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ETHYLLITHIUM: ADDITION TO AND METALATION OF AROMATIC HYDROCARBONS

by

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

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ACKNOWLEDGEMENT

I wish to dedicate this thesis to my grandfather, Abraham Schaeffer, without whose undying confidence in its achievement the road to success would have been more difficult.

I wish to express my sincere appreciation to Dr. Herman E. Zieger for his guidance, encouragement and friendship. I am also grateful to the staff and my fellow students for their helpful suggestions and discussions. In this regard I would like to pay particular thanks to Professor Leon Gortler and to my friend Mr. Bernard Schmall.

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ABSTRACT

It has been found that the bis amine, N,N,N',N'-tetramethyl-o-phenylenediamine (TMOPD), in cyclohexane, catalyzes the addition of ethyllithium to certain aromatic hydrocarbons to give lithio alkyl-dihydroaromatic adducts.

Additions of ethyllithium to anthracene either in cyclohexane with TMOPD or alone in tetrahydrofuran were found to give 9-lithio-10-ethyl-9,10-dihydroanthracene. Reactions of this organolithium with methyl iodide, ethyl bromide, and deuterium oxide were studied.

When methyl iodide or ethyl bromide is used to derivatize 9-lithio-10-ethyl-9,10-dihydroanthracene (in cyclohexane or tetrahydrofuran runs) only cis-9,10-dialkyl-9,10-dihydroanthracenes are obtained. It was shown that methyl iodide reacts with 9-lithio-10-ethyl-9,10-dihydroanthracene and that ethyl bromide reacts with 9-lithio-10-methyl-9,10-dihydroanthracene to give cis-9-methyl-10-ethyl-9,10-dihydroanthracene. Since it has been reported that the lithium compounds have the same structure, it was concluded that methyl iodide and ethyl bromide react in the same stereochemical manner with the intermediate lithium compounds.

The assignment of a cis configuration to the hydrocarbons obtained from the reaction of methyl iodide and ethyl bromide with 9-lithio-10-ethyl-9,10-dihydroanthracene was proven by a stereospecific synthesis of cis-9-methyl-10-ethyl-9,10-dihydroanthracene. This synthesis proceeded from the known cis-10-methyl-9,10-dihydroanthracene-9-carboxylic acid.

In contrast to the isolation of a single product from the reaction of 9-lithio-10-ethyl- (or 9-lithio-10-methyl-) 9,10-dihydroanthracenes, the addition of deuterium oxide to the former gives the mixture of cis- and trans-9-deuterio-10-ethyl-9,10-dihydroanthracene.

9-Lithio-10-ethyl-9,10-dihydroanthracene was also prepared by metalation of 9-ethyl-9,10-dihydroanthracene in tetrahydrofuran. Since reactions of this organolithium intermediate with methyl iodide, ethyl bromide and deuterium oxide gave products which were identical with those obtained from the intermediate secured by addition of ethyllithium to anthracene, it was concluded that the organolithium intermediate is a rapidly equilibrating mixture of cis- and trans-stereoisomers.

Conformational analysis of mono deuterated cis-dialkyl-9,10-dihydroanthracenes and 9-alkyl-9,10-dihydroanthracenes using infrared and nuclear magnetic resonance shows that conformations having axial alkyl groups are preferred.

It has been found that the ethyllithium-TMOPD complex adds to acenaphthylene, azulene and perylene, metalates benzene, and does not react with phenanthrene or napthalene. These results have been interpreted in terms of a free radical, single electron transfer mechanism for the addition process. This mechanism is based on the polarographic reduction potentials of the aromatic hydrocarbons. It has been used

to predict the reactions of other aromatic hydrocarbons with ethyllithium as well as the reactions of methyllithium, n-butyllithium and t-butyllithium with aromatic hydrocarbons.

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HISTORICAL

I Survey of the Reactions of Alkyllithium Reagents with Olefinic and Aromatic Hydrocarbons

Organolithium reagents are known to react with unsaturated hydrocarbons to give either addition products (eq 1)[1] or

(1) $\phi_2C{=}CH_2 + \underline{n}\text{-}C_4H_9Li \longrightarrow \phi_2C(Li)\text{-}(CH_2)_4CH_3$

hydrogen-metal exchange (metalation, eq 2).[2-4]

(2) $C_6H_6 + \underline{n}\text{-}C_4H_9Li \longrightarrow C_6H_5Li + \underline{n}\text{-}C_4H_{10}$

Ziegler discovered that alkyllithium reagents add to the double bond of stilbene or 1,1-diphenylethylene.[5] For example, the addition of n-butyllithium to 1,1-diphenylethylene in ether occurs as shown in equation (1).

The addition of n-butyllithium to butadiene yields (after hydrolysis) a mixture of straight chain (1,4 addition) or branched chain (1,2 addition) olefins differing by C_4 units.[6] Thus, in ether at room temperature, about 20% octenes, 5% 2,6-dodecadiene, 25% 5-vinyl-2-decene, and 50% of higher products are obtained.[6] Similarly, the addition of phenyllithium to cyclooctatetraene gives phenylcyclooctatetraene and lithium hydride.[7]

Ziegler found that n-butyllithium adds to ethylene under pressure (100-500 atmospheres) to give a mixture of alkyllithiums differing by two-carbon units.[8] The composition of the mixture was determined by the addition of formaldehyde and separation of the resulting C_7 - C_{13} alcohols by fractional distillation. In contrast

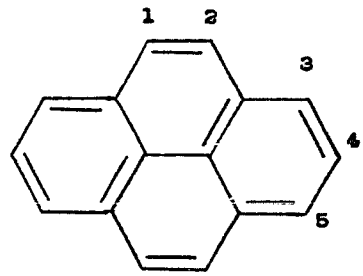
to the sluggish reaction of n-butyllithium,[8] Bartlett et al.[9] found that t-butyllithium in ether adds readily to ethylene at atmospheric pressure and -50° to give neohexyllithium. The presence of neohexyllithium was established by conversion to dineohexyl ketone with carbon dioxide.[9] In an extension of this work, Bartlett[9] reported that the addition of isopropyllithium to propene at -30° afforded a polymeric lithium alkyl. After reaction with carbon dioxide a carboxylic acid of molecular weight 308 was secured. In contrast, 1-hexene does not react with t-butyllithium in ether at -50°.[10]

The addition of organolithium reagents to certain cyclic olefins has been reported.[10] t-Butyllithium in ether at -40° or in ligroin at 64° reacts with norbornene. Exo-2-t-butylnorbornane was obtained in 33% yield after hydrolysis.[10] However, simple cyclic olefins such as cyclopentene, cyclohexene or cyclooctene did not react with t-butyllithium under the same conditions.[10] Interestingly, cyclopropene[11] undergoes addition of phenyllithium in ether to give phenylcyclopropyllithium. After carbonation with dry ice and esterification with diazomethane, vpc analysis indicated the presence of about 1% of methyl cis-2-phenylcyclopropanecarboxylate. No trans ester was detected.[11]

In contrast to these known addition reactions of olefins and dienes, aromatic hydrocarbons react with alkyllithium reagents in ether solvents via metal-hydrogen exchange to give aryllithium compounds.[2 - 4] For example, phenyllithium is secured quantitatively from benzene by metalation with n-butyllithium providing an equivalent of a catalyst (N,N,N',N'-tetramethylethylenediamine, TMEDA) is present to increase the activity of the n-butyllithium.[12]

The metalation of naphthalene by n-butyllithium in tetrahydrofuran (THF) was reported[13] to give isomeric naphthyllithiums as judged by the formation of 1- and 2-naphthoic acids (25 - 38%) after treatment with an ether slurry of dry ice. The structures of the neutral products formed were not ascertained.

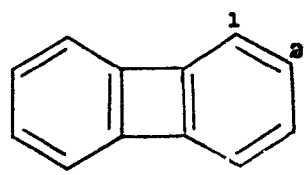
Using a low temperature carbonation technique, Berg[14] found that the metalation of pyrene (1) by n-butyllithium in THF gave an 85% yield



1

of three isomeric pyrene monocarboxylic acids. These acids were obtained in a ratio of 2 : 1 : 0.2 for the 1-, 3-, and 4- positions respectively.[14]

The metalation of biphenylene (2) with n-butyllithium has been

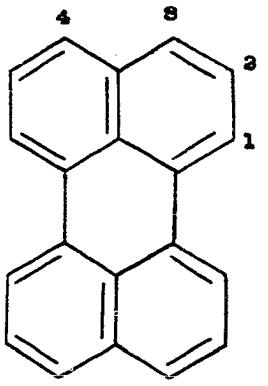


2

studied both from the experimental[15] and the theoretical[16] point of view. The latter study predicts that "aryl positions adjacent to a

fused strained ring have enhanced acidity."[16] For example, theory predicts metalation of biphenylene (2) in the 1-position.[16] This prediction is observed experimentally.[15]

In sharp contrast to the reactions of naphthalene, pyrene or biphenylene with n-butyllithium, perylene (3) reacts by addition to



3

give a lithio butyldihydroperylene.[17, 18] At -30° in THF this lithium intermediate eliminates lithium hydride to form 1-n-butylperylene (together with traces of 3-n-butylperylene).[18] Similarly, 1-ethylperylene (25-30%) was obtained[18] from the reaction of ethyllithium and perylene in benzene at 80° for 48 hours. Careful examination of data on the by-products suggested[18] that non-crystalline ethyldihydroperylenes were also formed. The addition of methyllithium to perylene in refluxing benzene, catalyzed by the addition of TMEDA, gave methyldihydroperylenes in 33% yield after hydrolysis. This material was dehydrogenated over 5% palladium on carbon to give 1-methylperylene.[19]

Although naphthalene reacts with n-butyllithium in THF at 25° to yield naphthyllithiums,[13] addition of n-butyllithium to naphthalene in

decalin at 160° gives 20% of 1-n-butylnaphthalene.[20] sec-Butyllithium produces 1-sec-butylnaphthalene in 20% yield, and t-butyllithium gives a mixture of 1-t-butylnaphthalene (30-45%) and di-t-butylnaphthalenes (50 - 30%). The structures of the latter compounds were not determined.[20]

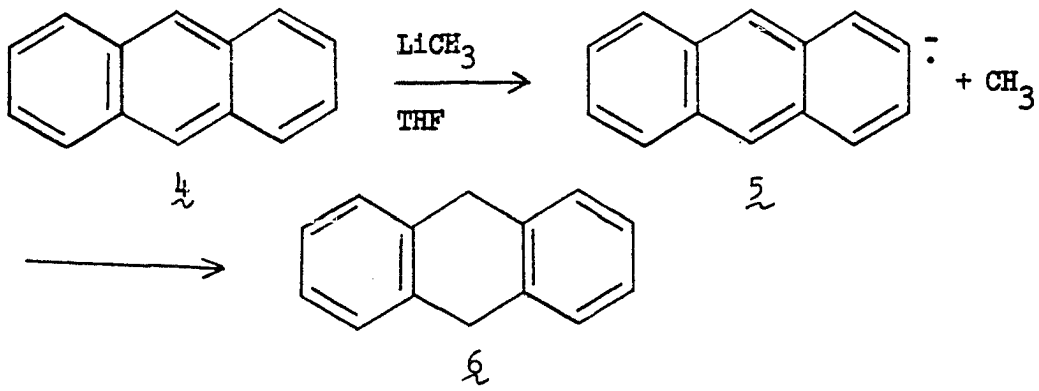
Naphthalene reacts with t-butyllithium in decalin at 60° to give both 1- and 2-t-butylnaphthalene in unreported yield. Further, a 17% yield of material boiling between these two products was isolated.[21] This material was identified as a mixture of 1-t-butyl-1,4-dihydronaphthalene and 1-t-butyl-1,2-dihydronaphthalene, in a ratio of 1 : 2, together with a much lesser amount of 2-t-butyl-1,2-dihydronaphthalene. The details of this analysis, which was based on nmr and ir spectra, are not given.[21]

Benzene was found to react with t-butyllithium in decalin at 160° to yield 15% of t-butylbenzene. Similarly, phenanthrene gave 9-t-butylphenanthrene in 50% yield. Other hydrocarbons which react with t-butyllithium (in decalin at 60°) are biphenyl, toluene and t-butylbenzene. However, no experimental details are provided, and the extent to which these hydrocarbons react was not reported.[21]

Winkler found that the addition of alkyllithium reagents (of two to ten carbon atoms) to aromatic hydrocarbons (anthracene, phenanthrene, naphthalene and biphenyl) in THF is catalyzed by ultraviolet radiation.[23] It was found that methyllithium reacted differently than the other alkyllithium reagents in this reaction.[23] When a 2 : 1 molar mixture of methyllithium and anthracene (4) in THF was photolyzed, extensive reduction of (4) to anthracene radical anion (5)[24-27] occurred. This radical anion (5) gave 9,10-dihydroanthracene (6) in 39% yield on

hydrolysis (eq 3).

(3)



II The Effect of Solvent on the Structure and Reactivity of Alkyllithium Reagents

The sluggish interaction of alkyllithium reagents like n-butyllithium with aromatic hydrocarbons[20-23] is believed to be due to the state of aggregation of the alkyllithium reagent.[13] This, in turn, is known to be a function of the solvent. Primary alkyllithium reagents are hexameric aggregates in hexane,[28] but dimeric in ether,[29] amines,[12] or tetrahydrofuran.[30]

The lower state of aggregation of butyllithium in ether or THF as compared to hexane has been interpreted as explaining higher reaction rates in the addition of alkyllithiums to olefins.[28b] In additions of n-butyllithium and ethyllithium to perylene, alkylation was extremely facile in THF but required heating when benzene was used.[18]

The enhanced reactivity of alkyllithium reagents in ether solvents often extends to the solvent itself.[1, 31, 32] Unfortunately, the decomposition of the solvent, for example, THF (by n-butyllithium)[31,32]

leads to the formation of alkoxides[31, 32] which complex with alkyllithiums reducing their reactivity.[33]

In order to avoid the problems arising from metalation of ether solvents by the alkyllithium reagent, recent workers have investigated the reactions of a TMEDA complex of the alkyllithium reagent in hydrocarbon solvent.[12, 34] For example, Langer found that n-butyllithium formed a complex with TMEDA.[12a] This complex is monomeric in hexane.[12a] The reagent is very effective as an anionic polymerization catalyst[12] and as a metalating agent.[12b] The complex formed between methyllithium and TMEDA has been used for the methylation of perylene.[19]

In summary, the structure of alkyllithium reagents is a complex problem. In many solvents alkyllithium dimers, tetramers and hexamers are the predominant species in solution.[13] In different solvents complex exchange phenomena occur within these aggregates. Current workers have viewed alkyllithium reagents as ion pairs,[70] salts of alkali metals[39] or as carbanions.[21]

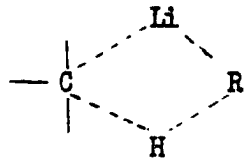
III Mechanism of the Metalation Reaction

Historically, the hydrogen-metal exchange reaction was pictured[2] as a nucleophilic attack on hydrogen by a carbanion. However, colligative property studies on simple alkyllithium reagents suggested that methyllithium, ethyllithium, butyllithium etc., exist as covalent aggregates in ether,[29] tetrahydrofuran,[30] or hydrocarbon[28] solvents. Consequently, the picture of simple carbanions attacking hydrogen atoms[2] in an aromatic substrate by an ionic process required modification. One proposal suggested the prior dissociation of dimeric

n-butyllithium (in THF)[30] into monomeric n-butyllithium with subsequent ionization into undetectable amounts[35b] of n-butyl carbanion. (eq 4)[52]

(4) $(\underline{n}\text{-}C_4H_9Li)_n \rightarrow (\underline{n}\text{-}C_4H_9Li)_2 \rightarrow \underline{n}\text{-}C_4H_9Li \rightarrow \underline{n}\text{-}C_4H_9^- + Li^+$

An alternate suggestion[36] proposes that a four-centered transition state (7) develops during a concerted protophilic attack on hydrogen.



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IV Mechanism of the Addition Reaction

The mechanism(s) of the addition of alkyllithium reagents to multiple bonds is(are) uncertain. Several mechanisms, and variations thereof, have been published. These mechanisms require different product-forming steps but fall into either the ionic or free-radical categories:

(Mechanism 1, eq 5) Nucleophilic (ionic) processes[9]

(5) $R^-Li^+ + \rangle C{=}C\langle \rightarrow R\text{-}\overset{|}{C}\text{-}\overset{|}{C}(-)Li^+$

(Mechanism 2, eq 6) Radical-radical anion combination[24, 26, 37]

(6) $R\cdot + (\rangle C{=}C\langle)^{\cdot -} Li^+ \rightarrow R\text{-}\overset{|}{C}\text{-}\overset{|}{C}\text{-}Li$

(Mechanism 3, eq 7) Free radical addition[38]

(7) $R\cdot + \diagup C{=}C\diagdown \rightarrow R\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\cdot$

Early research on the addition of isopropyllithium or t-butyllithium to ethylene and propylene[9] (see pp 1, 2) was interpreted in terms of a polar mechanism (eq 5). The latter reaction afforded a polymer. It was suggested that the intermediate was secondary alkyllithium (8) rather than primary alkyllithium (9).[9]

$H_3C\text{-}\overset{H}{\overset{|}{C}}(Li)\text{-}\ CH_2CH(CH_3)_2$ 8

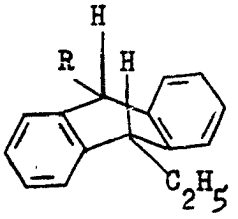
$LiCH_2\overset{H}{\overset{|}{C}}(CH_3)\text{-}CH(CH_3)_2$ 9

Subsequently, the alkylation of naphthalene by t-butyllithium in decalin at 60° (see p 5)[21] was interpreted as a nucleophilic attack on carbon of the naphthalene ring. This explanation was chosen because evidence for the transient formation of 1-lithio-2- and 1-lithio-4-t-butyldihydronaphthalenes was obtained.[22] When t-butyllithium-naphthalene mixtures were hydrolyzed shortly after mixing, t-butyldihydronaphthalenes and 1- and 2-t-butylnaphthalene were secured.[21,22] As the reaction progressed, the ratio of 1- and 2-t-butylnaphthalene to t-butyldihydronaphthalene increased. Since t-butyldihydronaphthalene was shown to be stable to the reaction conditions,[22] the formation of 1- and 2-t-butylnaphthalene was attributed to the elimination of lithium hydride from 1-lithio-2- and 1-lithio-4-t-butyldihydronaphthalene.[22] In reactions heated at 60° for long periods of time (20 hours), only 1- and 2-t-butylnaphthalene could be isolated.

