30.66; Br, 38.21.

Found: C, 28.49; H, 2.32; S, 30.60; Br, 38.11.

<u>The reaction of endo-7-bromobicyclo(4,1,0)-1,4-dithiacyclohept-2-ene (154) with lithium.</u>

A piece of clean lithium (ca. 0.01 g) was dropped in a solution of monobromoderivative <u>154</u> (0.1 g, 0.48 mmol) in 10 ml of dry THF at -70° C. The mixture was stirred at -70° C under nitrogen for one hour (no change at all) and then was warmed up to room temperature. After stirring for a further 2 hours, several pieces of dry ice (CO_2) were dropped into the solution and kept to stir for one hour. (Tlc showed only one spot corresponding to the starting material.) The solution was poured into aqueous KOH and the organic material was extracted with ether. The aqueous layer was neutralized with diluted hydrochloric acid and extracted with ether. The ether layers were combined, dried over anhydrous $MgSO_4$ and evaporated off. The starting material was recovered after the removal of solvent in ca. 95%. The same result was obtained, using potassium instead of lithium.

The reaction of endo-7-bromobicyclo(4,1,0)-1,4-dithiacyclohept-2-ene (154) with n-butyllithium.

To a stirring solution of 154 (0.14g, 0.67mmol) in 20ml of dry THF was added under nitrogen at -70° C, a solution of 2.45 M n-BuLi (0.28ml, 0.67mmol) in n-hexane. After stirring at -70° C for 30 minutes, the solution became deep violet-red color. Without warming up an excess of trimethylsilyl chloride was added quickly. The reaction mixture was allowed to stir at room temperature for one hour, followed by aqueous workup. The reaction mixture decomposed and a green polymer was obtained during the removal of solvent under the reduced pressure. (Temperature at 30-35° C.) After chromatography a trace of compound having a nmr spectrum δ 0.25 (s), δ 2.4 (AB system, J's ca. 7 Hz), δ 6.8 (s) was obtained; $R_f = 0.57$ (solvent: 1/2 benzene/pet. ether) on silica gel tlc plate.

The thermal rearrangement of endo-7-bromobicyclo(4,1,0)-1,4-dithiacyclohept-2-ene (154).

Without any solvent, endo-7-bromobicyclo(4,1,0)-1,4-dithiacyclohept-2-ene (154) was heated under nitrogen at 90° C for 30 min. The material melted and became a dark brown liquid, some black powder appeared. About 4 ml of carbon tetrachloride was added to dissolve the material and filtered off the black solid. After the solution was concentrated, the nmr spectrum showed an identical spectrum with the starting material.

Solvolysis of endo-7-bromobicyclo(4,1,0)-1,4-dithiacyclohept-2-ene (154) in Acetic Acid.

A. Compound 154 (0.14 g, 0.67 mmol) was dissolved in sodium acetate/acetic acid bulffer solution (0.4 g, of sodium acetate in 3 ml of acetic acid) and heated at 65° C (oil bath temperature) under nitrogen for 2 days. Tlc showed the starting material still remaining in solution. The temperature was raised to 84° C and the solution was held at this temperature for a further two days. After neutralized with 15% $NaHCO_3$, the reaction mixture was extracted with ether. After the removal of solvent, the starting material was recovered in ca. 85%.

B. Compound 154 (0.1 g, 0.48 mmol) was dissolved in silver acetate/acetic acid bulffer solution (0.2 g of silver acetate in 3 ml of acetic acid). The solution was heated at 65° C under nitrogen for one day. Tlc showed one spot which is the starting material. The reaction solution was heated at 85° C for a further two days. A series of spots was observed on tlc. The material seemed to be decomposed. No further study was done.

