ELECTRON TRANSFER REACTIONS:

THE REACTION OF LITHIUM NAPHTHALENIDE WITH QUATERNARY AMMONIUM SALTS AND BENZYLIC HALIDES

by

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ABSTRACT

It has been found that the reaction of lithium naphthalenide with benzylic halides and quaternary ammonium salts produces radicals.

Radicals produced by this reaction appear either as reduction products or as dimers. For example in reactions of lithium naphthalene with benzyl and benzhydryl derivatives (chlorides, bromides and quaternary ammonium salts) the radicals are converted into phenylated methanes (toluene and diphenylmethane) or phenylated ethanes (e.g. bibenzyl and symmetrical-tetraphenylethane).

In this thesis a study of the probable and possible mechanism of dimer formation is described. One possible mechanism for dimer formation is alpha coupling of two benzylic radicals, (Path A). An alternative pathway for dimer formation involves a second reduction step by $ArH^{\cdot}$ converting a radical into a carbanion which then reacts with more starting material in a normal displacement process (Path B or a carbanion mechanism).

It was found that path A could be favored by adding the aromatic radical anion slowly to the benzylic derivative. Conversely pathway B was favored by adding the benzylic derivative to the radical anion.

The effects of changing halogen from fluorine to chlorine to bromine were studied. It was found that fluorine departs much more slowly than the other halides during radical formation in harmony with recently published data.

Evidence for the intermediacy of radicals in reactions of lithium naphthalenide with quaternary ammonium salts comes from reaction with 5-hexenyltrimethylammonium iodide to produce 5-hexenyl-radicals which

cyclize to methylcyclopentyl radicals at a known rate. Methylcyclopentane (4%) was formed among the other products. Additional evidence for radical intermediates and the alpha coupling mechanism was obtained from competition experiments utilizing equimolar mixtures of benzhydryl chloride and benzyl chloride reacting with one equivalent of lithium naphthalenide to produce three phenylated ethanes (bibenzyl, 1,1,2-triphenylethane and symmetrical-tetraphenylethane) in the statistical ratio of 1:2:1 expected for path A.

Carbanion displacement studies parallel to the lithium naphthalenide reduction studies were carried out for each carbanion that could have formed from single electron reduction of the intermediate radical (i.e, path B). It was found that benzylic carbanions displaced bromine and chlorine much more rapidly than fluorine and the rates appeared to be comparable with the very fast naphthalenide ion reductions of benzylic chlorides and bromides.

Evidence that these displacements occur with 100% inversion of configuration was secured by conversion of R (+) - α - phenylethyltrimethylammonium iodide with benzhydryllithium to give R (+) 1,1,2-triphenylpropane. The absolute configuration of 98.5% optically pure R (+) 1,1,2-triphenylpropane was determined by its synthesis from S (+) hydratropic acid.

Further, it was found that triphenylmethyl chloride (or bromide) could oxidize triphenylmethyl carbanion to produce two trityl radicals. However, triphenylmethyl fluoride gave little or no reaction in tetrahydrofuran solvent. All attempts to oxidize benzylic carbanions with diphenylmethyl halides to produce radicals proved fruitless.

ACKNOWLEDGEMENTS

I wish to dedicate this thesis to my wife, Barbara, without whose confidence, encouragement, and most of all patience, the road to success would have been very difficult.

I wish to thank Prof. Herman E. Zieger for his friendship, encouragement, and most of all for his liberal attitudes in allowing me to carry out many off-track experiments. I would also like to thank Prof. Leon B. Gortler and Prof. Norman Goldman for their helpful suggestions and discussions.

I wish to thank my mother, my brothers, my mother in law, father in law, and sister in law for their moral support.

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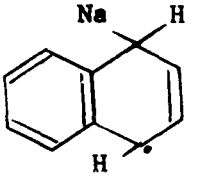
HISTORICAL[a]

INTRODUCTION

Formation of an aromatic radical anion was first recorded in 1867 when Berthelot described the appearance of a black addition product on fusing metallic potassium with naphthalene.[1] Stoichiometric investigations were carried out by Schlenk and coworkers some years later on sodium anthracene adducts.[2,3]

Early representation of the compounds formed from the addition of an alkali metal to aromatic hydrocarbons originated with Willstatter[4] who visualized that the metal was bonded to the ring as shown for naphthalenide in 1



1

Use of this type of designation continued unquestioned until 1936 when it became evident that the adduct was ionic rather than electrically neutral. Pertinent observations were that the adduct was formed in the more polar ether solvents such as dimethyl ether or tetrahydrofuran, but not diethyl ether or benzene,[5] and that solutions also conducted electric current.[6] Hückel and Bretschneider, therefore, modified the Willstatter formula, suggesting for the first time the idea that the adduct was formed via electron transfer.[7]

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[a]Abbreviations used in this dissertation are found on page 137

Final verification of the radical anion nature of the adducts was made by Weissman and his associates using electron spin resonance (esr) spectroscopy by 1953.[8,9]

A better understanding of the ionic and free radical character of the aromatic hydrocarbon-metal adducts was provided by physical measurements such as ionic conductivities, polarographic and potentiometric determination of aromatic hydrocarbon electron affinities and electron exchange rates measured by kinetic electron spin resonance (KESR). A heavy emphasis on the physical chemistry research of aromatic radical anions occurred during the period 1953-68, and critical reviews have been published by Szwarc.[10,10a] The significant conclusions of these and other physical measurements will be discussed in a later section.

As progress toward understanding the physical properties and structures of aromatic radical anions developed, interest, progress and results in studies on their chemistry expanded, slowly at first in the nineteen fifties and very rapidly from 1960 to the present. The review articles by Garst[11] provide the most critical analysis of the chemistry and physical properties of aromatic radical anions, and the recent review by Holy[22] serves as a good lexicon to the fundamental literature.