Laski and Zieger isolated a 1-methyl-1,X-dihydroperylene (3, p 4)

from the reaction of methyllithium with perylene in refluxing benzene.[19] These workers inferred that it was formed from an X-lithio-1-methyl-1,X-dihydroperylene precursor.

The best evidence that an alkyldihydroaromatic lithium intermediate is involved in the alkylation reaction was obtained by Nicholls and Szwarc.[40-42] Using vacuum-line techniques,[43] these workers investigated the reaction of recrystallized ethyllithium with anthracene in THF. From the reaction of equimolar quantities of anthracene and ethyllithium, a quantitative yield of 9-ethyl-9,10-dihydroanthracene (10) was secured after hydrolysis. Deuterolysis of the intermediate carbanion (11) gave cis-9-deuterio-10-ethyl-9,10-dihydroanthracene (12). The nuclear magnetic resonance spectrum of the deuterated product (12)



10 R = H

11 R = Li

12 R = D

shows a sharp band, corresponding to the aromatic protons, at 7.14 δ. The CH_2 group is a quintet (due to splitting by H_{10} and the methyl group) at 1.63 δ with J = 7 cps. The proton at H_{10} appears as a triplet at 3.75 δ (J = 7 cps). A second triplet, with the peaks in a ratio of 1 : 1 : 1, J = 2.5 cps, was centered at 3.74 δ . This

triplet arises from H_9-D splitting. These chemical shifts were interpreted as being consistent with the assignment of cis-diequatorial stereochemistry to 12.[40] However, this conclusion, while possibly correct, must be regarded as open to serious question because of the naive assumption that the upfield aliphatic proton is axial by analogy with simple cyclohexanes. This assumption is unjustified, especially since the opposite assignments have been unambiguously confirmed in the more similar 7,12-dihydropleiadenes.[67] Obviously, some additional conformational studies are necessary to clear up discrepancies in dihydroanthracene stereochemistry (see p 35).

Based on the deuterolysis study reported above, it was inferred that "the molecule of the carbanion (11) must...be bent, the ethyl group preferring the thermodynamically stable equatorial conformation. The lithium ion...is probably located under the "roof" (see 11) where it is stablized by interaction with the π electrons of the aromatic rings."[40]

Electronic spectra[41] and nmr spectra[42] of the carbanion (11) support the idea[40] that there is interaction between the charge on the lithium ion and the aromatic ring. Examination of the ultraviolet spectrum of 9-lithio-10-ethyl-9,10-dihydroanthracene, (11), in THF at 20° showed two peaks of approximately equal intensity at λ_{max} 450 and 400 mμ. These absorption maxima (for 11) occur at longer wave length than the absorption maximum in the corresponding hydrocarbon (10, λ_{max} = 275 mμ).[23] The existence of a bathochromic shift in molecules such as 11, has been interpreted as evidence for the delocalization of an incipient negative charge over the entire pi

system.[44]

In contrast to the nmr spectrum of the hydrocarbon (10 or 12, p 11), the spectrum of 9-lithio-10-ethyl-9,10-dihydroanthracene (11) shows the aromatic protons to be magnetically non-equivalent.[42] The absorption for these protons occurs in the 5.75-6.60 δ region at 60 mc. The 9-proton gives rise to a singlet at 4.19 δ and the absorption for the 10-proton appears as a triplet, J = 7 cps, centered at 3.41 δ . This nmr assignment has been used to bolster the argument that 11 represents the correct configuration (cis) and conformation (diequatorial) of the lithium salt. As in the case of the hydrocarbons 10 and 12, this assignment of structure to the salt (11) may be incorrect (see p 42).

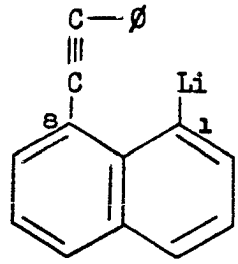
The formation of alkyldihydroaromatic lithiums in naphthalene,[20-22] perylene,[19] and anthracene,[40-42] is the sole evidence that alkylation proceeds by nucleophilic addition to aromatic carbon.[21]

The original claim that an ionic mechanism (eq 5) is operative in the alkylation of naphthalene by n-butyllithium in decalin at 165°[22] may be incorrect. At the high temperatures of their studies (160°) the alkyllithium reagent decomposes to form olefin and lithium hydride. n-Butyllithium gives pure 1-butene (no 2-butene, produced by isomerization, was detected).[6,45] sec-Butyllithium gives three isomeric butenes[46] and t-butyllithium gives isobutylene.[35] Consequently, the alkyllithium reagent is disappearing to form olefin simultaneously with its reaction with naphthalene to give 1- and 2-naphthyllithium (metalation).[13] A mechanism involving the addition of naphthyllithium to

an olefin is conceivable.

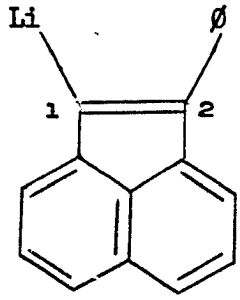
Dessy has proposed[47] that the intramolecular cyclization of 8-phenylethynyl-1-naphthyllithium (13) to 2-phenyl-1-acenaphthyllithium (14) is a carbanionic process (eq 8).

(8)



13

ether, 25°



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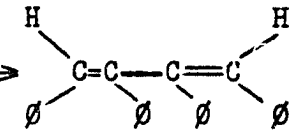
Recently, work on the addition of t-butyllithium to diphenylacetylene[26,27] (ligroin, 95°) has led to the suggestion[27] that addition may be a radical process. The isolation of a dimeric product (cis, cis-tetraphenylbutadiene, 16) was interpreted as evidence for the existence of an intermediate radical (15) (eq 9).

(9) $t\text{-}C_4H_9Li + Ø\text{-}C{\equiv}C\text{-}Ø \rightarrow Ø\text{-}\dot{C}{=}C(Li)Ø \longrightarrow$ 

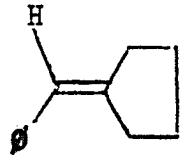
15 16

The cyclization (eq 10) of 6-bromo-1-phenyl-1-hexyne (17) to benzylidenecyclopentane (19) with n-butyllithium was studied[48] with the aid of nuclear magnetic resonance spectroscopy. The observation[48] of emission signals was interpreted as evidence for the fleeting existence of a radical intermediate, 18. These emission signals, which

(10)

$$\text{Ø-C}\equiv\text{C-(CH}_2\text{)}_3\text{-CH}_2\text{Br} + \underline{\text{n}}\text{-C}_4\text{H}_9\text{Li} \longrightarrow \text{Ø-C=C-(CH}_2\text{)}_3\text{CH}_2\cdot + \text{LiBr} + \text{C}_4\text{H}_9\cdot$$

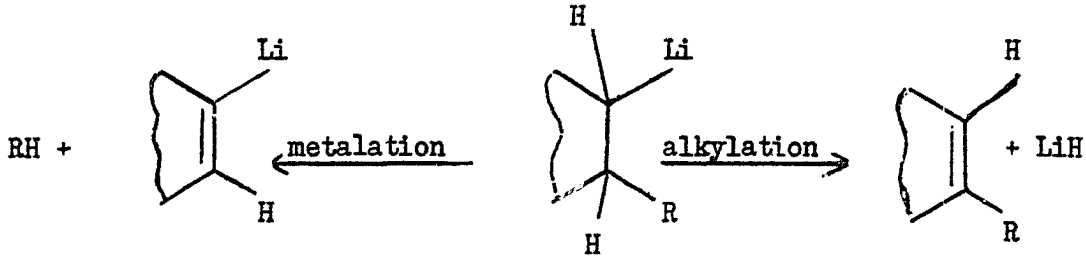
17 18



19

develop shortly after mixing of the butyllithium and 17, are believed[48] to be due to a dynamic polarization of the proton spins by the unpaired electron on the radical (18). This emission process is known[49] as Chemically Induced Dynamic Nuclear Polarization, CIDNP. Similar phenomena have been observed during the thermal decomposition of peroxides and azo compounds[50] and in the reactions of alkyl halides with lithium alkyls.[51]

Theoretically, both alkylation (eq 1) and metalation (eq 2) could occur simultaneously in a given system,[41,42] thereby increasing the complexity of product mixtures. Indeed, current researchers[52] have been led to suggest that regardless of the mechanism(s) actually involved, metalation and alkylation could occur through a common intermediate, 20.



20

Such an intermediate may conceivably explain the isolation of alkylnaphthalenes[20-22] in hydrocarbon solvents at elevated temperature or metalated naphthalenes[13] in THF at low temperature. Although intermediates such as 20 form in alkylation reactions,[41,42] no evidence for the formation of 20 in a metalation reaction has been presented.[52]

STATEMENT OF THE PROBLEM

Interest in the addition of bis-amine complexed alkyllithium reagents to aromatic hydrocarbons arose when it was discovered that methyllithium would add to perylene if a molar equivalent of TMEDA were present to catalyze the reaction[19] (see p 4).

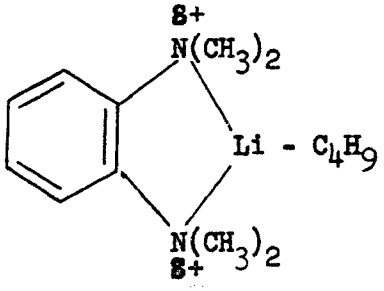
The objectives of this research were to prepare an ethyllithium-N,N,N',N'-tetramethyl-o-phenylenediamine (TMOPD) complex in a hydrocarbon solvent and study its reactions with the aromatic hydrocarbons, benzene, napthalene, phenanthrene, anthracene, and acenaphtylene.

It was expected that all of these hydrocarbons would react to give either alkylation products or metalation products. It was hoped that one or more of the hydrocarbons would give products characteristic of both reactions so that further study would show whether alkylation proceeds by a different mechanism than metalation.

It was known that a lithium-alkyl dihydroaromatic intermediate formed[40-42] during the alkylation process. Consequently, one of the objectives of this research was to prepare a lithio alkyldihydroaromatic compound in order to study its reactions with alkyl halides, carbon dioxide and deuterium oxide.

Ethyllithium was chosen for study because it is intermediate in its (addition) reactivity between methyllithium[19] and n-butyllithium.[17,18] Since the formation of methyllithium-TMEDA complex had exhibited enhanced reactivity in alkylation of perylene, study of ethyllithium-bis tertiary amine complexes was undertaken in the belief that enhancement

of reactivity would be found. It was felt that TMOPD would form a more stable complex with ethyllithium than would TMEDA. The former is capable of decreasing any positive charge (which develops on the nitrogen) by the inductive effect of the aromatic ring.



RESULTS

I THE REACTION OF ETHYLLITHIUM WITH AROMATIC HYDROCARBONS

A. Anthracene

1. Formation of 9-Lithio-10-ethyl-9,10-dihydroanthracene (I-3) by Addition of Ethyllithium to Anthracene.

It has been found that equimolar quantities of ethyllithium and N,N,N',N'-tetramethyl-o-phenylenediamine (TMOPD) form a monomeric complex in cyclohexane (p 88). This complex adds ethyllithium to anthracene in cyclohexane giving 9-lithio-10-ethyl-9,10-dihydroanthracene (I-3). Hydrolysis gives 9-ethyl-9,10-dihydroanthracene ((I-2) Chart 1 p 25) in 93% yield. When (I-3) is prepared from ethyllithium and anthracene in THF (no amine), a 98% yield of (I-2) is secured after hydrolysis.

Rapid addition of deuterium oxide to a solution of 9-lithio-10-ethyl-9,10-dihydroanthracene complexed with TMOPD in cyclohexane, provided a 3 : 2 mixture of cis- and trans-9-deuterio-10-ethyl-9,10-dihydroanthracene ((I-6) and (I-7), fig. 1, p 26, table 2 p 27). If the lithium compound is prepared by the addition of ethyllithium to anthracene in THF, a 1 : 1 mixture of deuterioanthracenes, (I-6) and (I-7), is obtained after deuterolysis. When deuteriotriphenylmethane is used as the acid, a 43/57 ratio of (I-7) to (I-6) is obtained from the intermediate lithium compound (I-3) prepared in cyclohexane and complexed with TMOPD.

When (I-3), obtained in cyclohexane with TMOPD, was allowed to react with methyl iodide, cis-9-methyl-10-ethyl 9,10-dihydroanthracene ((I-4) fig 2 p 28, table 2 p 27) is obtained. This same hydrocarbon

is also secured after the reaction of methyl iodide with a tetrahydrofuran solution of (I-3).

The reaction of ethyl bromide with (I-3), formed by the addition of ethyllithium to anthracene in cyclohexane in the presence of TMOPD, furnishes cis-9,10-diethyl-9,10-dihydroanthracene ((I-5), table 2 p 27). The material obtained in this reaction is contaminated with approximately 4% of another compound (possibly the trans isomer, table 3, p 34). Compound (I-5) is also obtained from the reaction of ethyl bromide and (I-3) in tetrahydrofuran (in 91% yield).

2. Formation of 9-lithio-10-ethyl-9,10-dihydroanthracene (I-3) by Metalation of 9-ethyl-9,10-dihydroanthracene (I-2) with n-butyllithium in Tetrahydrofuran.

When n-butyllithium is added to a THF solution of 9-ethyl-9,10-dihydroanthracene, (I-2), 9-lithio-10-ethyl-9,10-dihydroanthracene, (I-3), is formed (Chart 1 p 25, table 1, p 23,24). After the rapid addition of deuterium oxide to this solution, a 1 : 1 mixture of cis- and trans-9-deuterio-10-ethyl-9,10-dihydroanthracene ((I-6) and (I-7)) is secured. This same ratio of (I-6) to (I-7) has also been obtained by deuterolysis of (I-3) formed by addition of ethyllithium to anthracene in THF (p. 18). When the addition of deuterium oxide to (I-3) is performed slowly, the ratio of (I-6) to (I-7) becomes 64 : 36.

When the intermediate obtained from the reaction of n-butyllithium with (I-2) in THF is treated with methyl iodide, cis-9-methyl-10-ethyl-9,10-dihydroanthracene, (I-4), is obtained. When ethyl bromide is used to derivatize (I-3) (formed by metalation of (I-2)), cis-9,10-diethyl-9,10-dihydroanthracene (I-5) is secured. Trans-

isomers were not detected in these reactions.

Hydrocarbon (I-4) is also obtained from the addition of ethyl bromide to 9-lithio-10-methyl-9,10-dihydroanthracene, (I-9), in THF. The addition of methyl iodide to (I-9) gives cis-9,10-dimethyl-9,10-dihydroanthracene, (I-10). Trans isomers were not formed to an nmr detectable extent in these reactions.

3. Miscellaneous Observations on the Reactions of 9-lithio-10-ethyl-9,10-dihydroanthracene, (I-3).

The reaction of ethyllithium (complexed with TMOPD) to anthracene in cyclohexane requires less than three hours to go to completion. In tetrahydrofuran at + 10° the addition of uncomplexed ethyllithium to anthracene is over in less than 45 minutes. By contrast, the metalation of benzene in cyclohexane is 20% complete after three hours at 25° with ethyllithium-TMOPD.

Although addition of ethyllithium to anthracene may proceed faster in THF than in cyclohexane with TMOPD, the latter reagent affords cleaner products. In tetrahydrofuran, cleavage of the solvent by (I-3) proceeds to an appreciable extent if the reaction is run at room temperature or for periods of one hour or more. By contrast, (I-3) formed in cyclohexane with TMOPD, is unchanged after twenty-four hours at room temperature.

4. Conformational analysis and the structure of 9-lithio-10-ethyl-9,10-dihydroanthracene, (I-3).

Using infrared spectroscopy it has been determined that 9-alkyl-and cis-9,10-dialkyl-9,10-dihydroanthracenes exist predominately ($>50\%$) in the conformation in which the alkyl group (s)

is (are) axial.

The structure of (I-3) could not be determined with certainty. The nmr spectrum (fig 4 p) is in accord either with a trans structure or with a rapid (nmr time scale) equilibration of cis- and trans isomers. It is felt that the reactions of (I-3) with deuterium oxide and alkyl halides are more in accord with a rapid cis-trans equilibrium than with a single isomer.

B. Other Aromatic Hydrocarbons

9-Methylanthracene reacts with ethyllithium in THF to yield cis-9-methyl-10-ethyl-9,10-dihydroanthracene, (I-4), after hydrolysis. The addition of TMOPD complexed ethyllithium to this hydrocarbon was not investigated.

The reaction of TMOPD complexed ethyllithium with naphthalene phenanthrene, perylene, acenaphthylene, azulene and benzene were examined.

Naphthalene and phenanthrene did not react with this reagent at room temperature. Reactions at elevated temperatures were not investigated.