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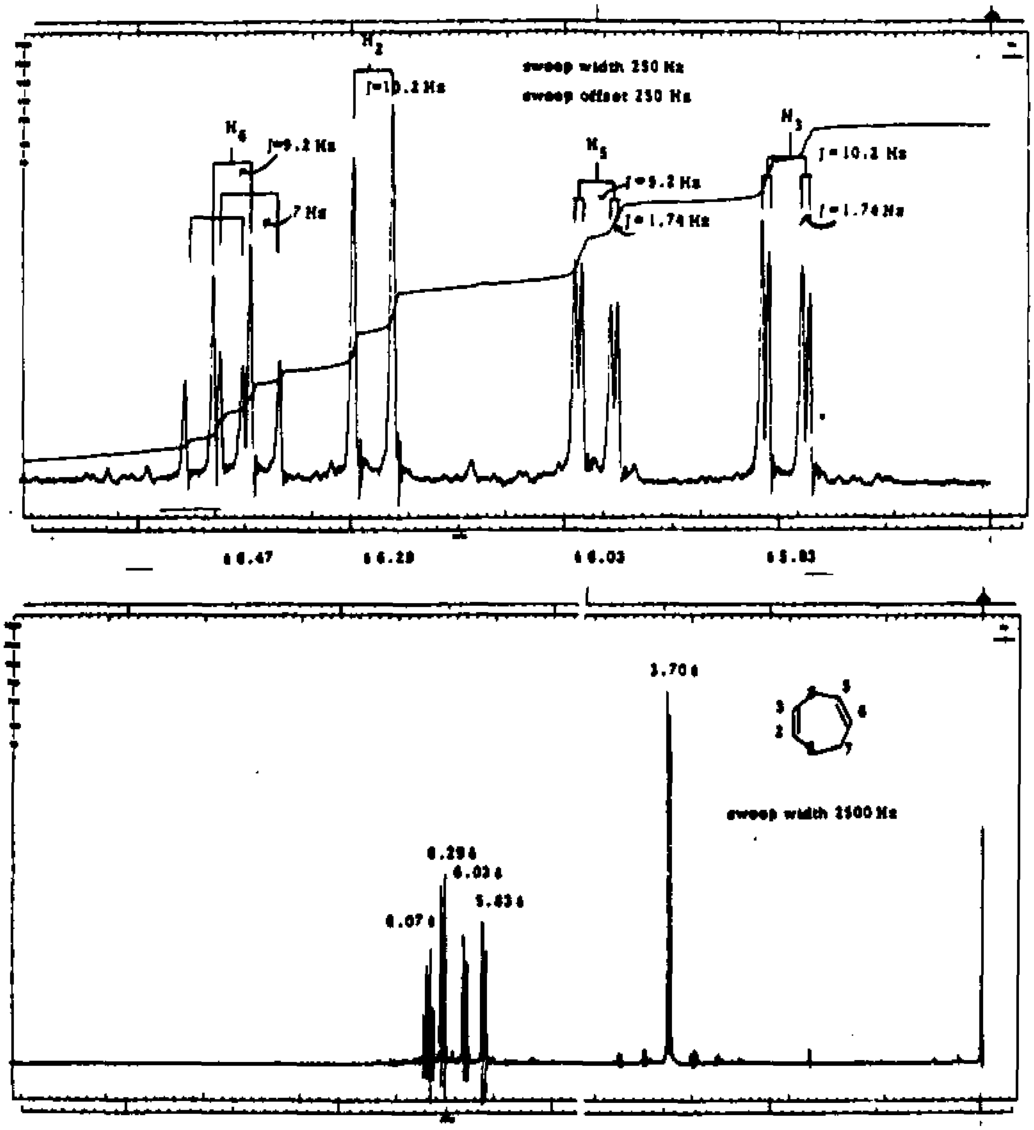
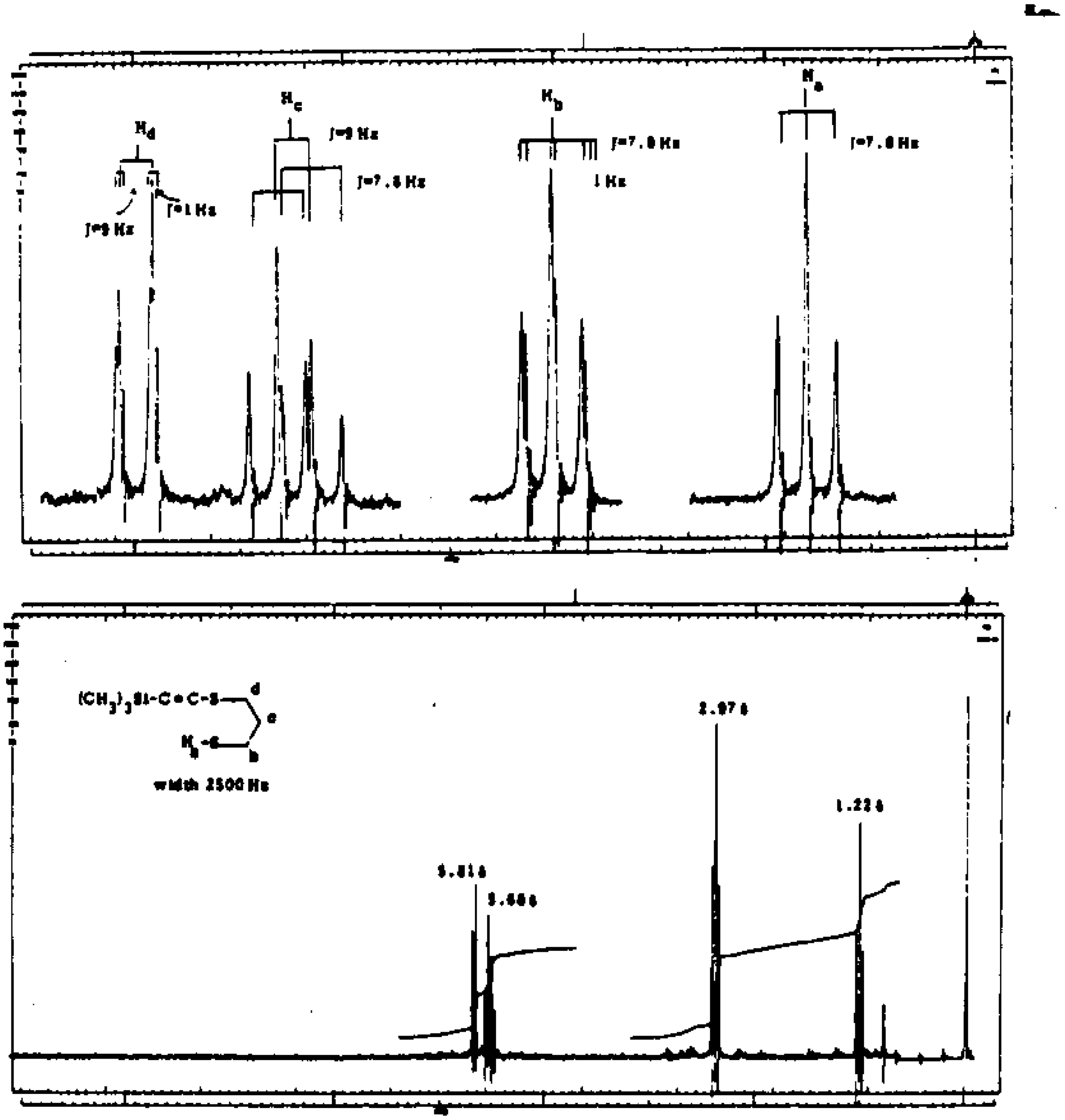