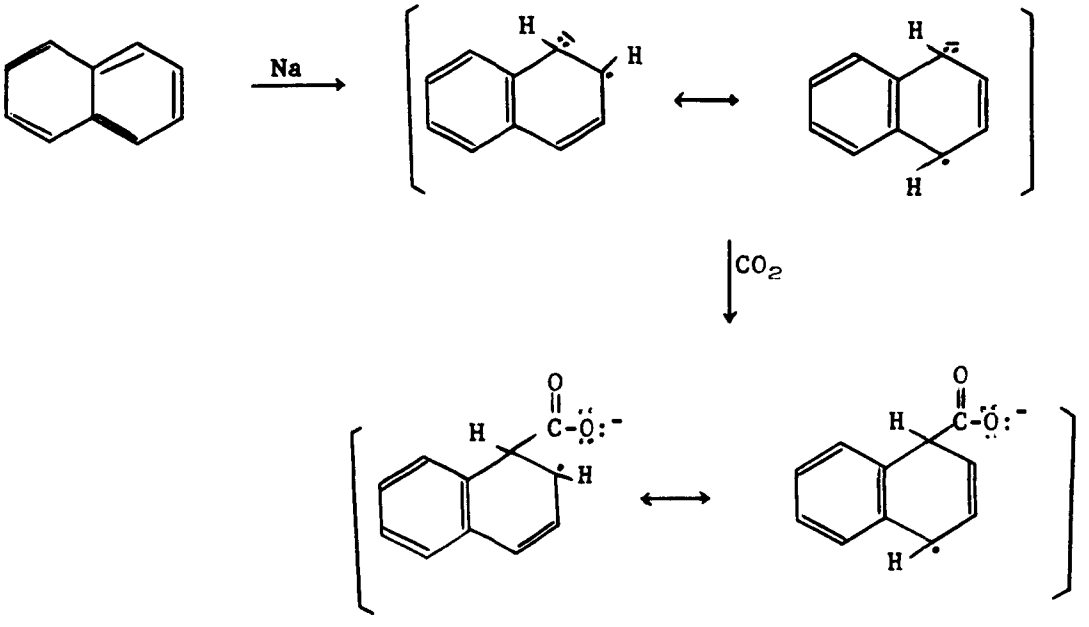
Chemistry of Aromatic Radical Anions

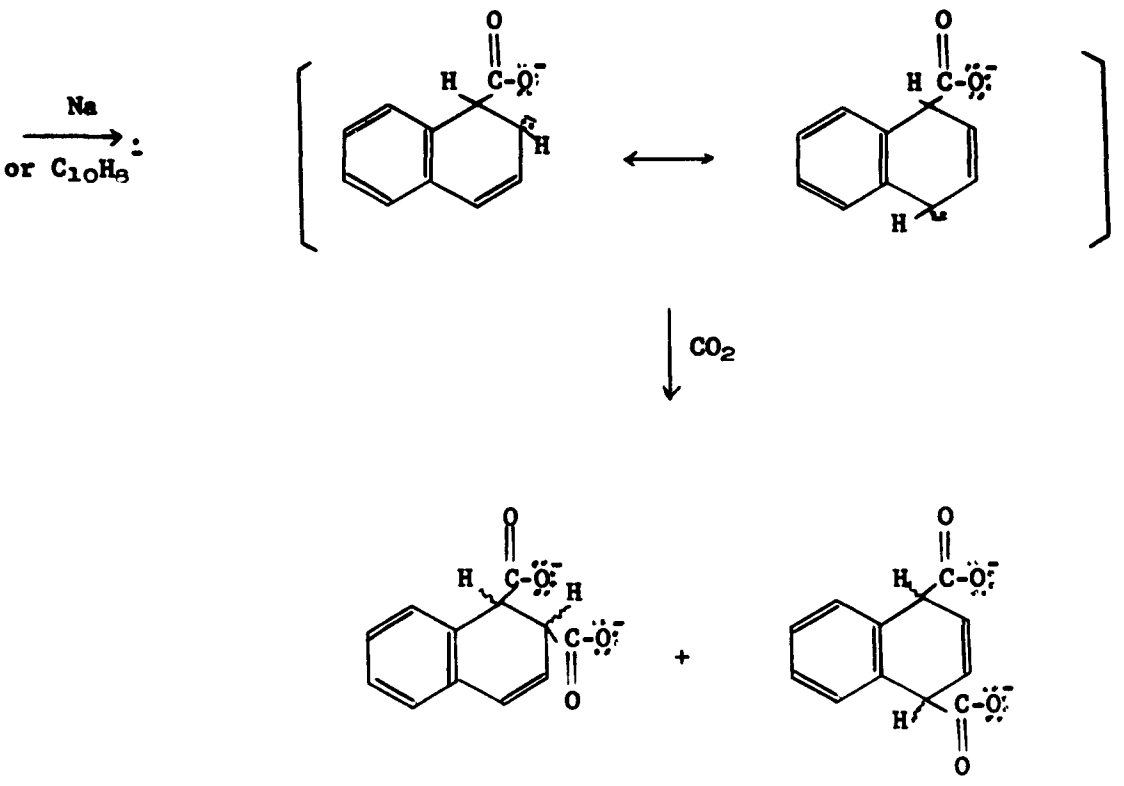
Aromatic radical anions function as reducing agents in their reactions with other compounds. The general mechanism by which they trigger chemical reaction is through transfer of an electron to the reacting partner with regeneration of neutral aromatic hydrocarbon. The most widely utilized aromatic hydrocarbons are naphthalene and biphenyl. Clearly these compounds would be expected to have different

electron affinities and therefore different reducing powers. A good comparison for the reducing power of aromatic radical anions would be with sodium or potassium dissolved in liquid ammonia. It will become apparent that aromatic radical anions are weaker, and therefore, more selective reducing agents than alkali metals in liquid ammonia.

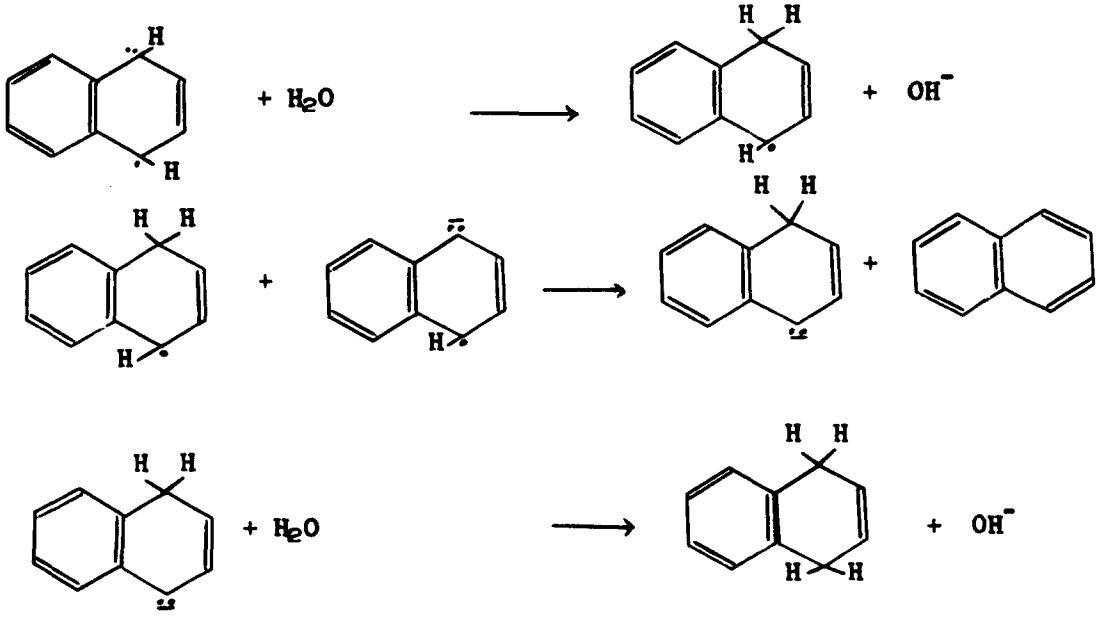
Although the most widely studied reaction of aromatic radical anions has been with halogen containing organic compounds, the earliest reliable work concerned itself with reactions of water and carbon dioxide with sodium naphthalenide. In reactions of this type, two experimentally determined facts are paramount: (1) dihydro, or substituted dihydro derivatives of the parent hydrocarbon are formed; (2) in the absence of excess alkali metal, half of the original hydrocarbon is recovered unchanged, whereas in the presence of excess alkali metal, the original hydrocarbon is completely converted to dihydro compound.

With these observations at hand, Paul, Lipkin, and Weissman[12] presented the following mechanistic scheme to explain the carbonation of naphthalene mononegative ion:





Clearly, reductive protonation with water would follow the path as shown below, to give the corresponding dihydronaphthalenes.



In order to test this proposed mechanism, Bank and Closson[13] treated the radical anion of naphthalene with tritiated water. The composition of the reaction mixture was naphthalene (58.7%), dihydronaphthalenes (40.7%), and tetralin (0.6%). All of the radioactivity was concentrated in the dihydronaphthalenes and tetralin; no activity was found in naphthalene. Recently, Bank and Bockrath[14] provided more support for this mechanism by measuring the kinetics of protonation of the radical anion. All of the evidence is consistent with the above mechanism and definitely excludes the following alternative mechanism that accounts for the observed products by a radical disproportionation reaction (Naph$^{\cdot}$ represents naphthalenide ion).

$$\text{Naph}^{\cdot} + H_2O \longrightarrow \text{NaphH}\cdot + OH^-$$

$$2\text{NaphH}\cdot \longrightarrow \text{NaphH}_2 + \text{Naph}$$

If such a mechanism were operative, disproportionation of the labeled radical (NaphH$\cdot$) to naphthalene and dihydronaphthalene would lead to incorporation of tritium in the recovered naphthalene.

The use of aromatic radical anions as electron transfer agents is well known.[8,11,12] They have been of particular use as initiators in anionic polymerizations[8,15,16,17,18] and more recently have been used to generate alkyl free radicals by electron transfer to alkyl and aryl halides.[19]

II Electron Transfer to Alkyl and Aryl Halides

Organic chlorides, bromides, and iodides react rapidly with naphthalene or biphenyl radical anions with cleavage of the halogen-carbon bond to produce an organic radical and a halide anion. Presumably this electron transfer reduction involves formation of halide radical

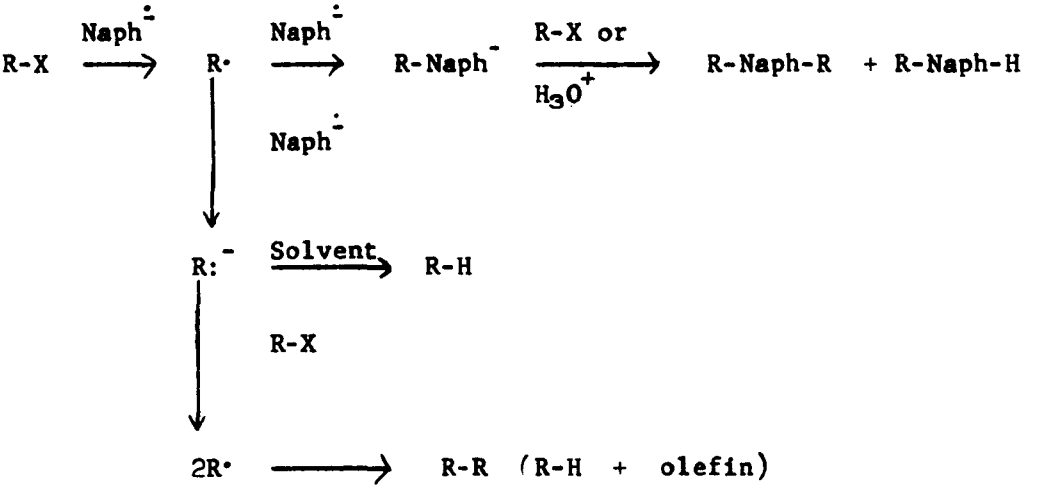
anion, 2, prior to departure of halide anion.

(1) $R\text{-}X + Naph^{\cdot -} \longrightarrow C_{10}H_8 + \underset{2}{R\text{-}X^{\cdot -}} \longrightarrow \underset{3}{R\cdot} + X^-$

However, most researchers, with the exception of Bunnett, ignore 2 because radicals, 3, appear to be formed so rapidly that no physical evidence for 2 has ever been found. Since 5-hexenyl fluoride has been reported to react slowly with aromatic radical anions, it would seem that intermediates such as 2 should possess lifetimes long enough for esr measurements.

During reductive cleavage of halogen by an aromatic radical anion a variety of reduction products is formed. These products and the probable pathways to their formation are shown in scheme 1.