Perylene gave a quantitative yield of 1-ethyl-1,X-dihydroperylene. When the addition of ethyllithium to perylene in cyclohexane in the absence of TMOPD was attempted at 25°, only perylene was secured on hydrolysis. Since the ethylation of perylene by ethyllithium in boiling benzene is known,[18] the observation that ethylation does not occur at 25° in the absence of TMOPD demonstrates moderate catalytic properties of the bis amine.

Azulene gave 4-ethyl-4,X-dihydroazulene, and acenaphthylene gave a complex mixture on reaction with ethyllithium-TMOPD in cyclohexane.

Benzene was slowly metalated by this reagent. The phenyllithium produced by metalation was isolated as triphenylmethanol after the addition of benzophenone.

Products Obtained from the Reaction of 9-Lithio-10-alkyl-9,10-dihydroanthracenes with Water, Deuterium oxide, and Alkyl Halides

Product	Source of the 9-lithio-10-alkyl-9,10-dihydroanthracene (Yield)			
	Anthracene + C_2H_5Li + TMOPD in cyclohexane	Anthracene + C_2H_5Li in THF	9-Ethyl-9,10-dihydroanthracene + n-C_4H_9Li in THF	9-Methyl-9,10-dihydroanthracene + n-C_4H_9Li in THF
(I-2) mp 42-43° 9-Et-9,10-DHA[a]	93%	98%	-----	-----
(I-4) mp 105-106 ° cis-9-Me-10-Et-DHA[a]	89 ± 4%	98%	98%	95%
(I-5) mp 58° cis-9,10-diEt-DHA[a]	80%	96%	96%	-----

TABLE I

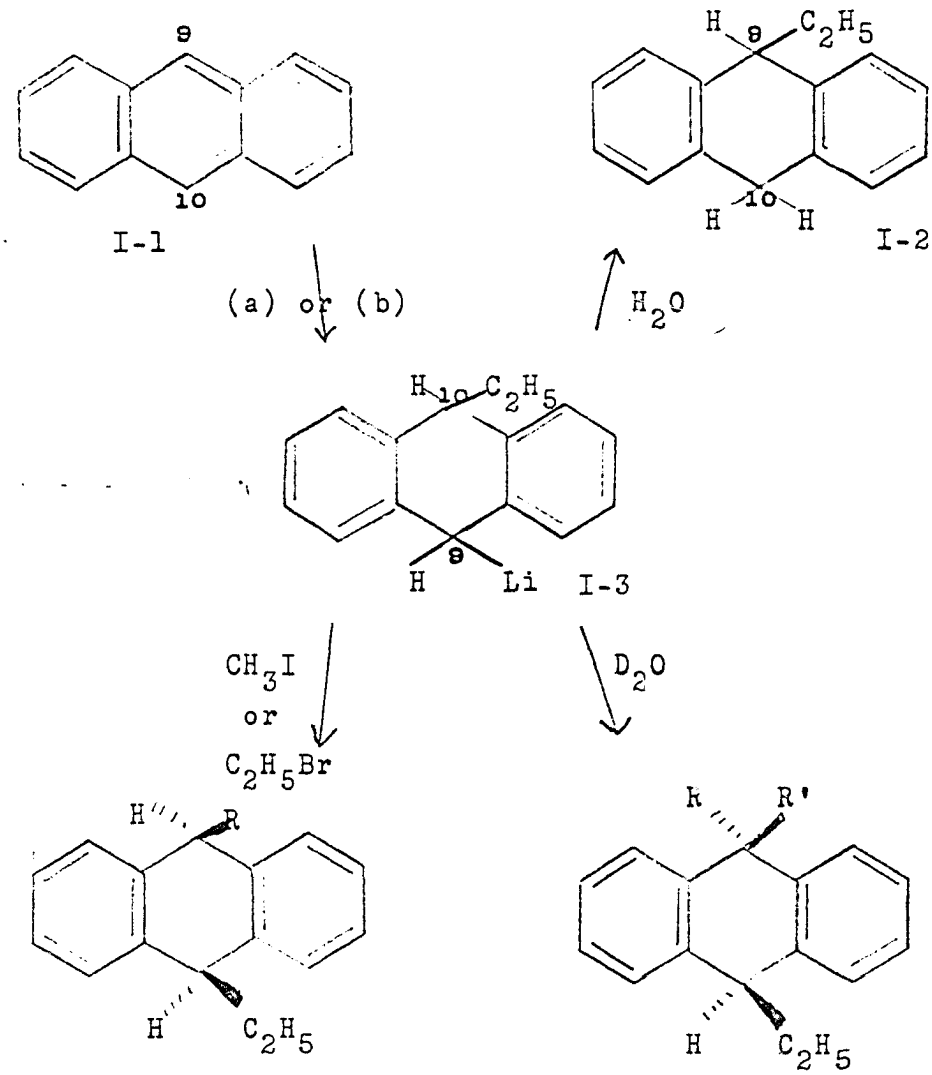
Product	Anthracene + C_2H_5Li + TMOPD in cyclohexane	Anthracene + C_2H_5Li in THF	9-Ethyl-9,10-dihydroanthracene + $n\text{-}C_4H_9Li$ in THF	9-Methyl-9,10-dihydroanthracene + $n\text{-}C_4H_9Li$ in THF
(I-6) / (I-7) mp 42°	2/3 (D_2O) 92 ± 3%	1/1 98%	1/1 rapid addition of D_2O (98%)	-----
cis / trans-9-D-10-Et-9,10-DHA[a]	43/57 (ϕ_3CD)		64/36 slow addition of D_2O	
I-10 mp 127-128° cis-9,10-diMe-9,10-DHA[a]				100%

a = dihydroanthracene

TABLE I - continued

CHART I Part A

ADDITION OF ETHYLLITHIUM TO ANTHRACENE: PRODUCT STEREOCHEMISTRY



I-4 R = CH_3

I-5 R = C_2H_5

I-6 R = H, R' = D

I-7 R = D, R' = H

(a) C_2H_5Li (0.005 mole) + TMOPD (0.005 mole) in cyclohexane or

(b) C_2H_5Li (0.005 mole) in tetrahydrofuran, with anthracene (0.005 mole).

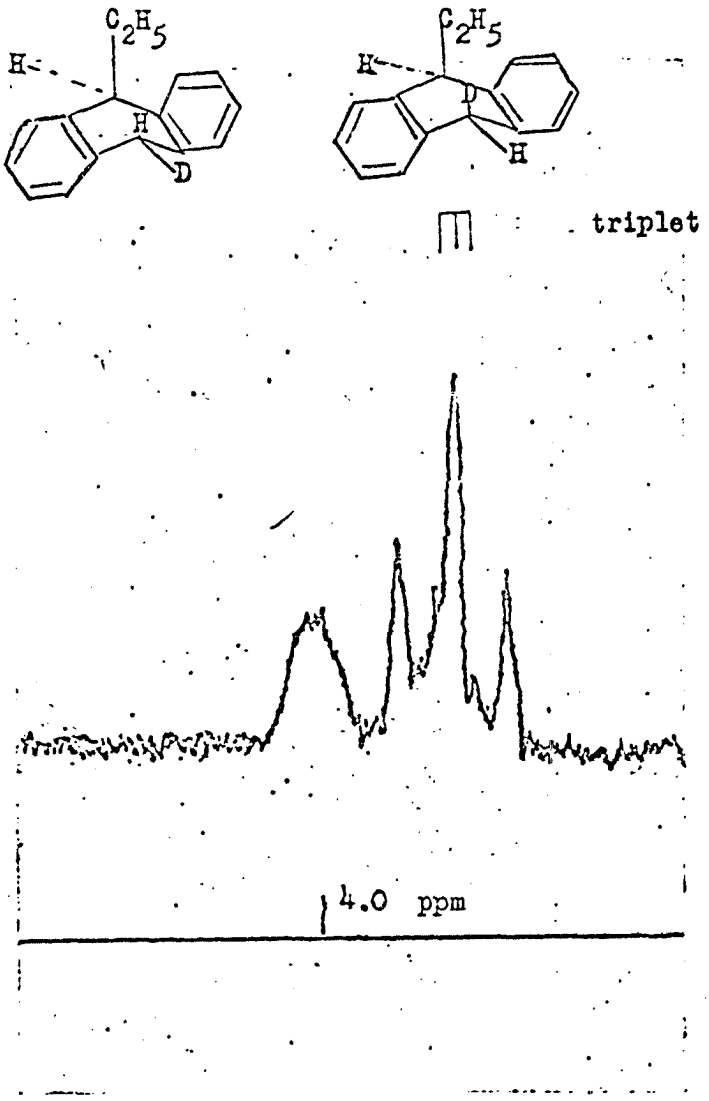


Figure 1 The benzylic region of the 60 mc nmr spectrum of cis- and trans-9-deutero-10-ethyl-9,10-dihydroanthracene

N M R Data on 9,10-Disubstituted-9,10-dihydroanthracenes #

Ar - R_1 R_2 in $CDCl_3$

	R_1	R_2	Aryl	Benzylic		$-CH_2-$	Methyl
				C-9	C-10		
cis	C_2H_5-	D-	428 (s)	225. (t) J=7.	224.4 (t) J=2.5	99. (qu)	49. (t)
trans	C_2H_5-	D-	428 (s)	241. (br.)		99. (qu) J=7.	49. (t) J=7.
cis	CH_3-	C_2H_5-	433 (s)	244. (q) J=7.	226. J=7.	108. (qu) J=7.	92. (d) J=7.
cis	C_2H_5-	C_2H_5-	427 (s)	223. (t) J=7.		108. (qu)	58. (t) J=7.
cis	CH_3-	CH_3-	435 (s)	244. (q) J=7.5		--	92. (d) J=7.5
cis*	CH_3-	-COOH	440	318.5 (s)	248. (q) J=7.0	--	104. (d)
---	CH_3-	H-	435 (s)	244. (q) J=7.5		--	92. (d) J=7.5
cis	CH_3-	$-CH_2OH$	434 (s)	215.-258. (m) (4 H) including $-CH_2OH$		110.(s,1H-OH)	90. (d) J=7.
cis	CH_3	$-CH_2O-SO_2C_7H_7$	432 (m)	247. (m)		139.(s,3H) ($RO_3S-C_6H_4\underline{CH_3}$)	75. (d) J=7.5

s - singlet
d - doublet
q - quartet
qu - quintet
m - multiplet
t - triplet
br - broad
* - in deuteriopyridine

- This work. Chemical shifts in this work at 60 MHz.

TABLE 2

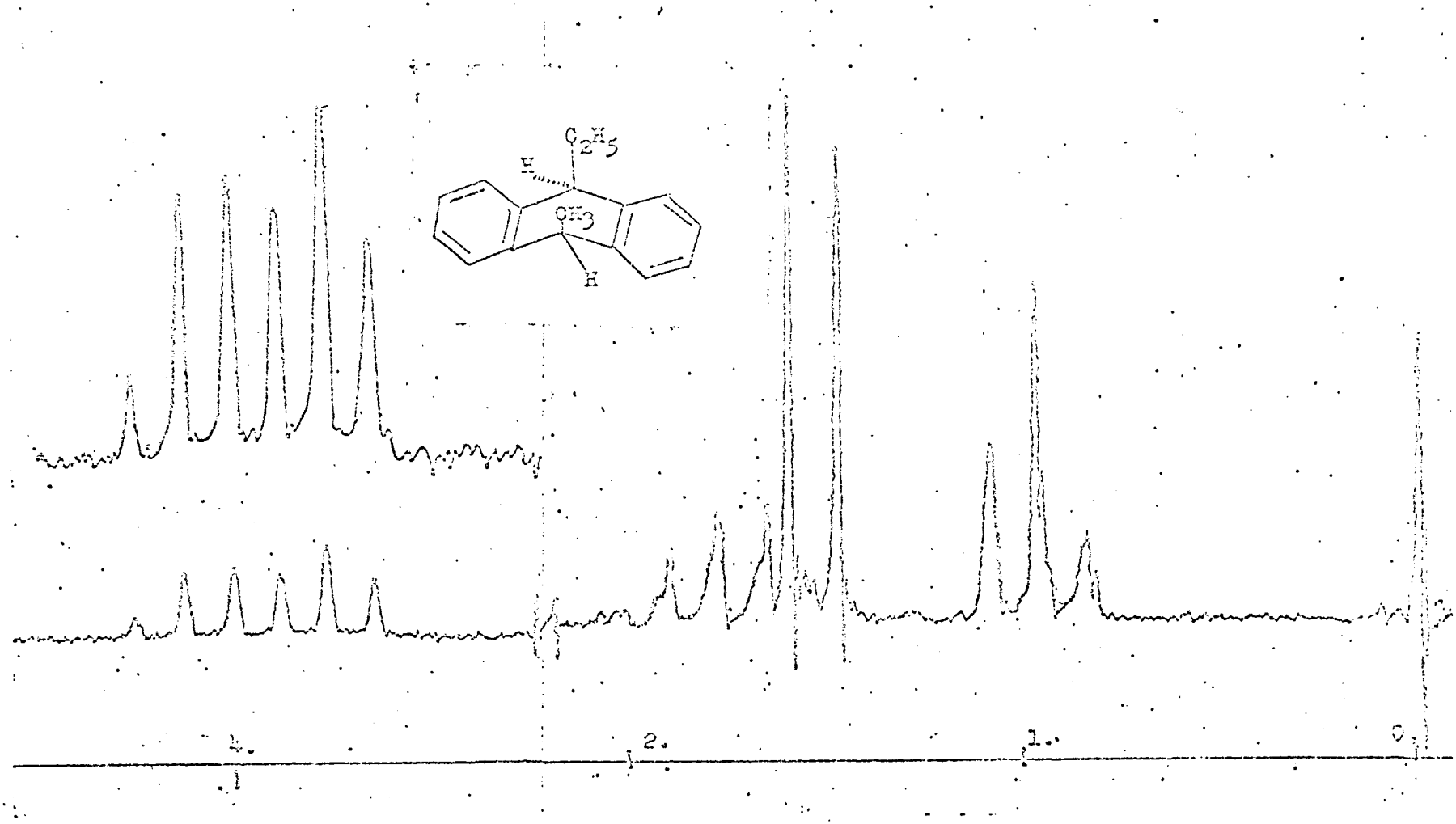
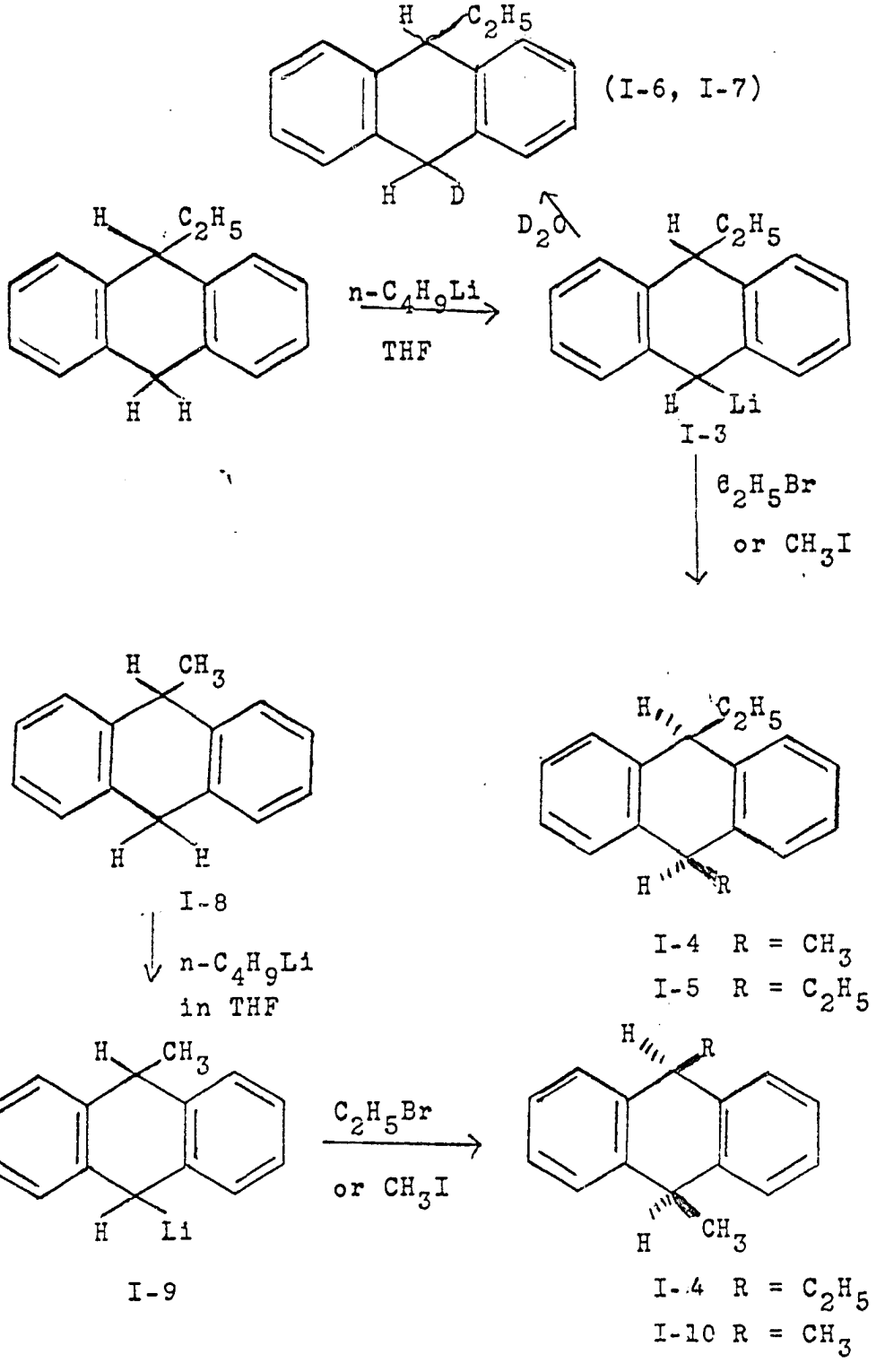


Figure 2 cis-9-methyl-10-ethyl-9,10-dihydroanthracene (60 mc nmr in $CDCl_3$).