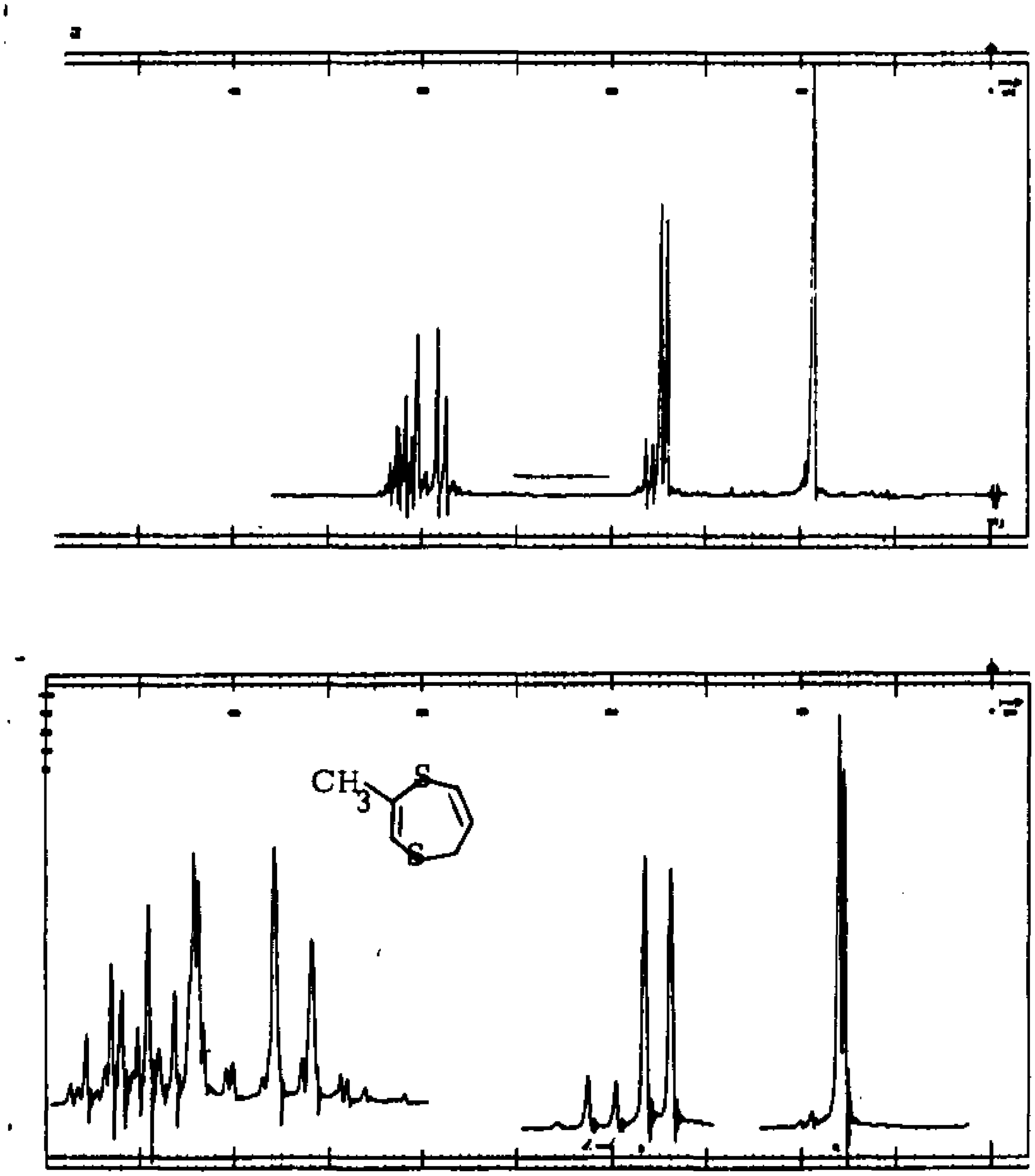