Scheme I



(Note: In this scheme, metal counter ions and regenerated aromatic hydrocarbons, and solvent derived products are omitted to avoid cluttering of the diagram.)

Although there has been considerable research in this area, only the radical anions of naphthalene, biphenyl, and anthracene have received attention, and most of the available data are from naphthalenide reactions.[11]

Among the alkali metals relative rate constants for M^+ naphthalenide with 5-hexenyl fluoride have been determined and show that Li^+Naph^- reacts faster than Na^+Naph^-. See table 1.

Table I[a] - Metal Ion Effects on Rates of Reactions of Alkali Naphthalenes with 5-hexenyl fluoride in DME at 25°.

Alkali Radical Anion	10^4k (ℓ. $mol^{-1}sec^{-1}$)
LiNaph	270 ± 20
Na Naph	2.8 ± 0.5
K Naph	0.02
Cs Naph	No Reaction

a. Data from J.F. Garst and F.E. Barton II, J. Amer. Chem. Soc., 96, 523 (1974).

In the mechanism, the individual steps seem reasonably certain except that for formation of the "dimer", i.e.

$$R^- \xrightarrow{R\text{-}X} 2R\cdot \longrightarrow R\text{-}R \qquad (2)$$

which is subject to debate.

The first step is a fast electron transfer to the alkyl halide followed by a rapid expulsion of halide anion. In the mechanism, the step involving electron transfer reduction of the radical, 2, to a carbanion seems firmly supported by data in the literature. However, whether "dimer" formation occurs by the coupling of two radicals has been a subject of continuing controversy.

Only rates for reaction of sodium Naph$^{\cdot}$ with 5-hexenyl fluoride are found to have rate constants of about 5×10^{-4} ℓ. mol.$^{-1}$sec^{-1}. For other halogens expulsion is fast and complete, as indicated by the use of sodium biphenylide for quantitative halogen analysis.[25] One product formed from the radical is a alkane, conceivably by either of two competing pathways.

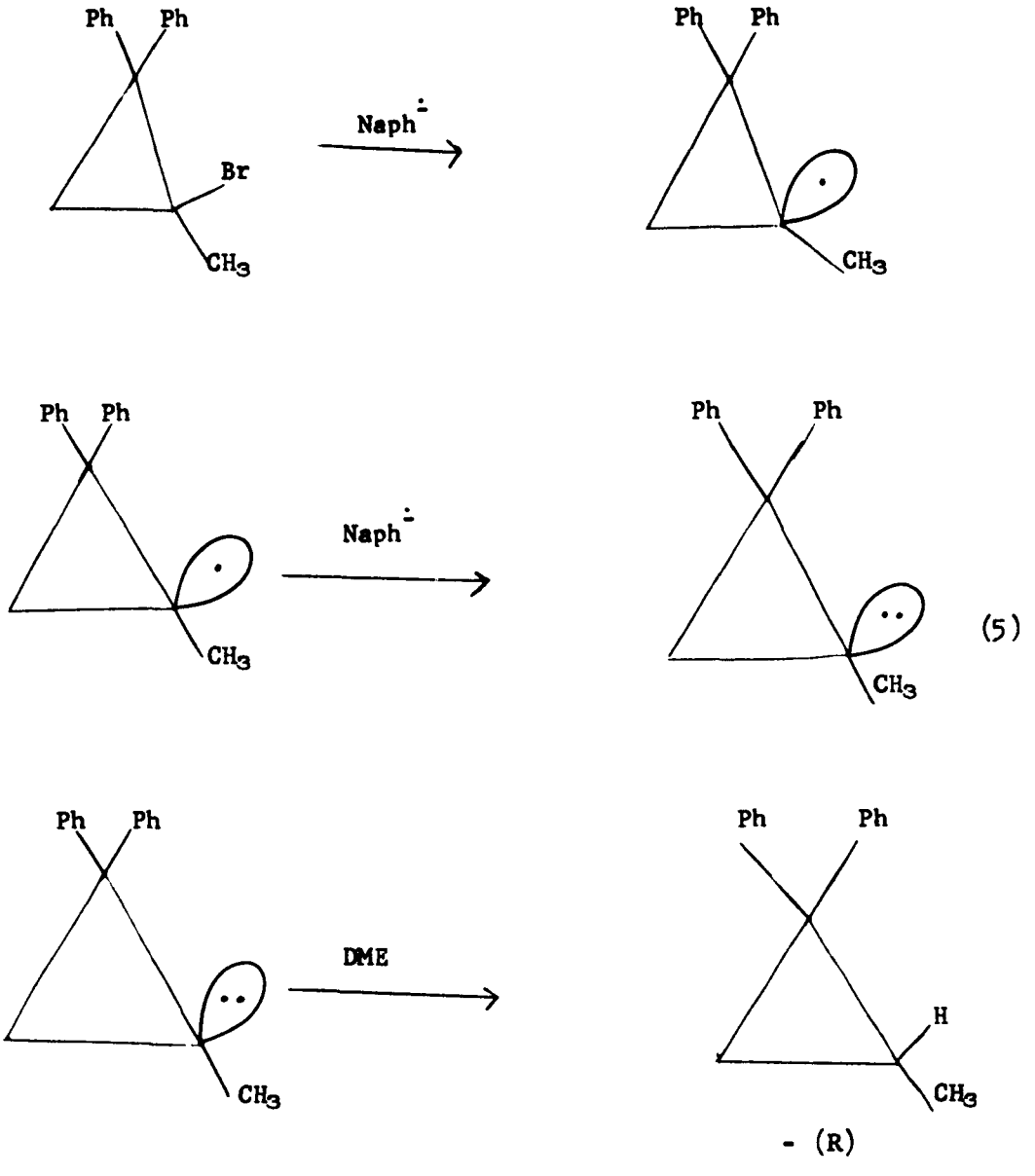
$$\text{R}\cdot \xrightarrow{\text{S-H}} \text{R-H} + \text{S}\cdot \qquad (3)$$

$$\text{R}\cdot \rightarrow \text{R:}^{-} \xrightarrow{\text{S-H}} \text{R-H} + \text{S}^{-} \qquad (4)$$

From an analysis of the rate of cyclization of 5-hexenyl radical to cyclopentylmethyl radical ($k = 10^{5}$ sec^{-1}) contrasted with the rate of electron transfer from naphthalenide ion to radicals ($k \approx 2 \times 10^{9}$ ℓ. mol^{-1} sec^{-1}), Garst[19,66] has concluded that the carbanionic route predominates over hydrogen atom abstraction from the solvent. The carbanion has even been trapped by anhydrous magnesium bromide which forms the Grignard reagent in good yield.[26]

The rate of electron transfer between naphthalenide and the alkyl radical is virtually diffusion controlled, (10^{9} - 10^{10} M^{-1} sec^{-1}). The chemical consequences of such a high rate for radical reduction can be seen in the stereochemical study of Jacobus and Pensak, concerning the

reduction of an optically active cyclopropyl bromide.[27] Treatment of optically pure (+)-(S)-1-bromo-1-methyl-2,2-diphenylcyclopropane with sodium naphthanide in DME yields 29% optically pure (-)-(R)-1-methyl-2,2-diphenylcyclopropane (eq.5).



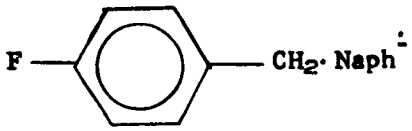
(5)

- (R)

Reduction of the optically active free radical must have a rate comparable to the inversion frequency of the cyclopropyl radical[28] (10^8-10^{10} sec^{-1}). In a similar reaction, Sargent and Browne were able to trap cis- and trans-isomers of vinyl radicals formed as intermediates in the reduction of cis- and trans-3-chloro-3-hexene with sodium naphthalenide.[39]

An elegant piece of work is that of Cristol and Barbour[20] who used a solution of sodium biphenylide to convert the isomeric chlorides, cholesteryl chloride 4 and β-cyclocholestanyl chloride 5, to monomeric hydrocarbon products in 58-84% yields. Chloride 4 gave only 5-cholestene 11 while chloride 5 gave mixtures of 11 and 3 α, 5α-cyclocholestene 10 according to Scheme II. Their results suggest that the course of reduction of 5 involves the initial transfer of an electron from the radical anion to the chlorine atom resulting in the loss of chloride ion and formation of the cyclocholestanyl free radical, 6, which is partly reduced to anion 8 and partly rearranged to radical 7 before reduction to anion 9. This reaction showed that the rate of reduction of radical 6 to carbanion 8 is comparable in speed to the rate of rearrangement of radical 6 to radical 7. The use of sodium biphenylide as an electron transfer agent provides for the most powerful reducing agent possible since its reduction potential is -2.165 v. Also, with 1,2-dimethoxyethane (DME) as solvent, the formation of completely dissociated ions is favored and electron transfer is not retarded as is the case with tightly bound ion pairs.[30,31,32]

The presence of an anion intermediate is further indicated by ^{19}F chemically induced dynamic nuclear polarization. Reduction of p-fluoro benzyl-halides (X=Cl, I) forms an intermediate which Rakshys interprets to be consistent with the collisional pair 12 of the p-fluorobenzyl radical and naphthalenide pair.[33]