CHART I Part B

THE METALATION OF 9-ALKYL-9,10-DIHYDROANTHRACENE WITH $n\text{-}C_4H_9Li$



DISCUSSION

The Addition of Ethyllithium to Anthracene: Configuration of the 9,10-dialkyl-9,10-dihydroanthracenes Obtained from the Reaction of 9-lithio-10-ethyl-9,10-dihydroanthracene (I-3) with Alkyl Halides

The nmr spectra (Table 2 p 27, Figure 2 p 28) and the melting points of the 9,10-dialkyl-9,10-dihydroanthracenes obtained in (Chart 1 p 25), agreed with the properties of compounds secured by the addition of alkyl halides to disodioanthracene.[54]

A tentative assignment of cis stereochemistry to these hydrocarbons was based upon the observation that 9-lithio-10-methyl-9,10-dihydroanthracene, (I-9), reacts with methyl iodide to give the known cis-9,10-dimethyl-9,10-dihydroanthracene.[55,56]

It has been shown by the use of ultraviolet[41] and nmr[42] spectroscopy, that 9-lithio-10-methyl-9,10-dihydroanthracene, (I-9), and 9-lithio-10-ethyl-9,10-dihydroanthracene, (I-3), have the same structure. The reaction of the methyllithio compound ((I-9)) with ethyl bromide produces the same 9-methyl-10-ethyl-9,10-dihydroanthracene as is obtained from the reaction of methyl iodide with the ethyllithio compound ((I-3)). Since the two lithio compounds have the same structure,[42] if the two halides reacted in a different stereochemical sense (i.e., if for example, methyl iodide reacted with retention of configuration and ethyl bromide reacted with inversion of configuration), then a different 9-methyl-10-ethyl-9,10-dihydroanthracene would be obtained from each of the lithium compounds. Since the same 9-methyl-10-ethyl-9,10-dihydroanthracene is obtained from the reaction of (I-9) with ethyl

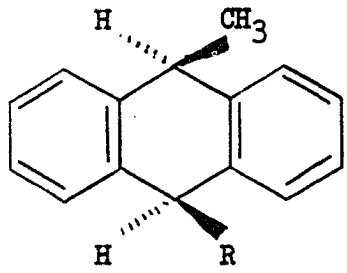
bromide and the reaction of (I-3) with methyl iodide, it is concluded that these halides react with the lithium salts in the same stereochemical manner--either inversion or retention of configuration. Further, the fact that the addition of methyl iodide to the methyllithio compound ((I-9)) produces the cis dimethyl compound, strongly suggests that the 9-methyl-10-ethyl- and the 9,10-diethyl compounds obtained by the reaction of (I-3) or (I-9) with alkyl halides are also cis.

The unproven criterion that aromatic protons of trans isomers give rise to a multiplet absorption in the nmr, and those (protons) of cis isomers give rise to a "singlet", enabled other workers to assign cis-sterochemistry to these compounds.[54] This criterion was based on the nmr spectra of the known cis-[55,56] and trans-[54, 55] 9,10-dimethyl-9,10-dihydroanthracenes. This method of making stereochemical assignments in 9,10-dihydroanthracenes may not rest on firm theoretical ground.

Interest in the question of whether the carbanion in (I-3) maintains its stereochemical integrity or equilibrates between cis and trans stereoisomers required an unimpeachable assignment of stereochemistry to the 9,10-dialkyl-9,10-dihydroanthracenes.

Confirmation of the cis stereochemistry of these compounds (Chart I) was obtained from the stereospecific synthesis of cis-9-methyl-10-ethyl-9,10-dihydroanthracene, (I-4). 9-Lithio-10-methyl-9,10-dihydroanthracene, (I-9), gave cis-10-methyl-9,10-dihydroanthracene-9-carboxylic acid (21, obtained in 60% yield),[56]

after treatment with carbon dioxide. Reduction of 21 with lithium



21 R = COOH
22 R = CH_2OH
23 R = CH_2OTs

hydride (to cis-alcohol 22)[56] and subsequent treatment with p-toluenesulfonyl chloride gave the known ester, 23.[56] Treatment of 23 with lithium dimethylcopper[58] gave a quantitative yield of authentic cis-9-methyl-10-ethyl-9,10-dihydroanthracene, (I-4). The properties of the 9-methyl-10-ethyl-9,10-dihydroanthracene obtained previously (p 25) were identical in all respects with those of authentic (I-4). Nmr data on compounds 21 - 23 is recorded in table 2, p 27.

It is interesting to note that although deuterium oxide gives a mixture of cis, (I-6), and trans, (I-7), deuterio compounds on reaction with 9-lithio-10-ethyl-9,10-dihydroanthracene, and that carbonation of 9-lithio-10-methyl-9,10-dihydroanthracene, (I-9), also forms a cis-trans mixture (21 and 24), the addition of methyl iodide or ethyl bromide gives only cis isomers. No evidence for the formation of trans isomers

in the alkyl halide quenching experiments could be obtained either by vpc or nmr. The alkyl halide quenching experiments of 9-lithio-10-ethyl-9,10-dihydroanthracene, (I-3), have been confirmed by other workers.[59]

TABLE 3

Additional NMR Data on 9-alkyl- and 9,10-dialkyl-9,10-dihydroanthracenes*

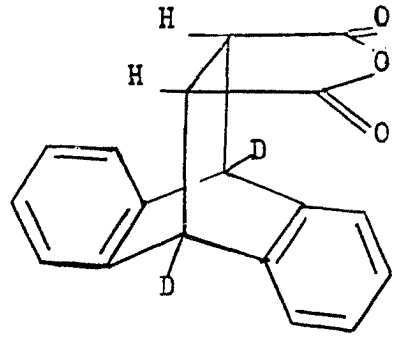
	R_1	R_2	Aryl	Benzylic	Methylene	Methyl
-----	C_2H_5	H	428 (s)	225 (t) J = 7; H_9 234 (q) J_{AB} = 18	97 (qu) J = 7	49 (t) J = 7
<u>trans</u>	C_2H_5	C_2H_5	438 (7)	239 (t) J = 6	125	48 (t) J = 7
<u>trans</u>	CH_3	CH_3	428 (m)	240.0 (q) J= 7.5		104.2 (d) J = 7.5
<u>trans</u>	CH_3	C_2H_5	435 (m)	231 (t) J = 7 240 (q) J = 7		53 (t) 106 (d) J = 7 J = 7

*Spectra taken in deteriochloroform on a Varian A-60 nmr spectrometer and expressed as cps relative to tetramethylsilane. We would like to thank Professor Ronald G. Harvey, Ben May Laboratories of the University of Chicago for supplying this data in advance of publication.[59]

III Conformation of Alkyldihydroanthracenes: the Assignment of Configuration of 9-deuterio-10-ethyl-9,10-dihydroanthracenes

The conformation of 9-alkyl-9,10-dihydroanthracenes is an unresolved question in the literature. Nicholls and Szwarc[40] (pp 10, 11) favor the conformation in which the alkyl group occupies an equatorial position. On the other hand, Eliel et al.,[60] and R. G. Harvey[59] favor an axially situated alkyl group. In the case of the bulky groups, 9,10-di-t-butyl-9,10-dihydroanthracene for example,[54,61] the central ring may be nearly planar. The report[62] that axial and equatorial deuterium in cyclohexane systems have different infrared stretching frequencies (table 4, p 36), suggested a means for determining the conformational preferences of alkyl groups in the dihydroanthracene system.

The Diels-Alder adduct of maleic anhydride and 9,10-dideuterioanthracene,[63] 25, represents a rigid system in which the deuterium



25

atoms at C-9 and C-10 must be equatorial. The infrared spectrum of this

TABLE 4

Infrared Data on 9-Deuterio-9,10-dihydroanthracenes

			C-D stretch in cm			ref.
cis	H	C_2H_5	2160, 2145	(neat)	(eq)	a
trans	H	C_2H_5	2110, 2088	(neat)	(ax)	a
cis	C_2H_5	C_2H_5	2137	(neat)	(eq)	a
cis	H	i-C_3H_7	2175, 2158	(neat)	(eq)	b
trans	H	i-C_3H_7	2115, 2090	(neat)	(ax)	b
cis	i-C_3H_7	i-C_3H_7	2128	(CCl_4)	(eq)	b
cis	i-C_3H_7	i-C_3H_7	2128	(KBr)	(eq)	b
trans	i-C_3H_7	i-C_3H_7	2137 (s), 2099 (w)	(CCl_4)		b
trans	i-C_3H_7	i-C_3H_7	2114	(KBr)		b
Diels-Alder adduct of 9,10-dideuterioanthracene and maleic anhydride			2136	(KBr)	(eq)	63
trans-4-deuterio-t-butylcyclohexane			2184, 2167		(eq)	62
cis-4-deuterio-t-butylcyclohexane			2114 - 2164		(ax)	62

References

a. This work

b. Sample prepared in this laboratory by Miss Regina Padronaggio

(ax) = axial deuterium
(eq) = equatorial deuterium
(s) = strong
(w) = weak

compound displays the C-D stretching absorption as a singlet, λ_{max}^{KBr} 2136 cm^{-1}. The C-D stretch of cis-9,10-diethyl-9-deuterio-10-hydroanthracene (neat liquid, p 76) occurs at 2137 cm^{-1}. The nearly identical C-D absorption frequencies strongly indicates that the cis-9,10-diethyl compound exists predominately in the conformation in which the ethyl groups are diaxial (table 3). It should be pointed out that the bridgehead proton of the non-deuterated Diels-Alder adduct is found at 2884 cm^{-1}. Methine protons are reported[64] to absorb at 2890 $\mp$ 10 cm^{-1}. On this basis it is concluded that bridging has not caused any unusual shifting of the infrared absorption frequency of the deuterated material. Thus, this compound serves as an excellent model for the diethyl compound.

The 9-proton of 9-ethyl-9,10-DHA and cis-9,10-diethyl-9,10-DHA have essentially the same chemical shift in the nmr (table 2, p 27). If the conformations of these compounds differed to an extent detectable by nmr, then appreciable differences in the chemical shifts of the 9-proton in the two compounds would be observed. Since such differences are not observed, the mono-ethyl and cis-diethyl compounds must be similar in conformation. That is, the predominate species corresponds to the conformation in which the alkyl group is axial.

The sample of 9-deuterio-10-ethyl-9,10-dihydroanthracene obtained in this work is a 1:1 mixture of cis- and trans-isomers. The replacement or exchange of deuterium for protium in 9-ethyl-9,10-dihydroanthracene should occur without affecting the conformational preference

of the ethyl group.[65] Therefore, by analogy with 9-ethyl-9,10-dihydroanthracene, both cis- and trans-9-deuterio-10-ethyl-9,10-dihydroanthracene exist predominately in the conformation in which the ethyl group is axial.

Equatorial protons in alkyldihydroanthracenes, such as those found in 9,10-ethano-9,10-dihydroanthracene,[66] appear as sharp bands in the 3.33-5.00δ region of the nmr spectrum. The 9-proton of 9-ethyl-9,10-dihydroanthracene and the 9,10-protons of cis-9,10-diethyl-9,10-dihydroanthracene appear as sharp absorptions in this region of the nmr spectrum. This indicates that these protons, like the 9,10-protons in 9,10-ethano-9,10-dihydroanthracene, are equatorial. This result is in accord with the infrared analysis of the conformational preferences of these systems. The 10-protons of 9-ethyl-9,10-dihydroanthracene form an AB quartet. The A portion is about 0.33δ downfield from the B portion, and is broader. Since equatorial protons in the 9,10- positions of 9,10-dihydroanthracenes are observed to give rise to sharp signals,[66] the broad peaks must arise from the 10-axial proton. This broadening arises from long-range coupling of this proton with aromatic protons in ortho and para positions.[67] "Extensive studies of such coupling by Sternhell and others[69] have shown that the greatest effect results when the benzylic C-H bond lies perpendicular to the aromatic ring, thus allowing efficient π overlap"[67] (see figure 3, p 41).

In the nmr spectrum of the mixture of cis and trans— 9-deuterio-

10-ethyl-9,10-dihydroanthracenes, (I-6) and (I-7), a broad, unresolved band appears about 0.33 δ downfield from the remaining 9,10-protons (table 2). This absorption occurs at 4.0 δ and is attributed to the 9-axial hydrogen of the trans isomer. The 10-proton of both the cis and trans isomers gives a signal at 3.75 δ (triplet, J = 7 cps). The 9-proton of the cis-isomer, a triplet[40] arising from coupling of the hydrogen with the axial deuterium, absorbs at 3.74 δ.

In contrast to simple cyclohexane systems in which the axial protons absorb at higher frequency than equatorial protons,[57] in dihydroanthracene the opposite is true in the case of the compounds listed in table 3 (p 34). Such a reversal has also been observed, but not explained, in the dihydropleiadene ring system.[67]

The absorption of the 9-equatorial proton in 9-alkyl- and 9,10-dialkyl-9,10-dihydroanthracenes (tables 2 and 3 and reference 54) shows a large upfield shift in going from methyl (4.67 δ) to ethyl (3.75 δ) to i-propyl (3.52 δ). This type of shift, caused by an alkyl group one carbon removed from the proton of interest, does not appear to have been observed in systems other than dihydroanthracene. This shift may be attributed to the greater diamagnetic anisotropy[91] of a methyl group as compared with an ethyl or i-propyl group. In cis-9-methyl-10-ethyl-9,10-dihydroanthracene (fig 3, p 41), for example, the carbon-hydrogen bond of the 9-methyl group shields the hydrogen (at C-9) to a lesser extent than does the carbon-carbon bond of the ethyl group to the hydrogen at C-10 (preferred conformation

based on the examination of Dreiding models). Since the shielding constant of a carbon-carbon bond is greater than that of a carbon-hydrogen bond,[91] it is not unreasonable that the equatorial proton at C-9 of cis-9-methyl-10-ethyl-9,10-dihydroanthracene will absorb at lower frequency than the equatorial proton at C-10. Apparently, the increased number of carbon-carbon bonds in an isopropyl group as compared to an ethyl group is responsible for the increased shielding of this group. This trend fails when the substituent is a t-butyl group (3.78 δ)[54] perhaps because of a change in the conformation of the central ring.[61]

Unlike monosubstituted or cis-disubstituted dihydroanthracenes which may exist preferentially in one conformation (alkyl groups axial), symmetrically substituted trans-dialkyldihydroanthracenes must exist as a 1:1 mixture of conformationally equilibrating isomers. If this equilibration is slow on the nmr time scale, the 9- and the 10-protons will absorb at different frequencies. If the equilibration is rapid, a single average signal will be observed. The latter result has been found in the room temperature nmr spectra of trans-9,10-dimethyl-9,10-dihydroanthracene (table 3, p 34), trans-9,10-diethyl-9,10-dihydroanthracene (table 3), trans-9-ethyl-10-methyl-9,10-dihydroanthracene (table 3), and trans-9,10,diisopropyl-9,10-dihydroanthracene.[54] However, the prediction that the 9- and 10-protons of these systems are distinguishable, is substantiated by the infra-red spectrum (table 4, p 36) of trans-9,10-diisopropyl-9-deuterio-10-hydroanthracene. The spectrum

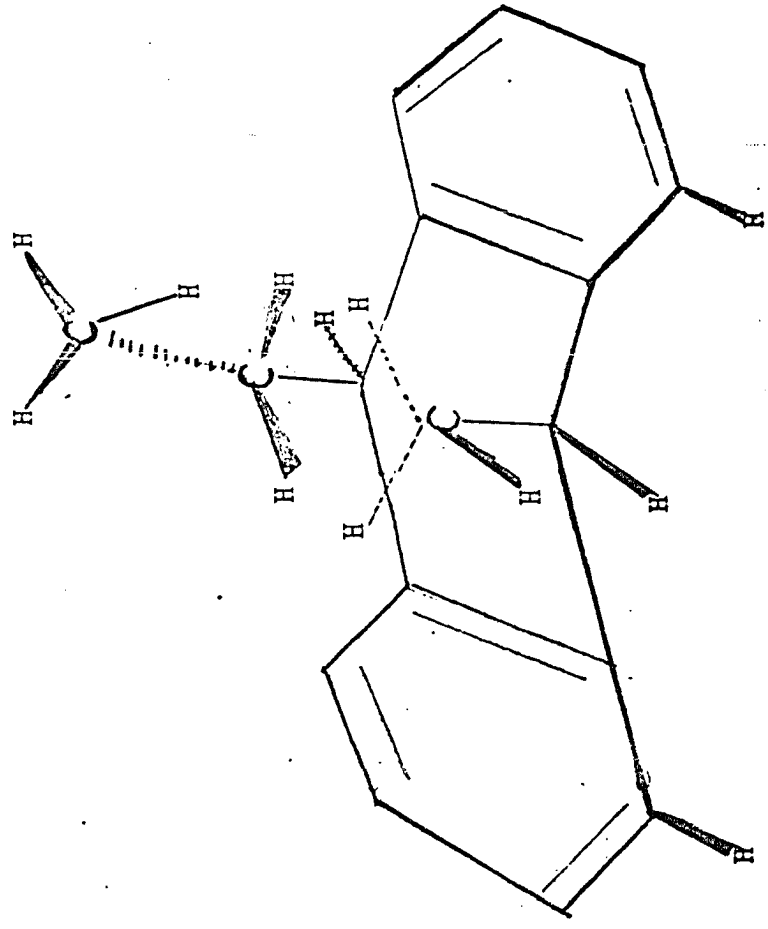


Figure 3 The conformation of cis-9-methyl-10-ethyl-9,10-dihydroanthracene

of this material shows a large peak at 2137 cm^{-1} attributed to the 9-equatorial deuteron, and a weak band at 2099 cm^{-1} arising from the 9-axial deuteron. Future study may show the existence of diastereotopic hydrogen atoms[90] (H_9 and H_{10}) in trans-9,10-diisopropyl-9,10-dihydroanthracene, if the energy barrier to interconversion is high enough such that low temperature nmr spectroscopy (on the Varian A-60 A spectrometer) is possible.