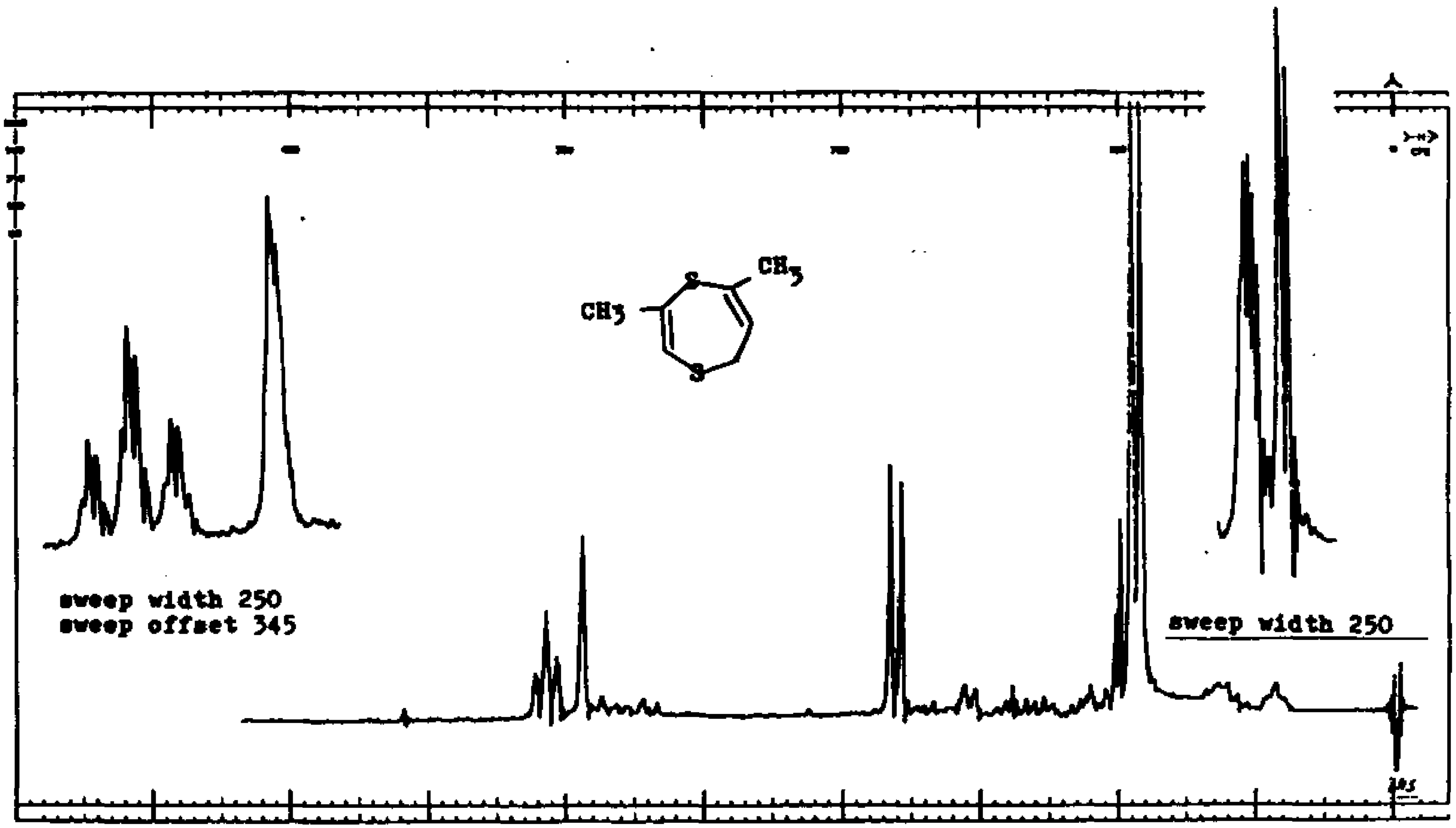
220 MH$_z$ NMR Spectrum of 1,4-Dithia-2,5-Cycloheptadiene



220 MHz ¹H NMR Spectrum of Acetylenic Trimethylsilane 112



100 MHz NMR Spectrum of 3-Methyl-1,4-Dithia-2,5-Cycloheptadiene



100 MHz NMR Spectrum of 3,5-Dimethyl-1,4-dithia-2,5-cycloheptadiene

AUTOBIOGRAPHICAL STATEMENT

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