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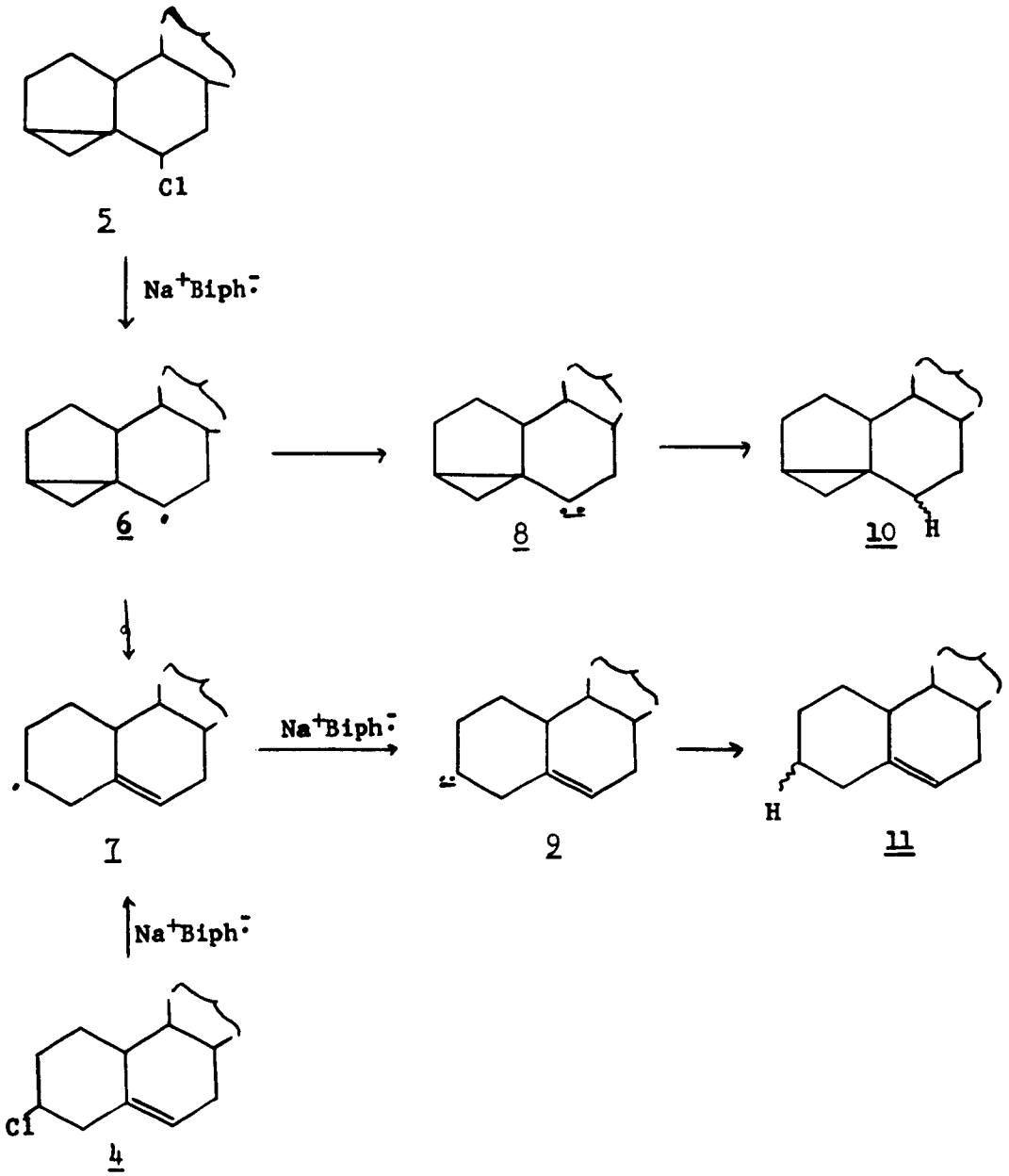
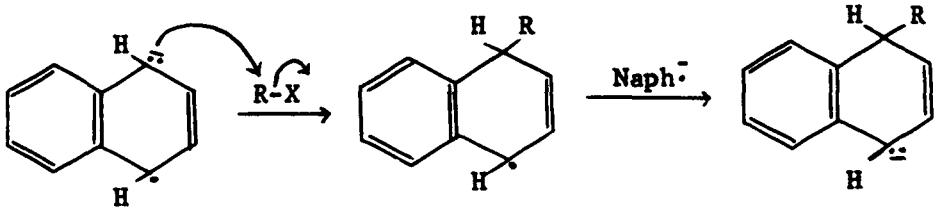
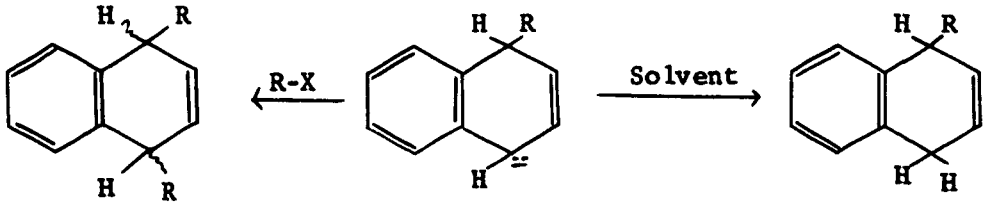
Scheme II



Alkylation of the aromatic nucleus typically accounts for between 5 and 60% of the alkyl halide. A number of mechanisms could conceptually account for these derivatives. An S_N2 displacement (eq.6) was postulated originally[34] but has since been ruled out for two principal reasons:[35-38]



(6)



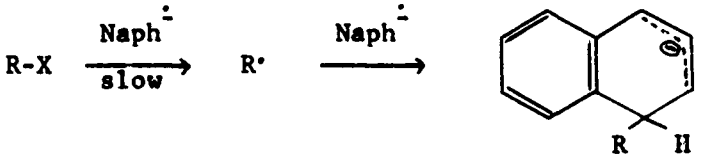
(1) the identity of the halogen has no effect on the amount of mono-alkylation product; (2) the percentage of alkylate increases in going from primary to tertiary halides, exactly opposite of what would be expected on the basis of an S_N2 reaction.

Another possible pathway suggested by Hoijtink involves direct attack of the alkyl radical on the aromatic nucleus, i.e., on naphthalene itself (eq.7),

(7)

but estimation of the rate constant, k, from an analogous reaction reveals that it must be too small for this route to be significant.[39] Furthermore, variation of the amount of naphthalene in the reaction does not affect the product distribution.[38] (This is the mechanism, however, which at present has the greatest support in the silylation of naphthalene with silyl halides).

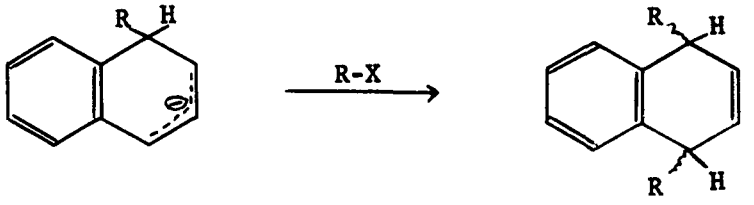
The first alkylation step is accounted for by eq. 8.



(8)

Coupling of the radical and the radical anion is consonant with the independence of the amount of monoalkylate with the identity of the halogen. It is also consistent with kinetic observations; the rate is first order in both naphthalenide and alkyl halide.[22] Furthermore, as the reduction potential of the alkyl halide increases on going from primary to tertiary intermediates (meaning less reduction of R· to R:⁻), there is a corresponding increase in alkylate. Coupling with naphthalenide (and presumably other radical anions) must be virtually diffusion controlled for this reduction to compete effectively with reduction of the alkyl radical to anion.

The second alkylation is believed to be simple S_N2 displacement from the anion; this is represented by eq. 9.



(9)

Sargent and Lux determined that neopentyl and tertiary halides do not yield dialkylate, but instead give only monoalkylate; this behavior is consistent with what would be expected from a displacement reaction.[38] The percentage of cis and trans isomers has not been specified.

Reductive dimerization is the least understood of the various reactions of alkyl halides.

$$2R\text{-}X \xrightarrow{Naph^{\cdot-}} R\text{-}R + 2X^{-} \qquad (10)$$

"Dimer" formation is appreciable only with alkyl iodides; it is not uncommon for 50% of the alkyl iodide to be accounted for by this route. With bromides the yield is usually about 5%; for the chlorides dimer formation is atypical and for fluorides this product apparently has not been observed. This trend was interpreted to imply radical-radical coupling.[21,38]

The high yields from iodides were viewed to be a consequence of the diminished reduction potentials of iodides compared to other alkyl halides which permitted such rapid production of free radicals that a sufficient radical concentration was achieved for appreciable coupling. A radical-radical coupling mechanism was further recommended by the observations that treatment of a equimolar mixture of n- and isopropyl iodides resulted in a statistical distribution of the possible dimers[21] and by the reaction of neopentyl iodide which forms a high yield of di-neopentyl.[38]

Zieger, Angres, and Maresca[40] have shown that for the case of the benzylic bromides and chlorides, high yields of dimer are formed. For example, when equivalent quantities of lithium naphthalenide were titrated with benzhydryl chloride, sym-tetraphenylethane (70-78%) was

produced. The formation of the above dimer may occur either by coupling of benzhydryl radicals or by S_N2 displacement between diphenylmethyl lithium and benzhydryl chloride. However, the slow inverse addition of one equivalent of naphthalenide to benzhydryl chloride also produces sym-tetraphenylethane (75%) under conditions where halide is in excess and no carbanion formation can be detected visually. Under these conditions radical coupling must be the predominant pathway for the formation of dimer. However, Closson[41] believes that dimer formation arises predominantly through the following pathway:

$$R\cdot + Naph^{\cdot -} \longrightarrow R:^- + Naph$$

$$R:^- + R\text{-}X \longrightarrow 2R\cdot + I^- \longrightarrow R\text{-}R + I^-$$

His evidence is based on efficient trapping of the carbanion intermediate with t-butyl alcohol.