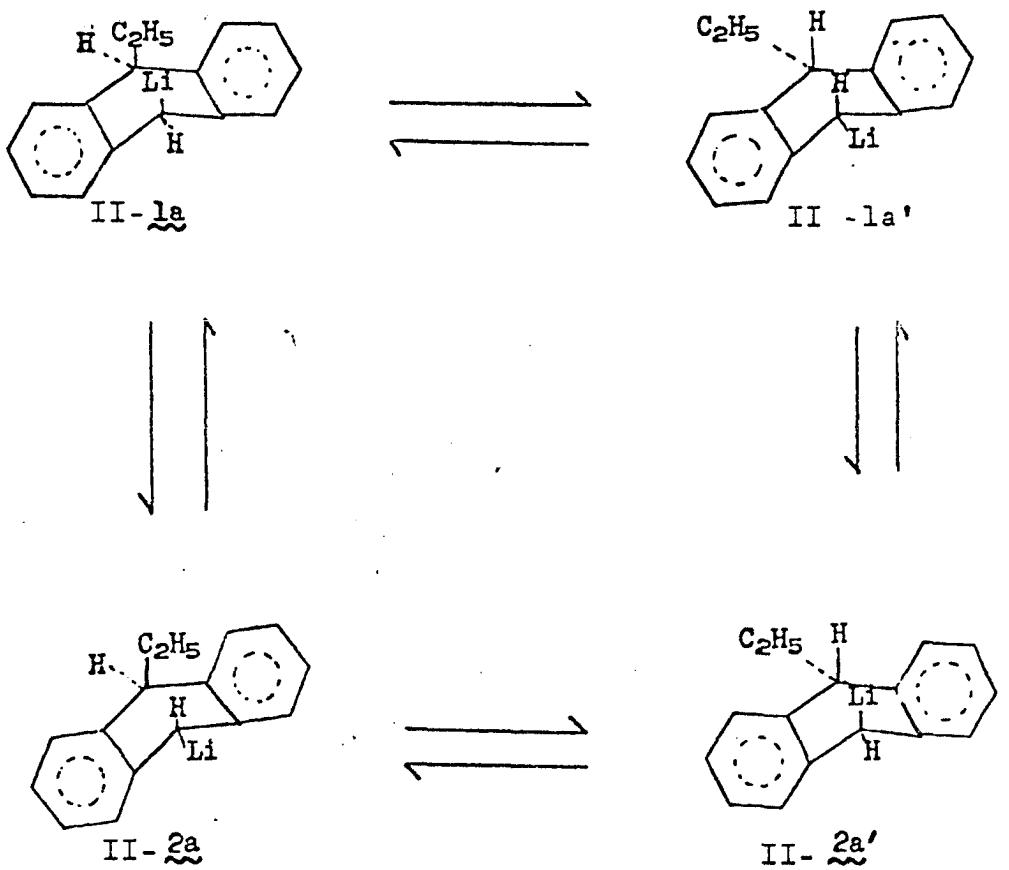
IV The Structure of 9-Lithio-10-ethyl-9,10-dihydroanthracene, (I-3)

Nicholls and Szwarc have tried to determine the structure of 9-lithio-10-ethyl-9,10-dihydroanthracene prepared by the addition of recrystallized ethyllithium to anthracene in THF.[40-42] The reaction of deuterium oxide with this intermediate over the temperature range of -70° to +55° gives only cis-9-deuterio-10-ethyl-9,10-dihydroanthracene.[41] This deuterolysis result has been interpreted in terms of cis-lithio compound 11. This assignment is supported by ultraviolet[41] and nmr spectroscopy[42] on the lithium compound (p 11).

When the intermediate lithium compound (I-3) is prepared by the addition of TMOPD-complexed ethyllithium to anthracene in cyclohexane, reaction with deuterium oxide gives a mixture of cis, (I-6), and trans, (I-7), deuterio compounds. This result suggested that in cyclohexane with TMOPD present, (I-3) is an equilibrium mixture of (II-1) and (II-2), p 43. In order to confirm the structure of the trans deuterio compound (I-7), it was desirable to have s sample of the pure cis isomer (I-6). Based on the results of the earlier workers[40-42]

Chart II

The conformational and configurational equilibria of 9-lithio-10-ethyl-9, 10-dihydroanthracene[a]



(a)

See E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, "Conformational Analysis" New York: Interscience Publishers (1966) p. 242.

the preparation of (I-6) by the addition of ethyllithium to anthracene in THF was attempted. We were surprised when a mixture of (I-6) and (I-7) was obtained in this solvent, too. The reason(s) for the difference between our results and those of Nicholls and Szwarc are not apparent. However, since these workers did not provide adequate experimental justification for their conclusions, the reliability of these conclusions is open to question.

The results given in table 1 (p 23,24) indicate that the ratio of cis : trans product is sensitive to the solvent (cyclohexane vs THF), the rate of addition of the acid to the lithium compound (fast vs slow addition of deuterium oxide), and the structure of the acid (deuterium oxide vs deuteriotriphenylmethane). These results are in accord with the equilibria pictured in chart II, p 43. The equilibria (II-1a) $\rightleftharpoons$ (II-1a') and (II-2a) $\rightleftharpoons$ (II-2a') represent inversion of conformation, for the cis- and trans-lithio compounds, respectively. The equilibria represented by (II-1a) $\rightleftharpoons$ (II-2a) and (II-1a') $\rightleftharpoons$ (11-2a') are changes in configuration.

It is known that the rate of reaction of an organolithium ((I-3)) with an oxygen acid (D_2O) is extremely fast, and is within the range of a diffusion controlled reaction, ($k_2 = 10^{11}$ M^{-1} sec^{-1}, $pK \approx 20$).[68] The transition state resembles the reactants (II-1, II-2). On the other hand, the rate of reaction of an organometallic with a carbon acid is slow ($k_2 = 10^{-7}$ M^{-1} sec^{-1}), and the transition state resembles the products (I-6, I-7).[68]

On this basis it is not surprising that reaction of a cyclohexane solution of (I-3) gives different product ratios when allowed to react with deuterium oxide and triphenylmethane-D. Judging from these results, in cyclohexane trans-lithio compounds, (II-2), are present in higher concentration at equilibrium than the corresponding cis isomers, (II-1). Theoretically, deuterium oxide is trapping these intermediates stereospecifically,[68] and the ratio of (I-6) to (I-7) in the products reflects the equilibrium ratio of (II-1) to (II-2). Apparently, the cis isomer, (II-1), reacts at a faster rate with a weak acid (triphenylmethane-D) than does the trans isomer, (II-2).

The addition of deuterium oxide to a THF solution of the lithium salt (I-3) affords a different mixture of products than is obtained from a cyclohexane solvated salt. This result implies that the ratio of cis-lithio compound, (II-1), to trans-lithio compound, (II-2), is different in these solvents. This solvent effect is not surprising[33] in light of recent work on the effect of solvent on the structure of ions and ion pairs.[70] Apparently, the cis-lithio compound, (II-1), reacts with deuterium oxide, present in insufficient amount in THF, faster than the trans compound, (II-2).

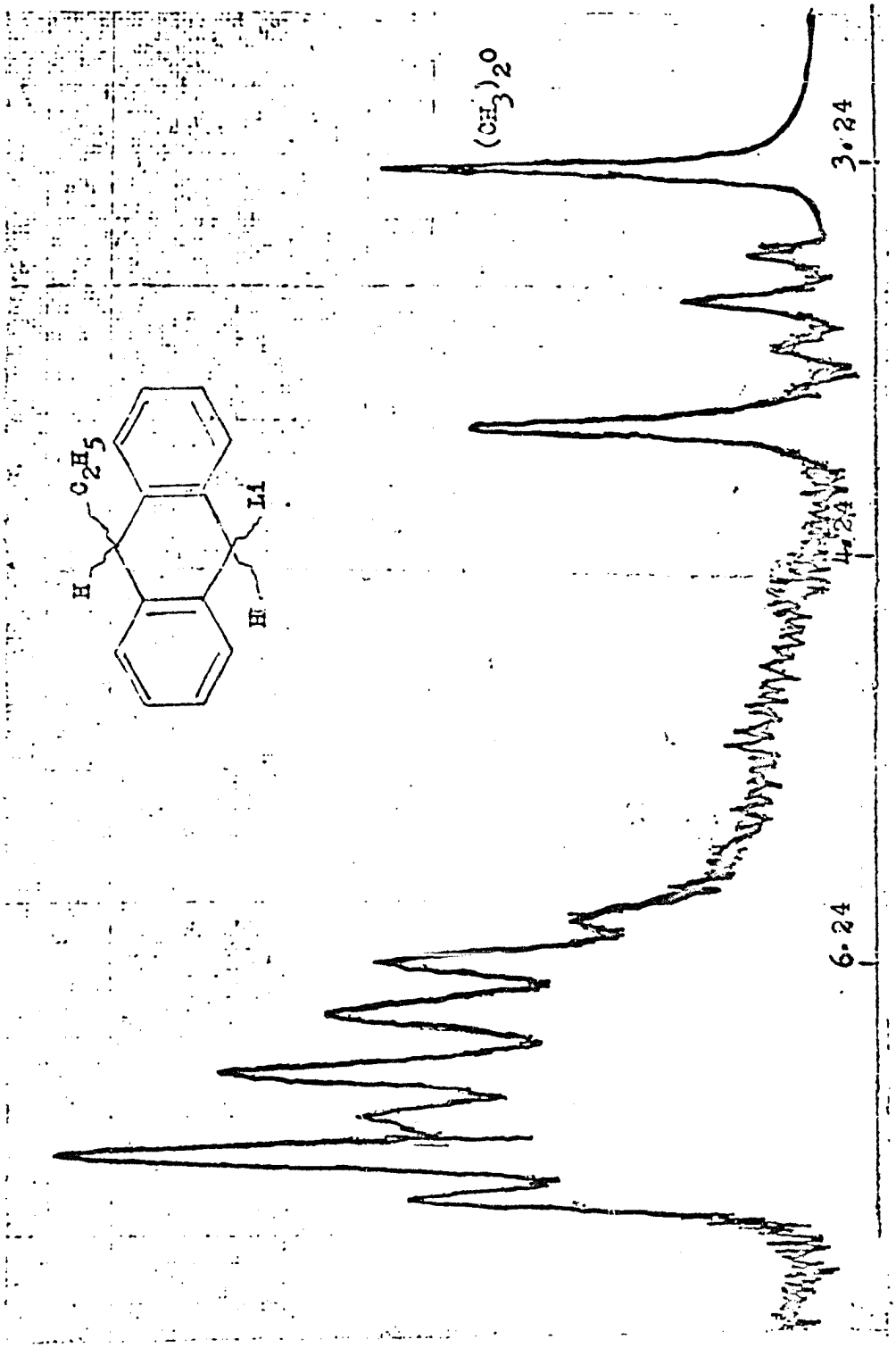
The reaction of alkyl halides with 9-lithio-10-ethyl-9,10-dihydroanthracene, (I-3), is expected[33] to be slower than the rate of reaction of (I-3) with deuterium oxide.[68] Therefore, it is expected that, in the absence of large steric factors present in the incoming halide,[54,61] the major product will be cis-9,10-dialkyl-9,10-dihydro-

anthracene. This, as we have already mentioned, (chart 1, p 25), is in accord with the experimental results.

The presence of equilibrating lithium compounds, (II-1) and (II-2), has been inferred from the reaction of 9-lithio-10-ethyl-9,10-dihydroanthracene, (I-3), with deuterium oxide and alkyl halides. However, no direct evidence[42] for their existence has been presented. Initial attempts to detect these compounds, (II-1) and (II-2), using nmr were unsuccessful due to the complexity of the reaction mixture, (chart 1, p 23,24). Eventually it was found that the system n-butyllithium, 9-ethyl-9,10-dihydroanthracene, methyl ether, afforded a solution of the desired salt, 9-lithio-10-ethyl-9,10-dihydroanthracene, (I-3). At + 35° the nmr spectrum* of this material (figure 4, p 47) showed a broad signal at 3.90 δ , attributed to the 9-proton. The 10-proton gave rise to a signal centered at 3.58 δ (triplet, J - 7 cps). Absorption in the region 5.84-7.0 δ (multiplet) was attributed to the aromatic protons.[42] This spectrum agrees well with the published spectrum[42] (see p 12) of this compound obtained from the addition of ethyllithium to anthracene in THF. The differences that do exist (e.g., chemical shifts) probably arise from differences in the solvating power[70] of THF as compared to methyl ether.

In the hydrocarbon (section III) it was shown that the benzylic

* Chemical shifts were measured relative to the dimethyl ether peak, taken as 194.4 cps downfield from TMS.



9-Lithio-10-ethyl-9,10-dihydroanthracene in dimethyl ether (from metalation)

Figure 4

proton on a carbon bearing an axial ethyl group gives rise to an absorption signal at 3.74-3.75 δ . This signal is sharper and occurs at higher field than the absorption of a benzylic axial proton. In the lithium compound the proton at C-10 gives an absorption signal at 3.58δ and the 9-proton signal appears at 3.90δ . These data are consistent with an equatorial C-10 proton (axial ethyl group, (II-1a), (II-2a)). The small upfield shift in the absorption of the lithium compound (C-10 proton) from that in the hydrocarbon is attributable to an increase in electron density at the 10-position.[44] Earlier workers,[42] using the criterion that axial protons absorb at higher frequencies than equatorial protons,[57] assigned the ethyl group an equatorial position, ((II-1a') and (II-2a')). This criterion, however, does not appear to be valid in the dihydroanthracene system, causing their assignment to be in error.

If the ethyl group is axial, then the broadness of the 9-hydrogen in (I-3) is compatible either with a single isomer or with a mixture in which one isomer predominated. If a single isomer is present, the broadness of the signal at C-9 indicates that this proton is axial. Since the proton at C-10 is equatorial and the lithium at C-9 is equatorial, then this compound must be the <u>trans</u> isomer, (II-2a). Previous workers[42] have also deduced that the lithium occupies an equatorial position (11).

Alternately, if the "carbanionic" center at C-9 is inverting rapidly on the nmr time scale ((II-1a) $\rightleftharpoons$ (II-2a)), then the proton

at C-9 will give a signal which is a weighted average of the separate signals arising from each of the salts. From the broadness of the peak, it would seem that the trans compound, ((II-2a), is predominant at equilibrium. This interpretation of the nmr spectrum of the salt, (I-3), is in agreement with the earlier analysis (p 44) of its structure.

Low temperature nmr studies on (I-3) should distinguish between a single species, (II-2a), and a mixture ((II-1a) and (II-2a)). Preliminary attempts to carry out this experiment were unsuccessful because the salt precipitated from solution (dimethyl ether-hexane) below room temperature.

In 9-lithio-10-ethyl-9,10-dihydroanthracene, (I-3), the aromatic hydrogens give rise to a multiplet which is shifted upfield from the position in the hydrocarbon. This effect has been discussed previously (pp 11,12). This upfield shift indicates[42] sp^2 hybridization of the "carbanionic" center with the aromatic nucleus. Such hybridization in no way invalidates the previous discussion of the geometry of the salt. The lithium can be cis or trans relative to the ethyl group regardless of the actual degree of planarity of the ring.

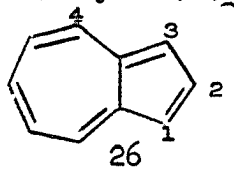
OTHER AROMATIC HYDROCARBONS

The facile addition of ethyllithium to anthracene seemed to provide a stepping stone for study of other aromatic substrates. Naphthalene and phenanthrene, both of which had been shown to react with butyllithium,[13,20] were studied next. Surprisingly, these hydrocarbons did not react with ethyllithium either in cyclohexane containing an equivalent

of TMOPD, alone in THF or with the amine in THF. Careful analysis of the cyclohexane reactions after addition of benzophenone indicated an almost quantitative recovery of hydrocarbon and unreacted ethyllithium.

The failure of naphthalene and phenanthrene to undergo addition or metalation with ethyllithium stands in sharp contrast to benzene. The ethyllithium-TMOPD complex metalated benzene slowly: 20% after three hours as judged by derivatization with benzophenone. All these studies were conducted at room temperature.

Study of the reactions of TMOPD chelated ethyllithium with aromatic hydrocarbons was extended to include perylene, (3, p 4),[17-19] azulene, (26),[71] and acenaphthylene, (14, p 13).[72]



26

Perylene gave a quantitative yield of ethyldihydrodroperylene with this reagent. A control run, identical except for the omission of TMOPD, afforded a quantitative recovery of unreacted perylene. The ethyldihydroperylene obtained from the addition of ethyllithium to perylene (in the presence of TMOPD) was converted to the known 1-ethylperylene[18] by dehydrogenation with chloranil. A compound, thought to be x-ethyldihydroazulene,[71] was obtained from the reaction of ethyllithium-TMOPD with azulene.

The reaction of complexed ethyllithium with acenaphthylene yielded a mixture.[72] Gas chromatography indicated the presence of

at least six components. The major component (20%), isolated by preparative gas chromatography, was shown to be the reduction product acenaphthene by the criteria of mixture melting point, gas chromatographic retention time and nmr spectral comparison. It was also established that at least one ethyldihydroacenaphthylene was present (see p 83).