Other investigations, however, suggest some other mechanism must be operative. The reactions of 1,4-diiodobutane and 1,5-diiodopentane forms no bimolecular reduction products, and, in fact, 99% of the starting material can be accounted for by the products cyclobutane, ethylene, and monoalkylation derivatives.[3e a,b] The reaction is believed to take the course shown in Scheme III. Thus the fate of the initially formed alkyl radicals is to be reduced by, or to combine with, sodium naphthalenide. Coupling of two alkyl radicals does not occur.

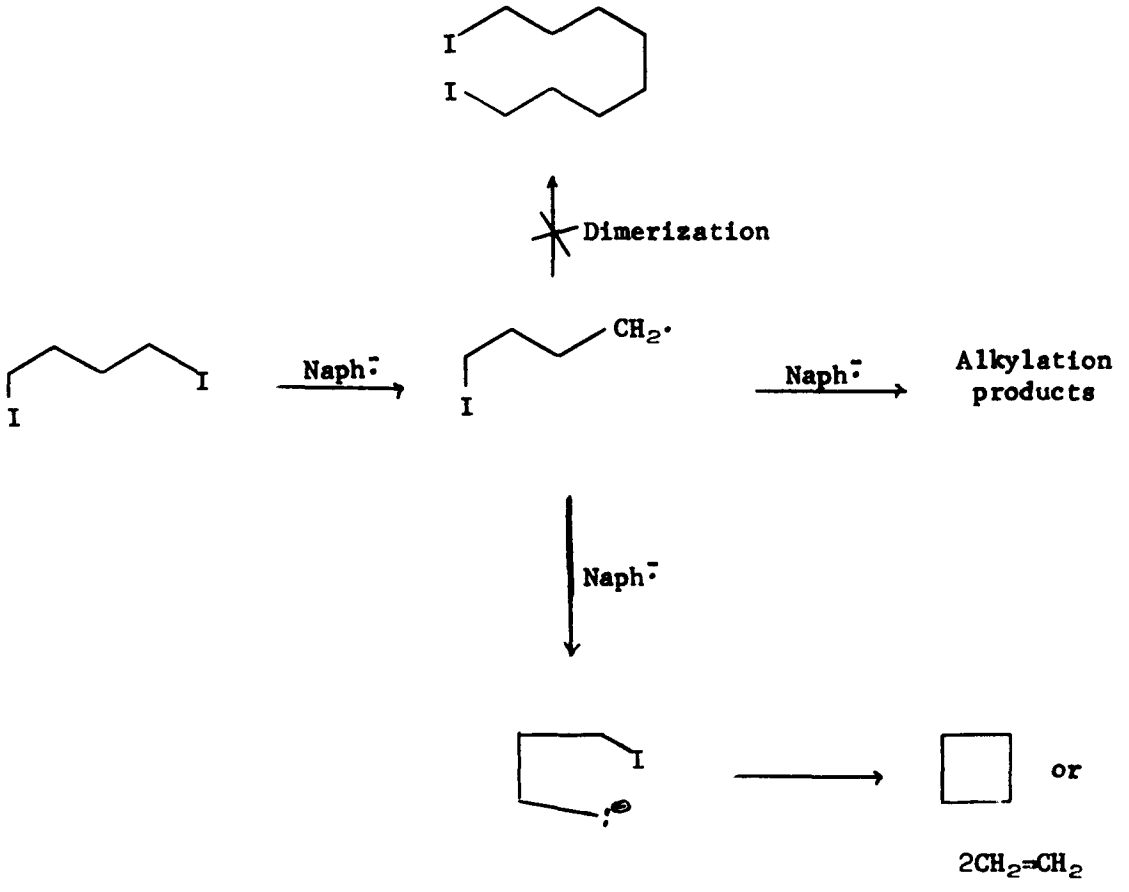
Thus there is something of a dilemma, there is evidence suggesting a radical pathway, and yet, according to other experimental data, it appears that it is not the radical which is the major pathway to bimolecular reduction product. An alternative is possible when one considers the reaction of alkyllithium with alkyl halides. These reactions

are known to have radical intermediates. Similar application of that mechanism to these reactions results in eq. 11,

$$(R^{-}Li^{+})_n + R' - X \longrightarrow R\cdot\ R'\cdot\ Li^{+}X^{-}\ (R:^{-}Li^{+})_{n-1} \longrightarrow R\text{-}R \quad (11)$$

in which radical pairs are generated in a cage by electron donation from the alkyllithium. The radical pairs may then combine, disproportionate, or diffuse apart. The intermediate radicals have been trapped,[42] observed by esr,[43,44] inferred from chemically induced nuclear spin polarization[45,46] and from stereochemical experiments.[47]

Scheme III

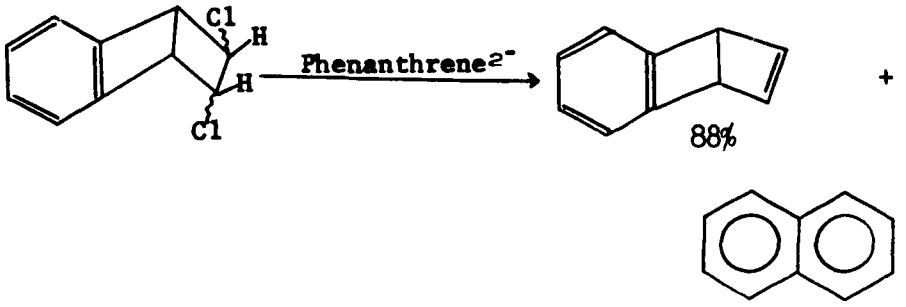


Most of the research on alkyl halide reactions has used naphthalenide as the radical anion. Other radical anions especially those which are less powerful reducing agents, should lead to somewhat different product distributions. It would be reasonable to anticipate less unimolecular reduction product because the radical anion would not as readily reduce the alkyl radical to carbanion. There is at least one sketchy report on reduction/alkylation which supports this possibility.[48] However, it is also entirely possible that little change in reduction/alkylation will be found as Bank has observed.[49]

In view of the facile reactions of alkyl halides, it is not surprising that vicinal dihalides react readily with naphthalenide. The dihalide is converted to olefin by dehalogenation and this may occur by either cis or trans elimination. This technique[50] gives higher yields of olefin using shorter reaction times, and therefore has real synthetic advantages over other methods.

Adam and Arce have found that upon treatment of threo and erythro 2,3-dibromo-3-methylpentane with sodium naphthalenide, dehalogenation occurs principally in a trans fashion.[51] The 2,3-dichloro-butanes dehalogenate with regioselectivity (same product mixture from meso and d,l isomers) while there is a slight stereospecificity observed for the reactions of 2,3-dibromobutanes (bromine being a better bridging atom than chlorine).

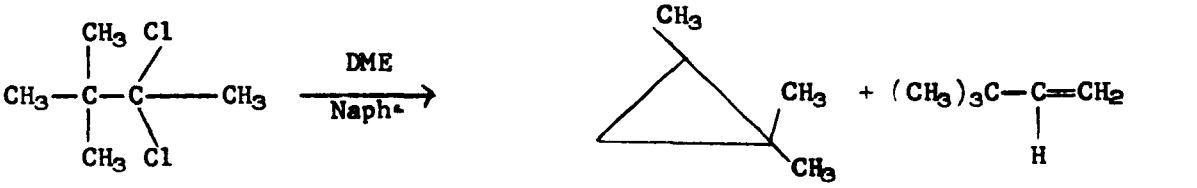
An elegant example of this kind of dehalogenation is illustrated in the reaction studied by McDonald and Frichey.[52] Treatment of compound 11 with disodium phenanthrene effects dechlorination in high yield. (eq. 12)



(12)

Treatment of stilbene dibromides with sodium naphthalenide formed many products.[51] One of these was diphenylacetylene which likely originates via dehydrobromination. (It remains to be proven that E2 dehydrobromination is a possible reaction pathway for these radical anions).

Sargent[53] has reported the results of a gem-dichloride reaction and has found evidence for a carbene radical anion, hitherto an unreported intermediate. The overall equation is



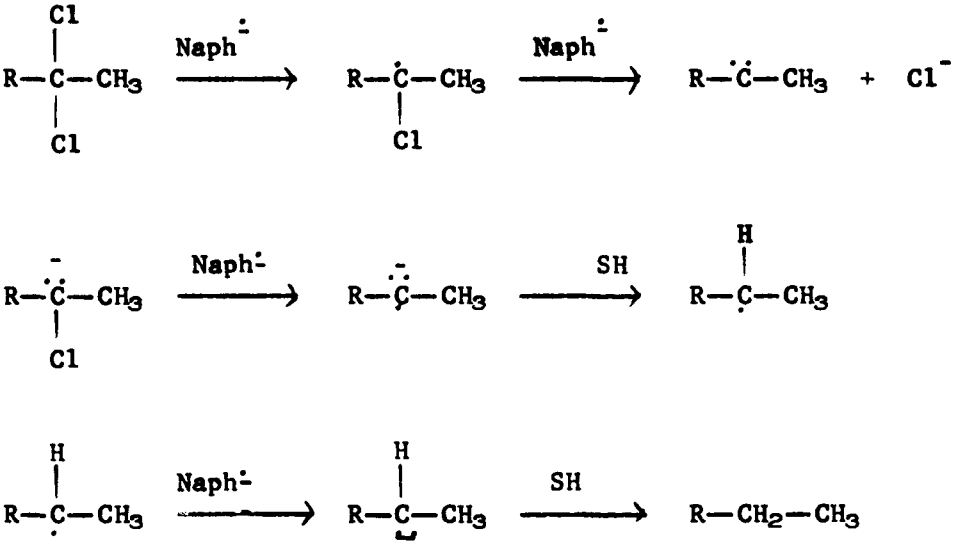
(13)

+ $(CH_3)_3C—CH_2—CH_3$

13

He suggests the cyclopropane derivative has a carbene or carbenoid origin, the alkene arising via "elimination and reduction reactions." The alkane 13 was proposed to be the product of a carbene radical anion intermediate (Scheme IV).

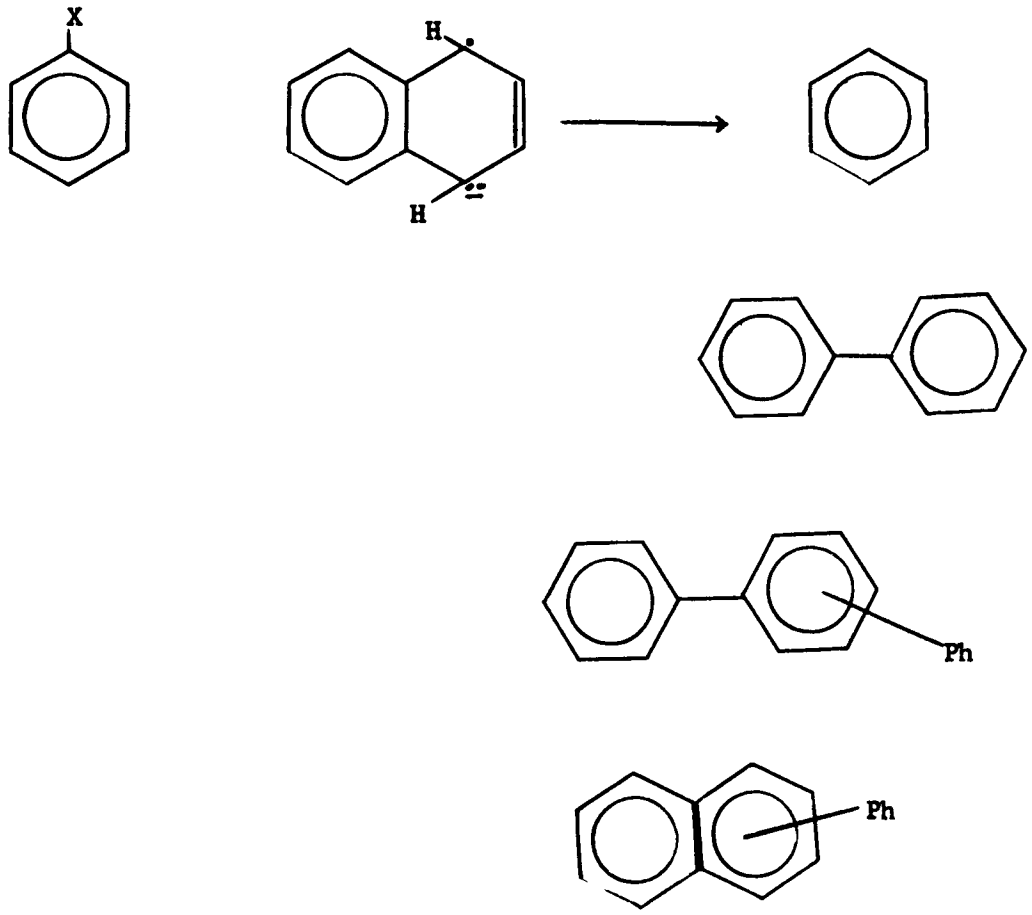
Scheme IV



Reaction of aromatic halides with an electron source was apparently recorded first in 1862 when it was found these compounds form their corresponding hydrocarbons upon treatment with metallic sodium.[54] Another early study was that of White, who reduced chlorobenzene with sodium in liquid ammonia.[55] Benzene was the major product, the author presumed this product to be derived from attack of phenyl radical on ammonia. Aniline, diphenylamine, and triphenyl amine were also recovered. Apparently biphenyl was not formed.

Studies with radical anions as the electron source showed the reactions to be fast.[56] Product studies were completed by Cheng, Headley, and Halasa,[57] The overall reaction of various aromatic halides with sodium

naphthalenide is summarized by eq. 14 with yields in Table II.



(14)

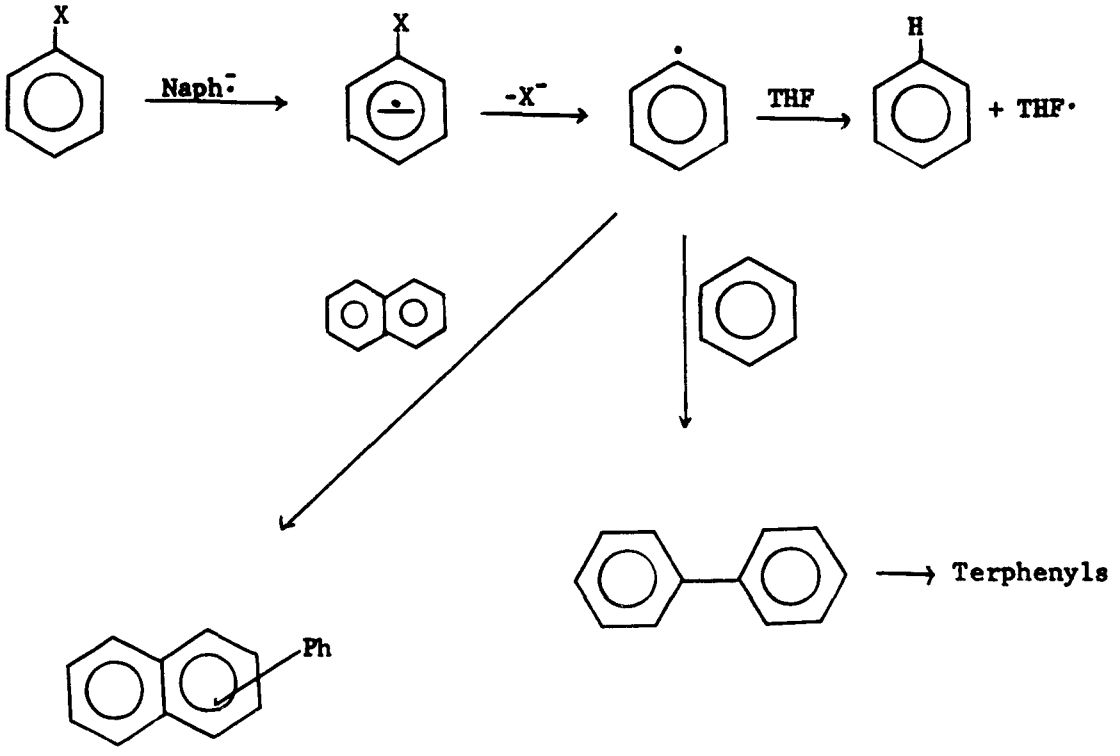
X = F, Cl, Br, I

From the yields it is evident that the product distribution, with the exception of the reaction of fluorobenzene, is independent of the halide. This suggests that the slow step in the reaction is not cleavage of the aryl-halogen bond. These results were interpreted by Cheng, et. al., to be accomodated by the mechanism in Scheme V.

Table II - Relative Amounts of Identified Products from the Reaction of Sodium Naphthalene with Halobenzenes before Hydrolysis.

ArX $\frac{Na^+Naph^-}{ArX}$	T°-C°	% benzene	% biphenyl	% o terphenyl	% m terphenyl	% p terphenyl	% α phenyl Naph	% β phenyl Naph
Bromobenzene								
1/1	-60°	86.9	8.7	1.1	0.1	0.1	1.4	0.9
Bromobenzene								
2/1	-60°	86.5	6.4	0.7	0.2	0.2	0.8	1.0
Bromobenzene								
1/1	27°	89.7	6.3	0.5	0.3	0.3	0.9	0.7
Bromobenzene								
2/1	27°	85.0	7.3	1.4	0.4	0.5	1.6	0.7
Fluorobenzene								
1/1	-60°	72.2	16.9	2.6			1.7	2.0
Chlorobenzeme								
1/1	-60°	82.4	8.6	1.7	0.3	0.2	2.4	1.5
Iodobenzene								
1/1	27°	84.8	9.8	0.6	0.3	0.3	1.1	0.2

Scheme V

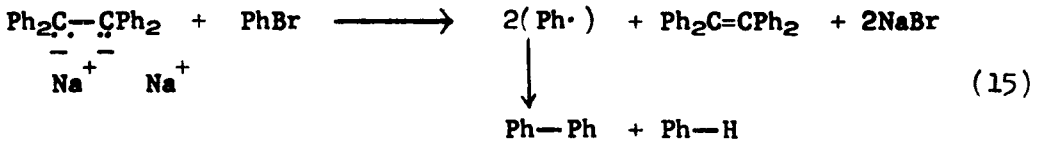


Phenyl Naphthalenes

Cheng, et.al., found the following observations to be consistent with the proposed mechanism. (1) The product distribution is independent of the $Na^{+}Naph^{\cdot -}$/ArX ratio; (2) a small amount of THF dimer is seen by mass spectroscopy; (3) quenching the reaction with D_2O did not result in the formation of any deuterated benzene, providing evidence against the intermediacy of phenyl anion.