V MECHANISM OF THE ADDITION REACTION

It was noticed that all of the unsaturated hydrocarbons which have been reported to undergo addition of ethyllithium possess low polarographic reduction potentials (Table 5, p 53). The aromatic hydrocarbons which exhibit ethyllithium addition at room temperature also possess low polarographic reduction potentials (Table 5, p 53), while hydrocarbons like naphthalene or phenanthrene that do not add ethyllithium have high reduction potentials comparable to that of benzene.

It was also clear that the ethyllithium-TMOPD complex in cyclohexane reacted slowly with benzene to give phenyllithium ($t_{\frac{1}{2}}$ = 4.0 to 5.0 hours) but quite rapidly with anthracene, acenaphthylene or perylene to give alkylation (reduction) products. A reasonable interpretation of these observations is that metalation is a slow process having a substantial activation energy barrier, while alkylation is a fast process having a low energy barrier for the three known aromatic hydrocarbons which exhibit the reaction. If this interpretation is correct, then metalation and alkylation proceed by different mechanisms.

Thus, the working hypothesis was developed that only aromatic hydrocarbons which are capable of forming radical anions relatively easily also exhibit alkylation, possibly by a scheme analogous to equations (11) - (13).

TABLE 5

Polaragraphic Reduction Potentials of Reactive Hydrocarbons [82]

Hydrocarbon	$E_{\frac{1}{2}}$ vs Hg pool	Reactivity with EtLi
benzene	-2.84v	metalation
naphthalene	-1.98v	no reaction
phenanthrene	-1.92v	no reaction
diphenylacetylene	-1.68v	addition [1]
anthracene	-1.46v	addition
perylene	-1.15v	addition
acenaphthylene	-1.13v	addition,reduction
azulene	-1.11v	addition

(11) Anthracene + $C_2H_5Li \rightleftharpoons$ (complex)$^{22,82d} \longrightarrow$

$C_2H_5\cdot$ + (Anthracene radical anion, 5) Li^+

(12) Anthracene + $C_2H_5\cdot \rightarrow$ 10-ethyl-10-hydroanthracene-9-(·)
27

(13) 27 + $C_2H_5Li \rightarrow$ 9-lithio-10-ethyl-9,10-DHA + $C_2H_5\cdot$
(I-3)

In the first step (eq 11) the organolithium reagent transfers an electron to the substrate[19, 24-27, 74] (anthracene).[73] This generates anthracene radical anion (5)[24, 25, 46, 73] and an ethyl radical. Transfers of this type are not reversible.[25] Recent workers have proposed that electron transfer occurs in most reactions of lithium alkyls.[24, 38, 48, 49, 73, 75]

In the second step (eq 12) the ethyl radical adds[76] to a fresh molecule of anthracene generating aralkyl radical 27. In the last step (eq 13), this radical (27) is reduced by fresh ethyllithium. This reaction yields 9-lithio-10-ethyl-9,10-dihydroanthracene ((I-3)) and a new ethyl radical.

Reduction of a radical by an alkyllithium reagent (eq 13) has not been demonstrated by others (See eq 9, p 13).[27] It was easy to show (visible spectroscopy) that n-butyllithium (or ethyllithium) reduces triphenylmethyl radical (yellow) to the known[42] triphenylmethyl carbanion (red) rapidly. By analogy to this reaction, the reduction

of radical 27 to salt (I-3) (eq 13) is expected to be rapid.

Equation (12) proposes that the ethyl radical formed in step 1 (eq 11), reacts with a fresh molecule of anthracene rather than coupling[27] with anthracene radical anion (5) (i.e., mechanism 2, equation (6), p 8). It has been shown[23] that the addition of n-butyllithium to anthracene radical anion (5) is slower than the addition of n-butyllithium to anthracene. It has been suggested[23] that the reactive substrate in this reaction is anthracene produced in the equilibrium[25] (equation 14):

(14) $5 \rightleftharpoons \frac{1}{2}$ (anthracene) $+ \frac{1}{2}$ (9,10-dilithio-9,10-DHA)

If a free ethyl radical were actually formed, as depicted in equation (11), a mixture of products, including dimers, might be expected.[76] Winkler has pointed out[23] however, that a "free" radical is unlikely but a "concerted radical attack during one electron transfer is conceivable."[27] Alternately, the electron transfer and radical addition steps (eq 11 and 12) may take place within a solvent cage.[27] Mulvaney has suggested that the reaction of t-butyllithium with diphenylacetylene[27] proceeds within such a cage (Eq 9, p 13). An electron transfer mechanism,[34] based on a kinetics study,[77] has been presented. The reaction which was investigated was the addition of n-butyllithium to diphenylacetylene.[77]

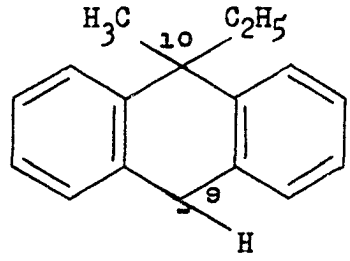
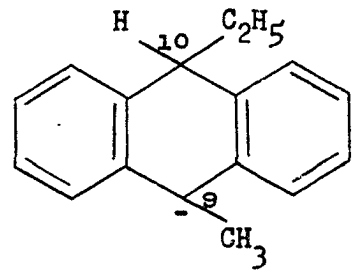
The idea that a radical addition to anthracene (eq 12) must give some dimeric material and a mixture of ring alkylated products[76] may not be correct.[23] It is known that the reactions of radicals with a given substrate are sometimes dependent upon the source of the radical[78-80] and the reaction conditions.[27,76] Thus, the absence of

these products is not conclusive evidence that a radical mechanism is not operative.

The minimum criterion that the proposed mechanism (eq 11 - 13) must meet, is that each one of the steps be thermodynamically possible. Unfortunately, the required thermodynamic data (free energies of reaction and formation) are not available in the literature. Other workers in the field of organolithium chemistry have also encountered this problem.[23] The only evidence of this type which can be presented for the porposed mechanism is that each individual step (eq 11-13) represents a known reaction. These reactions have been documented in the previous discussion. In summary, it would seem that the best evidence against a carbanion mechanism (eq 5 p 8) is that no one has demonstrated[20-22,52] the existence of simple alkyl carbanions[39] in these systems [i.e., methyllithium, ethyllithium etc. in hydrocarbons or tetrahydrofuran. The existence of carbanions in more complex systems (i.e., fluorenyllithium, diphenylmethyllithium, etc.)[42] is known.[42]] A radical-radical anion combination process (mechanism 2, eq 6) is perhaps the best documented[75] of the three mechanisms. However, this mechanism, like the carbanion mechanism, does not offer the best explanation for the addition reactions recorded.

The addition of ethyllithium to 9-methylanthracene (28) provides a system which can distinguish between mechanism 1 or 2 and 3 (p. 8). If alkylation involves a concerted ionic process, a 9-lithio-10,10-dialkyldihydroanthracene, 29, should be formed preferentially rather than 30, 9-lithio-9-methyl-10-ethyl-9,10-dihydroanthracene, because 2^{o} carbanions are of lower energy than 3^{o} car-

banions (eq 15)[39]

(15) 28 →  

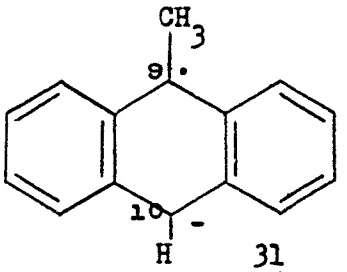
29 30

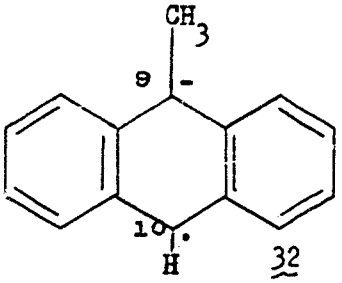
thermodynamically favored

thermodynamically unfavored

Conversely, mechanism 2 (involving radical anion formation) anticipates selective formation of 31 rather than 32. This prediction is supported by molecular orbital calculations which show that the π electron density at the 9-position is lower than the electron density at the 10 position (1.000000 vs 1.285714).[81] In the subsequent radical-coupling step (eq 16) 31 gives 29 while 32 yields 30.

(eq 16) 28 ⟶



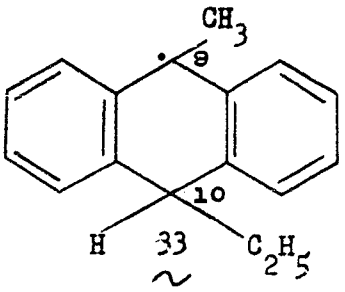


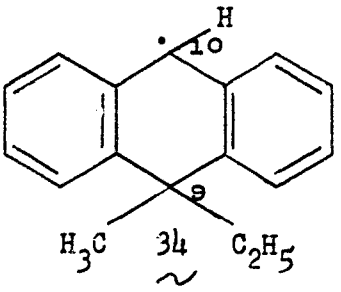
thermodynamically favored

thermodynamically unfavored

If the reaction proceeds via mechanism, 3, then tertiary radical 33 will be formed in preference to secondary radical 34 in the initial step (eq 17). Subsequent reduction of radical 33 would produce carbanion 30 whereas reduction of radical 34 would give carbanion 29 (eq 18)

(eq 17) 28 ⟶





(eq 18)

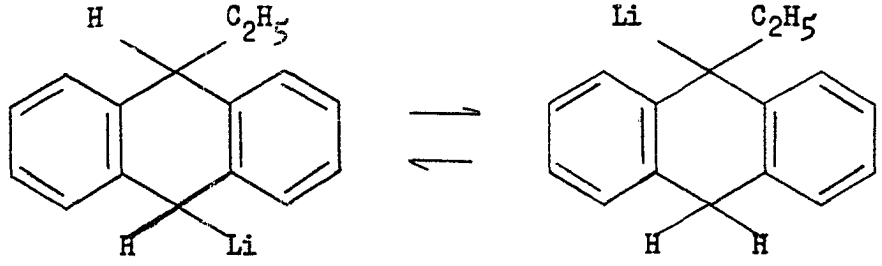
30

29

It was found that the addition of ethyllithium to 9-methylanthracene in THF yields, in addition to starting material, one major component (approximately 25% yield as judged by vpc) and several minor components. One of the minor components, obtained by precipitation with carbon tetrachloride, was a high melting (318°), presumably dimeric, hydrocarbon. The structure of this material was not determined. The major product, isolated by preparative vpc, was shown to be cis-9-ethyl-10-methyl-9,10-dihydroanthracene by the criteria of vpc retention time, melting point and mixture melting point with authentic material.

The isolation of cis-9-ethyl-10-methyl-9,10-dihydroanthracene is in accord with the predictions of mechanism 3 (radical addition). Deuterolysis studies reported earlier (p. 10) were interpreted as excluding equilibration of the secondary lithium compound (I-3) with

(19)



1-3 36

the (undetected) tertiary lithium compound, 36.[40] No evidence for a tautomeric equilibrium could be found during the present research. Reasoning by analogy with equation (19), it is clear that a secondary carbanion (in the 9,10-dihydroanthracene system) like 29 is of lower energy than a tertiary carbanion like 30. Further, there is no evidence that 29 and 30 formed from 9-methylanthracene are capable of interconverting.

If an ionic mechanism was operating, then the formation of the higher energy content system (30) might be explained in the terms of steric hindrance of a methyl group (preventing the formation of 29) or kinetic control of product formation. Since very little is known about the structure of the starting alkyllithium complex,[22,82d] and since the mechanism of the addition process is unknown, the effects of steric factors and kinetic control of products cannot be evaluated. In 9-methylanthracene, steric inhibition by the methyl group probably is not sufficiently great to favor the selective formation of 30 over 29.

If a radical-radical anion combination mechanism were operating, a mixture of 29 and 30 would be expected to form. The preliminary results on 9-methylanthracene do not appear to give products arising from a mixture of 29 and 30, but rather, a mixture of cis and trans isomers derived from 30. Consequently, a mechanism involving formation of 33 rather than 34 (by attack of a radical on 9-methylanthracene) seems to be a better interpretation of the present data.

SUMMARY AND CONCLUSIONS

The addition of ethyllithium-TMOPD to anthracene in cyclohexane has been shown to proceed in a rapid. quantitative manner to afford 9-lithio-10-ethyl-9,10-dihydroanthracene. Reaction of this organolithium with deuterium oxide or alkyl halides gives high yields of 9-deuterio-10-ethyl-9,10-dihydroanthracene and 9,10-dialkyl-9,10-dihydroanthracenes, respectively. It has been found that in the case of methyl iodide or ethyl bromide a single 9,10-dialkyl-9,10-dihydroanthracene is produced. The stereochemistry of these compounds has been shown to be cis by a stereospecific synthesis of cis-9-methyl-10-ethyl-9,10-dihydroanthracene.

By the use of deuterium labeling and the infrared carbon-deuterium stretching frequencies of suitably labeled compounds, it has been shown that the alkyl group (s) in 9-alkyl- and cis-9,10-dialkyl-9,10-dihydroanthracenes prefer the axial or diaxial conformation, respectively.

Product analysis and nmr spectral studies have suggested that 9-lithio-10-ethyl-9,10-dihydroanthracene may exist as a pair of rapidly equilibrating cis-trans isomers, rather than as a single stereoisomer.[40-42]

Although benzene is metalated by the ethyllithium-TMOPD complex in cyclohexane, naphthalene and phenanthrene undergo neither metalation nor addition of ethyllithium under the same conditions. The reasons for the difference between benzene and naphthalene or phenanthrene are not clear, although differences in the structure or

the energy of the complex (7) formed between the aromatic hydrocarbon and ethyllithium may exist.[82d] Unfortunately, the structures of these complexes are unknown, and therefore, the validity of this idea cannot be tested.

One of the accomplishments of this research was the finding that ethyllithium-TMOPD afforded quantitative yields of 1-ethyl-dihydroperylene. This represents a marked improvement in the synthesis and yield of this difficulty accessible hydrocarbon.[18] Further, it provides a quantitative measure of the ethylating efficiency of this system in comparison with other ethyllithum alkylation systems.[18, 20-22]

The initial goal of establishing criteria for predicting those combinations of alkyllithium reagent and aromatic hydrocarbon which would react, was achieved. These criteria are based on the polarographic reduction potential of the aromatic hydrocarbon. The criteria seem to be effective in cyclohexane-TMOPD and THF solvent systems. Although quantitative work has to be performed to determine the precise limiting values, from the information currently available, the following generalizations can be made. Methyllithium will add to those hydrocarbons having a reduction potential lower than or equal to about -1.2 volts. Thus perylene ($E_{\frac{1}{2}}$ = -1.15 v) is predicted to be reactive, and anthracene is predicted to be unreactive. Unreported observations in this laboratory and the published report of Winkler[18] support this. Ethyllithium will be an effective ethylating agent for systems whose reduction potential is about -1.68 volts. For example, diphenylacetylene ($E_{\frac{1}{2}}$ = -1.68) adds ethyllithium, but phenanthrene ($E_{\frac{1}{2}}$ = -1.9) is unreactive. It is predicted that pyrene ($E_{\frac{1}{2}}$ = -1.6)

will add ethyllithium in cyclohexane-TMOPD, in contrast to its metalation with n-butyllithium in THF. n-Butyllithium seems to be an effective n-butylating agent for hydrocarbons with a reduction potential of about -2.0 volts. This includes naphthalene and phenanthrene, but excludes benzene, biphenyl and biphenylene. These give metalation products.[3,4] t-Butyllithium, perhaps in THF and with ultraviolet excitation,[23] should be effective in alkylating these latter systems.

Interestingly, this correlation may be extended to Grignard reagents. Although the exact details have not been determined in these systems, the following generalizations seem to apply. Simple alkyl Grignard reagents will add to systems whose reduction potential is about -1.0 volt. Pyridine and similar heterocycles, cyclooctatetraene[7] and some polynuclear aromatic hydrocarbons having reduction potentials in this range are expected to undergo addition. The reduction potentials[82] used for these predictions are relative to a mercury pool, and are about 0.52 volt lower than potentials measured relative to a saturated calomel electrode.

Finally, evidence has been obtained which suggests that the addition of ethyllithium to anthracene and 9-methylanthracene may be a free radical process. A mechanism involving radicals has been proposed. The first step of this mechanism requires single electron transfer from the ethyllithium to the aromatic hydrocarbons. In that the aromatic hydrocarbon suffers a single electron reduction, this step is analogous to polarographic reduction.[82] The proposed radical mechanism may be general for a variety of organometallic addition reactions, although it is not the exclusive mechanism in reactions of this type.

We did not obtain any evidence that a lithio alkyldihydro-aromatic (20, p 14) was present in the metalation of benzene. Further, 9-lithio-10-ethyl-9,10-dihydroanthracene, (I-3), did not give 9-lithioanthracene under the same (benzene) conditions. This suggests that 20 is not an intermediate in metalation.[52]

EXPERIMENTAL

Chemicals

Standard cyclohexane solutions of ethyllithium were prepared by distillation in vacuo of the benzene in commercial ethyllithium (Foote Mineral). After the addition of two volumes of dry, olefin-free cyclohexane, 5.0 ml aliquots were removed for analysis by titration.[83] (All transfers of alkyllithium reagents and dry solvents were made with hypodermic syringes). The analysis was accomplished as follows:

To 20 ml of dry cyclohexane, maintained under an argon atmosphere, was added by means of a syringe 5.0 ml of the cyclohexane solution of ethyllithium. To this was added 0.5 ml of a 0.025 M solution of phenanthroline in dry benzene. Phenanthroline forms a red-brown colored complex with the ethyllithium. This colored solution is titrated with a 1.0 M solution of sec-butanol in dry benzene. The end-point is indicated by the disappearance of the red-brown complex of phenanthroline with ethyllithium and the formation of a pale straw-yellow solution. Replicate analyses were accomplished by adding a fresh aliquot of ethyllithium and of phenanthroline to the flask. Titrations were reproducible to within $\pm$ 0.01 ml by this technique.

n-Butyllithium and methyllithium were titrated in the manner described above for ethyllithium.[83]

Cyclohexane was washed with aqueous potassium permanganate, sulfuric acid and water. It was dried over sodium ribbon. Spectral

grade benzene was stored over sodium ribbon and used without further purification. Tetrahydrofuran was dried by refluxing over sodium, and was distilled before use.