These results are compatible with those of Muller and Roscheisen,[58] who interpreted the reaction between disodium tetraphenylethylene and bromobenzene as being consistent with the scheme in eq. 15. Muller and Roscheisen used CO_2 as a diagnostic for the presence of the

phenyl anion. They isolated no benzoic acid and therefore concluded that a radical mechanism was operative.



(15)

In a somewhat different environment there is direct evidence for the phenyl anion. After treating fluorobenzene with dilithium biphenyl, carbon dioxide was bubbled into the reaction mixture and benzoic acid was isolated.[59]

Studies more seriously questioning the validity of a radical pathway were published by Sargent.[60] His interpretations are totally at odds with those of Cheng, et al. He cites the following observations:

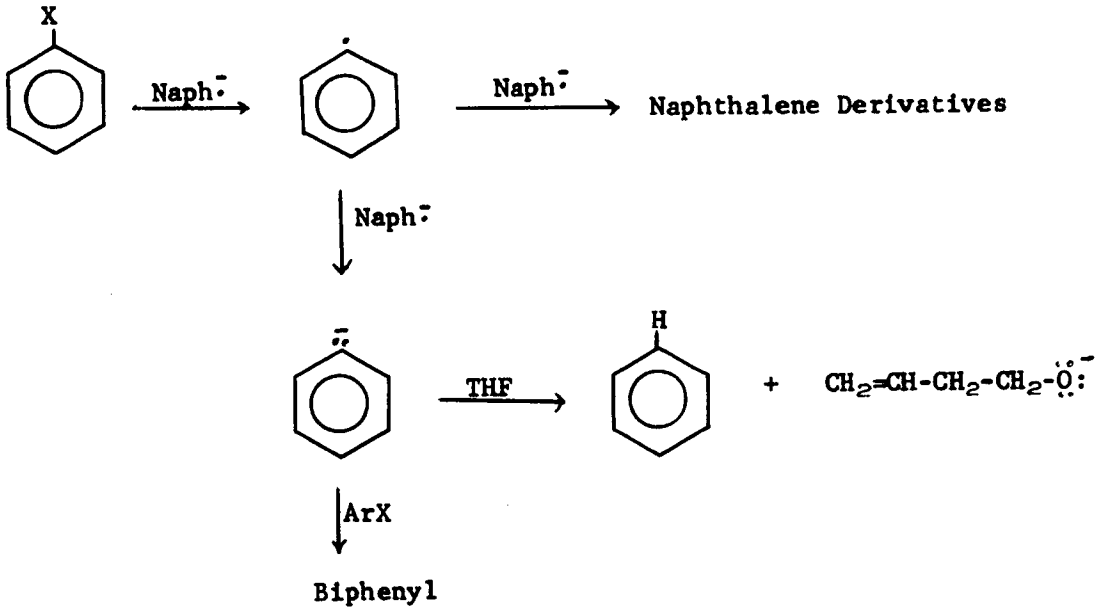
1. Garst has observed that abstraction of a hydrogen from THF by the 5-hexenyl radical does not compete with reduction of that radical to the corresponding anion.[19,35] Furthermore, Sargent has determined that the sp^2 hybridized 3-hexen-3-yl radical is reduced to the anion more rapidly than it can extract a hydrogen from THF[61]. These results are in conflict with those in Scheme V.
2. It is difficult to account for the formation of biphenyl on the basis of the coupling of phenyl radical with benzene. The benzene for this process can only come from a reaction of aryl halide with sodium naphthalenide. A reaction which concomitantly produces a molecule of naphthalene. Thus, the concentration of naphthalene must always be equal to or greater than that of benzene. Since the phenyl radical has greater affinity[62] for naphthalene then benzene by a factor of 24:1, more phenyl naphthalene than biphenyl would be anticipated by a radical mechanism. Increasing the concentration

of benzene by performing the reaction in a solvent which was 40-60 vol% benzene-THF produced no significant change in the yield of biphenyl.

3. Alkylation of naphthalene has clearly been demonstrated not to involve radical addition to naphthalene, but rather to be a consequence of alkyl radical-radical anion coupling. There are no prior data which would suggest that phenyl radicals behave differently.

Sargent proposed a mechanism which is fully in agreement with the reactions of alkyl halides and sodium naphthalenide. (Scheme VI).

Scheme VI



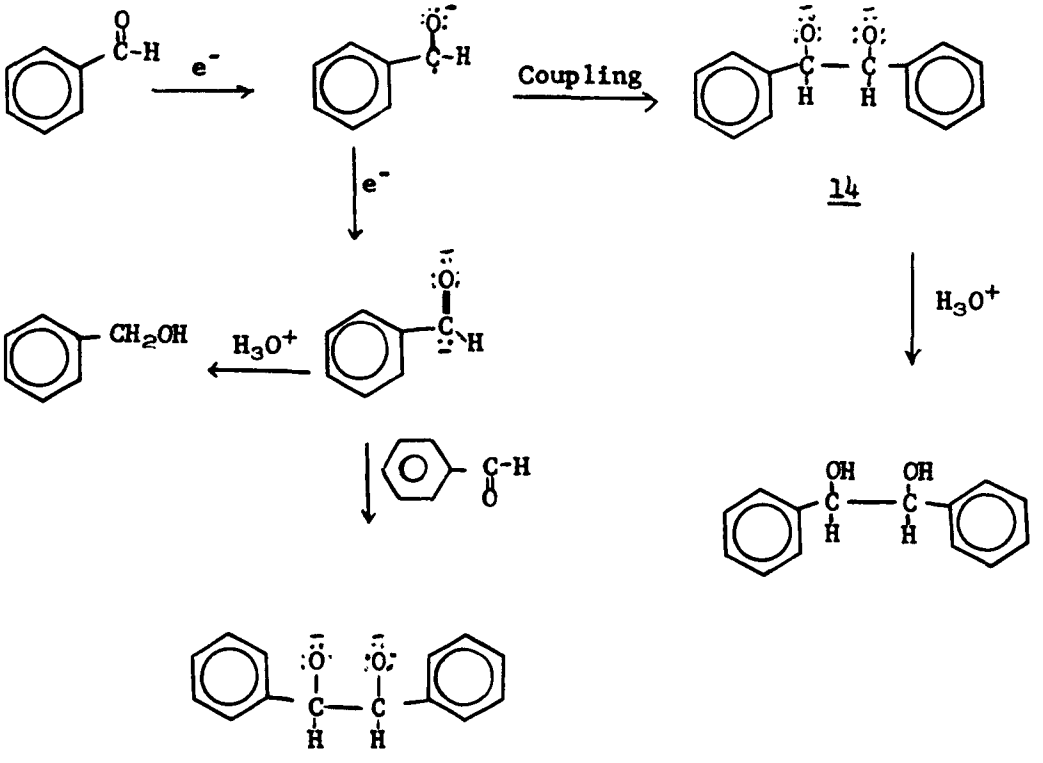
A comparison of the reactions of phenyl lithium and sodium naphthalenide is of interest. Upon treatment with phenyl lithium, fluorobenzene is converted to unstable ortho-fluorophenyllithium which decomposed to benzyne intermediates.[63] No evidence is seen in the results of Cheng, et.al., of similar behavior. Dilithium biphenyl does not preponderantly convert fluorobenzene to a benzyne intermediate

either.[59] Electron transfer is the favored process for both the radical anion and dianion.

III Electron Transfer to Aldehydes and Ketones

Reactions of aromatic aldehydes and ketones with sodium naphthalenide lead to two products which in all likelihood reflect either a one or a two electron reduction.[64] For benzaldehyde and related compounds the major product is diol. The products likely arise via the Scheme VII, which is consistent with electrolytic reduction.