Argon (Matheson) and prepurified nitrogen (Matheson) were dried prior to use by passage through a tower of calcium hydride dust. The apparatus described by W.S. Johnson and W.P. Schneider[84] was used to maintain an inert atmosphere over reaction mixtures.

Anthracene (Matheson, Coleman and Bell, fluorescent grade) was dried at 110° for 24 hours before use. Naphthalene and phenanthrene (Kodak, white label) were sublimed prior to use. Azulene (K & K Laboratories), acenaphthylene (Fluke), triphenylmethane (Kodak), and perylene (American Cyanamid) were used as obtained without further purification. TMOPD (Kodak) was distilled under nitrogen (bp 92°/ 10 mm). Recently (1 month) distilled amine was more effective than several-months-old samples.

Instruments

Gas chromatography was performed with an F and M model 500 instrument equipped with a ¼ inch O. D., two foot 25% Apiezon N column on Chromsorb P. The column temperature was held at 275° with a helium flow rate of 80 cc/min. The injection port was maintained at 320° and the detector block at 300°. The filament current was 100 ma. Under these conditions, the following retention times, relative to the retention time of anthracene, were found: 9,10-dihydroanthracene 0.61; 9,-methyl-9,10-DHA 0.62; 9-ethyl-9,10-DHA 0.69; cis-9-methyl-10-ethyl-

9,10-DHA 0.75; cis-9,10-diethyl-9,10-DHA 0.92; 9-ethylanthracene 1.68. Calibration curves were used for quantitative work.

Nmr spectra were obtained on a Varian A-60 A spectrometer equipped with a variable temperature probe. Spectra were obtained as solutions in carbon tetrachloride or deuterochloroform at a probe temperature of 35-39°, unless otherwise noted. Infrared spectra were taken on a Perkin-Elmer 137 Infracord or a Perkin-Elmer model 21 prism infrared spectrophotometer. Spectra were calibrated by means of a polystyrene calibration film. Ultraviolet spectra were recorded on a Perkin-Elmer model 202 ultraviolet-visible spectrophotometer. Mass spectra were run on a CEC Model 21-103 mass spectrometer in the Department of Chemistry, California Institute of Technology.

Other

Yields are computed from the total weight of product obtained and the theoretical yield based on the quantity of starting hydrocarbon used in the reaction. In cases where product mixtures are obtained, this weight yield is corrected for the presence of impurities as judged by nmr and vpc. For example, if 0.005 mole (0.89 g) of anthracene is allowed to react with ethyllithium, 1.29 g of product is obtained after hydrolysis. If this material is nmr and/or vpc pure, the 1.29 g of product represent 0.005 mole (100% yield) of product. If, however, nmr or vpc indicates that this material is only 80% pure, the yield of this component is 80%.

Quantitative Analysis of Reaction Mixtures

The purity of the major component obrained in a reaction was

determined from the total integral of the nmr spectrum obtained on the mixture. In all cases yields were calculated from the ratio of aromatic : benzylic : aliphatic hydrogens. Thus, for the mixture discussed previously, this ratio was: 97 (aromatic) : 38 (benzylic) : 50 (aliphatic, ethyl group). If each hydrogen in the ethylated product accounts for 10 integral inits (5 aliphatic hydrogens x 10 units/hydrogen = 50 units). then 80 (8 aromatic hydrogens x 10 units/hydrogen = 80 units) of the 97 aromatic units are from this compound. The purity of the 9-ethyl-9,10-dihydroanthracene obtained in this reaction is: 80 units aromatic hydrogen/97 units total aromatic hydrogen = 82%. The purity obtained in this manner is good to within $\pm$ 2%.

Vapor phase chromatography was employed as an alternate or additional method of quantitative analysis. For the above reaction, a solution (containing weighed amounts of 9,10-dihydroanthracene, 9-ethyl-9,10-dihydroanthracene and 9-ethylanthracene) was prepared in a volumetric flask. Aliquots of this solution (ranging in volume from 1.0 to 100.0 μl) were subjected to vpc analysis. From the area under each peak (area = peak height x peak width at half height) calibration curves of concentration vs area were prepared for each compound. A solution of the crude reaction product was then injected into the vpc. By the use of the calibration curves, the peak areas obtained for the crude reaction product were converted into molar concentrations. From these concentrations a material balance and percent purity could be calculated. The estimated error limits of results obtained by this

method are ± 2%.

Analyses performed using both the nmr and vpc methods usually agree to within ± 2%, eg. 80 ± 2% by vpc, 82 ± 2% by nmr.

The reactions of alkyllithium reagents with aromatic hydrocarbons were all performed in the manner described in detail below for the addition of ethyllithium-TMOPD complex to anthracene.

Addition of Ethyllithium-TMOPD Complex to Anthracene

A 100 ml three-necked flask (14/20 joints) was equipped with a glass encased magnetic stirring bar and a gas inlet tube in the center neck. A stream of dry argon was admitted through the gas inlet tube, and the flask was flamed with a blue bunsen flame for five minutes. The flame was removed and the side necks of the flask were closed with serum caps. A positive pressure of argon was maintained while the flask cooled.[84]

When the flask had cooled to room temperature, 10.0 ml of a 0.50 M solution (0.005 mole) of ethyllithium in cyclohexane and 30 ml of cyclohexane were added through one of the side necks to the flask. A hypodermic syringe fitted with a two-inch, 18 gauge needle was used to transfer these reagents. A slow stream of argon was passed through the flask, and 0.005 mole (0.89 g) of anthracene was added by momentarily removing one of the serum caps. After the serum cap had been replaced, the stream of argon was reduced so that a slight positive pressure of argon was maintained.[84]

To this stirred slurry of anthracene and ethyllithium in

cyclohexane was added 0.75 ml (0.8 g, 0.005 mole) of freshly distilled TMOPD. Within fifteen minutes the color of the slurry changed from pale yellow to orange, and then to a deep-red, opaque solution. After magnetic stirring for three hours* at room temperature, reactions were terminated with one of the following: (a) Deuterium oxide or water (b) Methyl iodide (c) Ethyl bromide

(a) Deuterium oxide:

One ml of deuterium oxide was added, by means of a hypodermic syringe, in one portion. The reaction mass was washed with 1:1 aqueous hydrochloric acid (5 x 50 ml), 5% aqueous sodium bicarbonate (2 x 50 ml), saturated sodium chloride (2 x 50 ml), and was dried over sodium sulfate. After filtration and concentration under reduced pressure on a rotary evaporator, a pale yellow oil (1.04 g, 100%) was isolated. Analysis (nmr and vpc) indicated that this was a mixture of cis- and trans-9-deuterio-10-ethyl-9,10-dihydroanthracene, ((I-6) and (I-7), 88-95% yield, range 8 runs), together with trace amounts of 9-ethylanthracene, 9,10-dihydroanthracene and anthracene. The cis-trans ratio (40 ± 3% cis, average of 4 runs) was determined from the integration traces of the benzylic hydrogens in the nmr spectrum (figure 1).

In the trans isomer, the hydrogen at C-9 appears as a broad

*Yields of 80% were obtained after 30 minutes when freshly distilled TMOPD was used.

(unresolved) signal at much lower field (δ = 4.01 ppm) than the proton at C-10 (3.75 δ) or the hydrogen at C-9 in the cis isomer (3.74 δ). See figure 1, p 26, for the nmr spectrum in $CDCl_3$ and table 2 for data.

An IR spectrum on a neat sample showed C-D stretching vibrations as a pair of doublets at 2110 cm^{-1} (strg.), 2088 cm^{-1} (weak) and at 2160 cm^{-1} (med.), and 2145 cm^{-1} (med.). These values show small deviations from axial and equatorial C-D stretching vibrations reported for cis- and trans-4-deuterio-t-butylcyclohexane.[62] (See Table 4, p 36) for data.

The mass spectrum showed a molecular ion at m/e = 209 and exhibited a fragmentation pattern in harmony with the loss of H, D, both H and D, and $C_2H_5^-$. When the m/e = 209 peak was set equal to 100, the peaks at 210 and 211 had relative abundances of 20.1 and 2.45% in good agreement for a monodeutero material. No ions were observed at m/e = 212-218. A trace impurity could be detected at m/e = 221.

Run 2 Hydrolysis of a parallel run with water gave 9-ethyl-9,10-dihydroanthracene as an oil. After low temperature recrystallization from ethanol, 0.7 g (70%) of crystalline hydrocarbon having a mp of 42-43° was secured. The nmr spectrum of this material was identical with the literature spectrum[40] (table 2, p 27).

(b) Methyl iodide: cis-9-methyl-10-ethyl-9,10-dihydroanthracene, (I-4)

Quenching with methyl iodide (3 ml) gave (I-4) (0.96 g, 100%). Analysis of this product by nmr and vpc indicated that it was 85-93% pure (9 runs). After recrystallization from ethanol white needles, mp 105-106° were secured in 70% yield. The melting point reported

in the Ph D Thesis of D. A. Redford for this compound is 108.0-108.5°.[54]

Anal. Calcd for $C_{17}H_{18}$: C, 91.84: H, 8.16. Found: C, 91.58, H, 8.16.

Trans-9-methyl-10-ethyl-9,10-dihydroanthracene could not be detected either by vpc or nmr (see table 3, p 34). A mass spectrum of (1-4) exhibited a small molecular ion at m/e = 222. The UV spectrum in ethanol had λ_{mu} (ε) values of : 258.5 (708.), 265.2 (1013.) and 272.4 (1038.) which compared well with values for the hydrocarbon obtained by reducing 9-methyl-10-ethylanthracene with sodium in alcohol.[54]

(c) Ethyl bromide: cis-9,10-diethyl-9,10-dihydroanthracene, (I-5)

Cis-9,10-diethyl-9,10-dihydroanthracene, mp 57.5°-58.5° (lit. 59-60°)[85] was isolated in 80% yield after addition of ethyl bromide (3 ml) to 9-lithio-10-ethyl-9,10-DHA (see table 2 for nmr spectral data). Nmr spectra on crude reaction mixtures indicated the possible presence of about 4% of the trans isomer (table 3, p 34), 51 cps (triplet, J = 7). This material could not be isolated. The mass spectrum for the purified hydrocarbon ((I-5, cis isomer) exhibited a molecular ion at m/e = 236 and a fragmentation pattern similar to spectra of (I-6) and (I-7).

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.50; H, 8.29.

Preparation of 9-methyl-10-ethylanthracene by Oxidation to cis-9-methyl-10-ethyl-9,10-dihydroanthracene, (I-4)

A mixture of (I-4) (1.2 g) and sulfur (0.4 g) were heated (in

a sealed tube) at 250° for three hours. The crude product, analyzed by nmr, had a spectrum consistent with its formulation as 9-methyl-10-ethylanthracene, 7.78 δ (aromatic, 8H, doublet of quartets, $J_{doublet}$ = 25 cps, $J_{quartet}$ = 3 cps); 3.60 δ (q, J = 7.5 cps, 2H, $C\underline{H}_2$-CH_3); 3.07 δ, (s, 3H, $-CH_3$); 1.32 δ (t, J = 7.5 cps, 3H, $-CH_2$-$C\underline{H}_3$). Recrystallization from ethanol gave yellow needles, (0.60 g, 50.5% yield), mp 128-9° (Lit. mp 145.5°).[53] Admixture with starting material (I-4) depressed the mp > 20°.

Triphenylmethane-D

To a solution of triphenylmethane (25 g, 0.10 mole) in 250 ml of dry THF maintained under argon at 0° was added 0.11 mole of n-butyllithium. The solution was allowed to stir for one hour, deuterium oxide (3.0 ml) was added, and stirring was continued for an additional three hours. The reaction was transferred to a separatory funnel, washed with water and the organic layer was concentrated to dryness affording 24.0 g (96%) of triphenylmethane-d,[68] mp 91-92°. This material contained better than 95% D as determined by nmr.

The reaction of 9-lithio-10-ethyl-9,10-DHA with triphenylmethane-D

To a solution of 9-lithio-10-ethyl-9,10-DHA prepared from 0.005 mole each of anthracene, ethyllithium and TMOPD in 50 ml of cyclohexane, was added 0.01 mole of solid triphenylmethane-D. After 24 hours deuterium oxide (1.0 ml) was added and the solution was allowed to stir an additional hour before the product was isolated. Nmr spectral analysis of the isolated product indicated a 43/57

ratio of trans- to cis-9-deuterio-10-ethyl-9,10-DHA. This ratio was nearly the reverse of that obtained when hydrolysis with deuterium oxide alone is accomplished.

Additions of Ethyllithium to Anthracene in THF

To 0.005 mole (0.89 g) of anthracene in dry THF (50 ml) maintained at 0-5° was added 10 ml of a 0.50 M solution (0.005 mole) of ethyllithium in cyclohexane. After magnetic stirring for 30 minutes at 0° to +10°, the reactions were terminated: (a) with rapid addition of excess deuterium oxide (1 ml): (b) with rapid addition of excess methyl iodide (2 ml); (c) with rapid addition of excess ethyl bromide (2 ml). After work up as described above (omitting the aqueous hydrochloric and sodium bicarbonate washes) the products obtained were: (a) a 1:1 mixture of cis- and trans-9-deuterio-10-ethyl-9,10-dihydroanthracene ((I-4) and (I-5)) in 98% isolated (crude) yield; (b) a 98% yield (isolated) of cis-9-methyl-10-ethyl-9,10-DHA, (I-4); and (c) a 96% isolated yield of cis-9,10-diethyl-9,10-DHA, (I-5). The melting points and nmr spectra of these compounds matched the melting points and spectral data for samples obtained by bis amine catalyzed reactions in cyclohexane.

Preparation and Reactions of 9-lithio-10-alkyl-9,10-dihydroanthracenes from Metalation of 9-alkyl-9,10-dihydroanthracene by n-Butyllithium in Tetrahydrofuran

To a stirred solution of 0.01 mole of 9-alkyl-9,10-dihydroanthracene (R = methyl or ethyl) under dry argon in THF at -60° was

added in one portion, 0.01 mole of n-butyllithium (Foote Mineral) in hexane. After warming to + 10° during 30 minutes, the deep-red colored solution was cooled to -30° and terminated with: (a) deuterium oxide; (b) methyl iodide; (c) ethyl bromide.

Metalation of 9-Ethyl-9,10-dihydroanthracene, (I-2)

(a) 9-Lithio-10-ethyl-9,10-dihydroanthracene, (I-3), was prepared from 0.01 mole of n-butyllithium and 0.01 mole (2.08 g) of (I-2) in 100 ml of THF. Deuterium oxide (1. ml) in 3.5 ml of dry THF was added in one portion, and a 1:1 mixture of (I-6) and (I-7) (nmr) was secured. The yield was 95% based on the weight of the product.

(b) Run 2: Slow addition of deuterium oxide to 9-lithio-10-ethyl-9,10-dihydroanthracene, (I-3)

To 0.005 mole of freshly prepared 9-lithio-10-ethyl-9,10-dihydroanthracene (from (I-2)) in 50. ml of THF, deuterium oxide (0.10 ml in 40. ml of tetrahydrofuran) was added dropwise during one hour at temperatures below -20°. Magnetic stirring for an additional hour with warming to + 25° was followed by addition of 0.1 ml of deuterium oxide. After product isolation, analysis of the benzylic proton portion (3.34 -5.00 δ) of the nmr spectrum indicated a 2:1 mixture of (I-6) : (I-7). This analysis is less precise than earlier analyses because of the formation of 9-ethyl-9,10-dihydroanthracene through reaction with the solvent (THF).

Run 3: Inverse addition of 9-lithio-10-ethyl-9,10-dihydroanthracene (I-3), to deuterium oxide

Rapid inverse addition of 0.005 mole of (I-3) to a solution of deuterium oxide (2 ml) in THF (15 ml) gave a 1:1 mixture of cis- and trans-9-deuterio-10-ethyl-9,10-dihydroanthracene.

Run 4: The addition of methyl iodide to 9-lithio-10-ethyl-9,10-dihydroanthracene, (I-3)

The addition of methyl iodide (3 ml) to 50 ml of a 0.1 M solution (0.005 mole) of (I-3) in THF gave a 98% yield of cis-9-methyl-10-ethyl-9,10-dihydroanthracene, (I-4).

Run 5: The reaction of 9-lithio-10-ethyl-9,10-dihydroanthracene (I-3), with ethyl bromide

The reaction of (I-3) (0.005 mole in 50 ml of THF) with ethyl bromide (3. ml) yielded cis-9,10-diethyl-9,10-dihydroanthracene (I-5) in 96% isolated yield.

Cis-9,10-diethyl-9-deuterio-10-hydroanthracene

To a solution of 9-deuterio-10-ethyl-9,10-dihydroanthracene (1. g, 0.005 mole) in 60 ml of THF was added 0.006 mole of n-butyllithium. The solution was warmed from -30° to +10° during thirty minutes. Ethyl bromide (2 ml) was added and cis-9,10-diethyl-9-deuterio-10-hydroanthracene, (mp 57-58°, 0.5 g, 40% yield), admixed with an equal quantity of (I-5), was isolated. The nmr spectrum of this material was similar to that of (I-5). The only discernible difference between the two spectra was a reduction in the relative

intensity of the benzylic proton integral of the deuterated material to the integral in (I-5). Infrared data are recorded in table 4, p 36.

Preparation of 9-Methyl-9,10-dihydroanthracene, (I-8)

9-Methyl-9,10-dihydroanthracene (100 g) was prepared in 94% yield by metalation of 9,10-dihydroanthracene (0.55 mole, 100.0 g) in dry THF (1200 ml) with n-butyllithium (0.075 mole, 360.0 ml of 1.6 N Foote Mineral solution in n-hexane) and subsequent addition of excess methyl iodide. After isolation and recrystallization from ethanol, the product had mp 54-55° (lit[86] mp 61°, see table 2, p 27 for nmr data).

The Reaction of Methyl Iodide with 9-lithio-10-methyl-9,10-dihydroanthracene, (I-9)

The addition of methyl iodide to 0.005 mole of 9-lithio-10-methyl-9,10-dihydroanthracene, (I-9), in tetrahydrofuran (50 ml) gave the known cis-9,10-dimethyl-9,10-dihydroanthracene (I-10)) in 100% yield, mp 127-128° from ethanol (lit.[56] mp 130°). See table 2, p 27 for nmr data.

The Preparation of cis-10-methyl-9,10-dihydroanthracene-10-carboxylic acid, 21

To a solution of 29.1 g (0.15 mole) of 9-methyl-9,10-dihydroanthracene in 500 ml of THF cooled to -50°, was added 100 ml of a 1.6 M (0.16 mole) solution of n-butyllithium in hexane. The cold bath was removed and the solution was allowed to warm to + 10° over 30 minutes. It was cooled to -22° and poured into 500 ml of ether saturated with

carbon dioxide at -70°. The reaction was warmed to room temperature over two hours. It was transferred to a separatory funnel and thoroughly extracted with 10% aqueous sodium hydroxide (5 x 200 ml). The aqueous phases were combined, extracted with ether (200 ml), cooled in ice and then acidified to give white crystals of crude acid. The acid was collected by filtration, washed with water and recrystallized from glacial acetic acid (275 ml), furnishing 20.0 g (56%) of white, delicate plates, 21 (mp 226-7°; Lit.[56,87] 225-226°). The nmr (deuteriopyridine) data are given in table 2. Neutralization equivalent = 238; calcd for $C_{16}H_{14}O_2$: 238.

Concentration of the acetic acid mother liquor to 25 ml gave 9.1 g (25.5%) additional acid, mp 170-210°. NMR spectra indicated the presence of 9% trans-10-methyl-9,10-dihydroanthracene-9-carboxylic acid, 24 (5.38δ for H-9; 1.61δ for CH_3- doublet, J = 7.4).

Evaporation of the neutral ether layers from extraction of the carboxylic acid salt solutions gave 3.14 g (12.5%) of 9-methyl-9,10-dihydroanthracene, (I-10).

Run 2: 9-Lithio-10-methyl-9,10-dihydroanthracene (from 30.0 g of 9-methyl-9,10-dihydroanthracene) was carbonated as in run 1. The crude lithium carboxylate was poured into 500 ml of a 1:1 mixture of water-hydrochloric acid, and the crude acids (31.4 g, 85%), obtained as a precipitate, were collected by filtration. After recrystallization from acetic acid 59.3% of cis acid 21 (21.84 g, mp 223-225°) was

secured. NMR analysis of the acids remaining in the acetic acid mother liquor showed the presence of cis and trans (70:30) acids or 77% cis and 8% trans overall.

Cis acid 21 (1.2 g, 5×10^{-3} mole) was dissolved in glacial acetic acid (23 ml). Concentrated hydrochloric acid (2 ml) was added and the solution was refluxed for four hours. The solution was cooled and the solvent was removed under reduced pressure. This gave the starting acid (mp 227-228°) quantitatively. The nmr spectrum exactly matched that of the starting cis acid, 21.

10-Methyl-9-hydroxymethyl-9,10-dihydroanthracene, 22:

Cis-10-methyl-9,10-dihydroanthracene-9-carboxylic acid (1.17 g, 0.0046 mole 21) in 50 ml of refluxing ether, was reduced with lithium aluminum hydride (0.8 g in the cup of a Soxhlet extraction apparatus) for six hours. After additional stirring at 25° (15 hours), the reaction mixture was hydrolyzed with aqueous hydrochloric acid, extracted with 5% sodium bicarbonate (3 x 50 ml), dried (sodium sulfate) and the ether was evaporated to dryness to afford 1.03 g of alcohol, (97%), mp 135-136°; (lit. 136-137°).[56] Table 2 contains nmr data in $CDCl_3$.

The cis-tosyl ester (23) was prepared by the reaction of 22 (1.0 g, 0.46 mole) and p-toluenesulfonyl chloride (0.009 mole) in pyridine (50 ml, for two hours at 0° and 13 hours at room temperature). The product (mp 134-134.5°, lit.[56] 133.5-134.5°), was obtained in

86% yield after recrystallization from isopropyl ether. The nmr ($CDCl_3$) data are listed in table 2.

Cis-9-ethyl-10-methyl-9,10-dihydroanthracene, (I-4), from the Tosyl Ester (23) of cis-10-methyl-9-hydroxymethyl-9,10-dihydroanthracene

The conversion of tosyl ester 23 to (I-4) was accomplished using lithium dimethylcopper.[58]

To a suspension of cuprous iodide (4.0 g, 0.021 mole, Fisher Scientific) in dry THF (40. ml) was added 0.042 mole of methyllithium in ether. Tosyl ester (1.5 g, 0.0039 mole of 23) was added to the organocopper reagent. After stirring 24 hours at 25°, methyl iodide was added and stirring was continued for 1.0 hour. Water was added and after removal of copper salts, the product was isolated by crystallization from ethanol (0.69 g, 79% of authentic (I-4), mp 103-104°). Admixture of this material with a highly purified sample of material obtained earlier showed no depression of melting point. An nmr spectrum was identical with the spectrum obtained on samples prepared from 9-lithio-10-ethyl-9,10-dihydroanthracene, (I-3), and 9-lithio-10-methyl-9,10-dihydroanthracene, (I-9).

Attempted Isomerization of cis-10-methyl-9-hydroxymethyl-9,10-dihydroanthracene (22)

To a solution of lithium dimethylcopper prepared as above (5×10^{-3} mole) in 20 ml of THF and 7 ml of ether was added 0.25 g (10^{-3} mole) of cis alcohol 22. After 7 hours, water was added and

the product isolated as above, using chloroform as the extractant. This furnished a pale yellow solid, 0.25 g (100% recovery), mp 130-132°. This material showed no depression of melting point on admixture with starting alcohol, mixture mp 134-135°. This result suggests that cis-tosyl ester 23 was probably not epimerized by the lithium dimethyl-copper reagent.

The Reaction of n-butyllithium with Triphenylmethyl Free Radical

Triphenylmethyl free radical was prepared as a solution in benzene according to the method of Gomberg[88] vis. λ_{max} 483, 495, and 522 mμ. The addition of n-butyllithium to a yellow solution of triphenyl-methyl free radical produces a red solution, vis λ_{max} 463 mμ. This spectrum exactly matches that of triphenylmethyllithium, λ_{max} 463 mμ, prepared from triphenylmethane-D and n-butyllithium in benzene.*

Reaction of Naphthalene with Ethyllithium, N,N,N',N'-tetramethyl-o-phenylenediamine (TMOPD)

To a solution of naphthalene (0.005 mole) and ethyllithium (0.005 mole) in 40 ml of cyclohexane was added 0.005 mole of TMOPD. The solution was stirred for three hours at room temperature and then an equivalent of benzophenone was added. The product was isolated by washing with 1:1 hydrochloric acid-water, 5% aqueous sodium bicarbonate, brine

* (Tetrahydrofuran, 0.1 ml, was added to promote reaction in each case. Triphenylmethyl free radical does not react with THF).

and removal of the solvent under reduced pressure. The nmr spectrum of the crude reaction mixture integrated properly for a 1:1 mixture of naphthalene and products derived from the reaction of ethyllithium with benzophenone (1,1-diphenylpropene and 1,1-diphenylpropane-1-ol).

Reaction of Phenanthrene with Ethyllithium, N,N,N',N'-tetramethyl-o-phenylenediamine (TMOPD)

In the manner described for naphthalene, the reaction of phenanthrene with ethyllithium was studied. The products obtained after the addition of benzophenone analyzed correctly (nmr) for a 1:1 mixture of phenanthrene and products derived from the addition of ethyllithium to benzophenone.

The Metalation of Benzene by Ethyllithium in Cyclohexane

a. N,N,N,',N'-tetramethylethylenediamine (TMEDA) Catalysis

Run 1 To a solution of benzene (0.40 g of 0.005 mole) and ethyllithium (0.005 mole) in cyclohexane (60 ml), was added 0.006 mole of TMEDA. After 4.0 hours 0.005 mole (0.91 g) of benzophenone was added in one portion.

The crude reaction mixture was transferred to a separatory funnel, diluted with an equal volume of ether, and washed with 1:1 hydrochloric acid-water (4 x 50 ml), 5% aqueous sodium bicarbonate (2 x 50 ml), saturated sodium chloride solution (1 x 50 ml), dried over sodium sulfate, filtered and evaporated to dryness under reduced pressure on a rotary evaporator. This gave a yellow liquid (1.38 g, 100% recovery). From the integrated nmr spectrum of this mixture, it was determined that (52 ± 5)% of the ethyllithium had been consumed; (52 ± 5)% of

triphenylmethanol (based on starting benzene) had been produced.

Run 2 The reaction was repeated in the manner described above. After 6 hours benzophenone (0.005 mole, 0.91 g) was added. After isolation the product was analyzed by nmr. This analysis showed that (62 ± 4)% of the benzene used in this experiment had been metalated by the ethyllithium. Corresponding to this, (38 ± 4)% of the ethyllithium originally present was isolated as a mixture of 1,1-diphenylpropene and 1,1-diphenylpropan-1-ol.

b. N,N,N',N'-tetramethyl-o-phenylenediamine (TMOPD) Catalysis

When TMOPD was used in place of TMEDA, reaction with benzophenone after 3.0 hours gave a solid mixture. Nmr analysis of this material indicated that 20.% of the benzene originally present had been metalated.

Reaction of Acenaphthylene with Ethyllithium

To a solution of 0.005 mole each of ethyllithium and TMOPD in 40 ml of cyclohexane was added 0.005 mole of acenaphthylene.* After 18 hours the reaction was terminated with water. The reaction mixture was extracted with 1:1 hydrochloric acid-water (3 x 50 ml), aqueous sodium bicarbonate (1 x 50 ml) and brine (1 x 50 ml); dried over sodium sulfate, filtered and evaporated to dryness under vacuum (20 torr). The crude oil obtained in this fashion was triturated with methanol (75 ml) yielding a soluble and insoluble fraction. Nmr examination of the insoluble material indicated a complex mixture: 7.22 δ (m); 3.37 δ (m); 1.81 δ (q); 0.98 δ (t, J = 6.5).

*The acenaphthylene used in this experiment contained 5% of acenaphthene, as judged by vpc and nmr spectral analysis.

From the total integral this material is approximately 50% ethylated, assuming only monoethylation. Gas chromatography showed that both the soluble and insoluble fractions were complex mixtures of about the same composition. The fractions were combined and subjected to preparative gas chromatography. The major identifiable component was the reduction product, acenaphthene (approximately 20% of the total material as judged by vpc). The structure of this component was proven by melting point, mixture melting point, vpc, mixture vpc and nmr comparison with authentic acenaphthene. The other components (at least four) could not be separated in sufficient quantity for identification.

The Addition of Ethyllithium to Perylene: 1-Ethylperylene

To a solution of 0.0102 mole of ethyllithium and 0.005 mole of TMOPD in 72 ml of cyclohexane was added 0.005 mole of perylene. The solution immediately turned emerald green and within 30 minutes the perylene was completely dissolved. After 1.5 hours a 3.0 ml aliquot was removed and the product was isolated as above. From the integrated nmr spectrum this material was estimated to be approximately 92% pure 1-ethyl-x,y-dihydroperylene.

After a total of 20.5 hours, water was added to the remainder of the reaction mixture. The product, 1.386 g (97.5%) of a yellow oil, was pure 1-ethyl-x,y-dihydroperylene as judged by nmr. This material was dissolved in 30 ml of benzene, slightly more than one equivalent of chloranil was added, and the solution was refluxed for 6.5 hours. The solution was cooled, washed with 10% aqueous sodium

hydroxide (200 ml), water (4 x 100 ml), and brine (1 x 50 ml), dried over sodium sulfate, filtered and concentrated to dryness under reduced pressure. This gave 1.30 g (100%) of 1-ethylperylene[18] whose nmr spectrum exactly matched the published spectral data.[18] nmr: 7.80 δ (m, 11 H); 3.14 δ (q, J = 7, $-\underline{CH}_2CH_3$); 1.46 δ (t, J = 7, $-CH_2\underline{CH}_3$); mp 81-82° (ethanol); lit.[18] 84°.

A control experiment showed that in the absence of TMOPD no reaction occurred under the same conditions.

The Reaction of Azulene with Ethyllithium

To a solution of ethyllithium (0.0025 mole) in 35 ml of cyclohexane was added 0.32 g (0.0025 mole) of azulene. After five minutes TMOPD (0.0025 mole) was added and the reaction was allowed to stir for 20 hours. The reaction was hydrolyzed by the addition of 5 ml of water, and the crude product was isolated after washing the organic layer with aqueous acid, water and brine, drying over sodium sulfate, filtration and removal of the solvent. The blue liquid obtained by this procedure is presumed to be 4-ethyl-3a,4-dihydroazulene, by analogy with the numerous additions of alkyllithium reagents to azulene reported by Hafner.[71] NMR indicated that approximately 75% of the mixture is this component and 25% represents unreacted azulene. nmr: aromatic 8.42-5.00 δ (integral: 155 mm); benzylic 3.42-1.7 δ (integral: 55 mm); aliphatic 1.83-0.58 δ (integral: 110mm); methyl triplet, J = 6, 0.87 δ (integral: 52 mm). If the methyl triplet represents ethylated material, and the only other component is azulene, then the percent purity of the ethylated material is: (5)(52)/363 = 73%, where the

number 52 represents the integral for three hydrogens and multiplication by 5 gives the integral for the 15 hydrogens of ethyldihydroazulene.

The Addition of Ethyllithium to 9-methylanthracene in THF

To a solution of 0.95 g (0.005 mole) of 9-methylanthracene in THF (60 ml), maintained below 10°, was added 0.005 mole of ethyllithium. The reaction was monitored by hydrolyzing 0.5 ml aliquots and subjecting the hydrolyzed material to vpc analysis. By this technique it was found that after 40 minutes no further consumption of starting material occurred. After 160 minutes an additional 0.005 mole of ethyllithium was added to the reaction mixture in an effort to increase the extent of conversion of 9-methylanthracene to products (about 30%). A sample removed for vpc analysis 40 minutes after innoculation with ethyllithium indicated that an additional 15% conversion had been achieved. Again, no further change was noted in subsequent aliquots. Five hours after the commencement of the experiment the reaction was hydrolyzed by the addition of water (30 ml). The reaction was diluted with ether (30 ml), transferred to a separatory funnel, and the layers were separated. The organic layer was washed with water (4 x 50 ml), dried over sodium sulfate, filtered and concentrated on a rotary evaporator. The addition of carbon tetrachloride (5-10 ml) to the crude reaction mass caused the precipitation of a solid (0.1 g), mp 318°. This material was not identified but its high mp is in accord with its formulation as a dimer. Replacement of the carbon

tetrachloride with an equal volume of ethanol gave a second precipate (0.08 g), mp 227-233°. This material depressed the melting point of anthracene. No further characterization of this material was attempted.

Replacement of the ethanol with 2-3 ml of hexane resulted in a yellow solution which was purified by filtration through florisil (45 ml), with hexane as the eluent. Vpc monitoring of the chromatography indicated that no separation of the major component (shorter retention time) and 9-methylanthracene occurred. However, the components having a longer retention time than 9-methylanthracene were absent. Approximately 700 ml of hexane were required to elute all the 9-methylanthracene. Since vpc had shown that only two major components were present in the eluent, the fractions were combined and reduced to dryness on a rotary evaporator. The addition of ethanol (8 ml) to the semi-solid mass which was obtained, furnished a precipitate of 9-methylanthracene (0.21 g), identified by nmr.

The remaining material, subjected to preparative vpc, yielded a small amount of cis-9-ethyl-10-methyl-9,10-dihydroanthracene, mp 103-105° (from ethanol). Admixture with authentic hydrocarbon did not depress the melting point (mixture mp 104-106°). This component represents about 70% of the product mixture, as estimated by vpc and nmr.

Molecular Weight of the Ethyllithium N,N,N'N'-tetramethyl-o-phenylenediamine Complex by Freezing Point Depression

Cyclohexane-ethyllithium:

The freezing point of a purified sample of cyclohexane was found to be 6.32 ± 0.02°. A solution of ethyllithium in cyclohexane, 8.80 ml of a 6.10 x 10^{-1} M solution, solidified at + 1.80°. The calculated molality, m = B/Δt, (where B, the molal freezing point depression constant has a value of 20.0), is 0.226. The theoretical molality of ethyllithium in cyclohexane, for this solution, assuming no aggregation, is 0.91. The calculated aggregation factor, 3.98, agrees well with literature values.[16]

Cyclohexane-ethyllithium N,N,N',N'-tetramethyl-o-phenylenediamine (TMOPD)[89]

To the above solution of ethyllithium in cyclohexane was added 0.86 g (5.26 mmoles) of TMOPD. From the freezing point (-12.0 ± 0.5°) of this solution the molality is calculated to be 0.91, in good accord with the theoretical value for a monomeric complex of 0.89.

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