Scheme VII



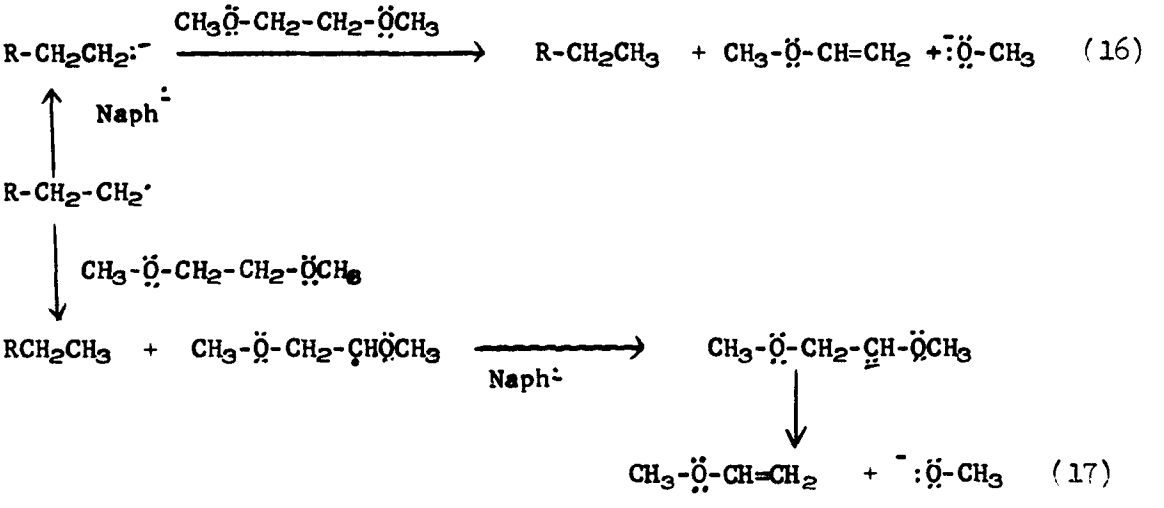
Alcohol could conceivably arise via disproportionation of the dianion 14, but this is not probable in view of the constancy of the yield with a variation in reaction time and method of quenching.[64]

IV Ether Cleavage

Ethers are the solvents of choice in the preparation and reactions of alkali metal-aromatic radical anions. Formation of these adducts is highly dependent on solvation, especially of the cation. But ethers themselves react with radical anions, albeit more slowly than other functional groups. The overall reaction of the ethers is cleavage, and this may occur by electron transfer or proton abstraction. (See appendix A).

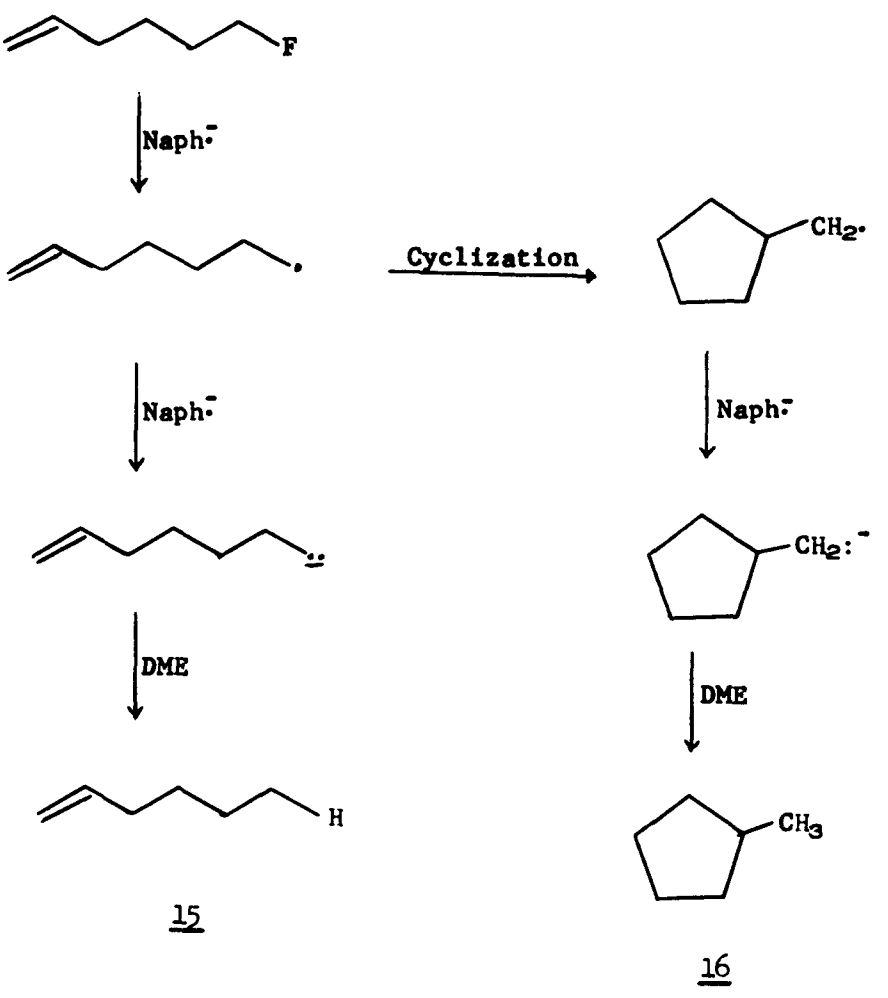
The quenching of many of the intermediates considered earlier was shown to occur by reaction between the intermediate and the ether solvent. One prominent example involved the quenching of intermediates derived from alkyl halides. In DME the possible routes are shown in eq. 16 and 17.

Studies on 5-hexenyl fluoride are helpful in choosing between (16) and (17).



Garst found that the reduction of 5-hexenyl fluoride with sodium naphthalenide yielded 1-hexene, 15, and methyl cyclopentane 16, the reaction paths given in Scheme VIII have been suggested.[65]

Scheme VIII



15 16

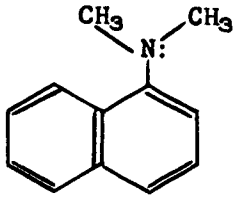
With an excess of sodium naphthalenide the ratio 1-hexene:methylcyclopentane is as much as 40:1; it never falls below 2:1. Consequently, the reaction path via (17) is less likely than via (16) because it is known that cyclization of these radicals is much faster than hydrogen atom transfer.[19,66,67] Hence in this reaction the favored path involves proton abstraction from the solvent.

In ethers having one or more components capable of undergoing reduction, the major cleavage mechanism appears to involve electron transfer. This conclusion is based entirely upon the products derived

from the reactions found in published reports because mechanistic studies have not been made. Therefore, a summary of these reports on ethers is provided in Appendix A together with reactions of aromatic radical anions with H_2, N_2 and compounds containing sulfur and nitrogen.

V. New Synthetic Aspects

In general, radical anions are good reducing agents, however, product isolation involves separation from the radical anion precursor (e.g. naphthalene) and is often difficult.[68] Bank and Platz[69] have solved the problem by using a conveniently recoverable radical anion precursor. The precursor is α-dimethylaminonaphthalene (DIMAN) 17.



17

By stirring freshly cut sodium, DIMAN, and solvent, THF or DME, in a dry oxygen free vessel there is obtained a dark green color in minutes and reaction is completed in several hours. For their comparative studies, four characteristic and diverse sodium naphthalenide reactions were investigated: cleavage of cyclohexyltosylate to cyclohexanol, elimination in 1,2 cyclododecane dimesylate to cyclododecene, preparation of benzyltrimethylsilane from benzyl chloride and trimethyl silylchloride and reaction with hydrogen to give activated sodium hydride. In each instance DIMAN was quantitatively removed by successive washings with aqueous acid. Yields with sodium DIMAN are comparable to those

with sodium naphthalene, although somewhat lower. More significantly, the isolated yields of pure products are substantial and should render the reagent of synthetic use. They found no evidence for cleavage of the dimethylamino group. Sodium DIMAN reacts slowly with THF, however, to give both cis and trans crotyl alcohol and for this reason synthetic reactions are run preferentially in DME, as solvent decomposition products if any, do not interfere with product isolation. No mechanism is given by Bank as to the reaction of the radical anion with THF to give cis and trans crotyl alcohol.

The rapid and extensive formation of sodium DIMAN radical anion indicates that the conjugative effect of the dimethyl amino group does not significantly raise the reduction potential of the naphthalene ring. Quite possibly the operative effect is an internal solvation of the sodium ion, similar to that observed for various other organometallic compounds.[70]

VI. Review of Some of the Physical Chemistry of Radical Anions

1. Electron affinity

The single characteristic most important in defining the reactivity of radical anion is the ease with which the nucleus is reduced; one measure of this is given by the electron affinity in the gas phase, (see Table III).

From Table III one may see that the difference in electron affinity between naphthalene and anthracene, is 0.40 eV with anthracene being the more easily reduced.

In solution the difference in electron affinity between any two compounds varies with the stabilization afforded by solvation. The degree of stabilization is not uniform and depends on the area of the

TABLE III - Electron Affinities[a]

Compound	Electron Affinity eV
Naphthalene	0.152 ± 0.016
Phenanthrene	0.308 ± 0.024
Chrysene	0.419 ± 0.036
Anthracene	0.552 ± 0.061
Azulene	0.587 ± 0.065

[a]W.E. Wentworth, E. Chen, and J.E. Lovelock, J. Phys. Chem., 70, 445 (1966) R.S. Becker and E. Chen, J. Chem. Phys. , 45, 2403 (1966).

radical anion; solvation is more important in those radical anions of rather small area but not as important in larger rings in which solvation becomes nearly constant.[71,72] Thus, in solution there is an increase in the difference between the electron affinities of small (e.g. naphthalene) and large (e.g. anthracene) molecules.

Another method of determining electron affinity was pioneered by Hoijtink and his associates.[73] Essentially the method involves potentiometric titration of aromatic compounds with a standard solution of biphenyl and biphenylenide (biphenyl has a high reduction potential). One electrode was in the biphenyl-biphenylenide solution, the other in the aromatic hydrocarbon to be reduced. The potential difference was measured as the biphenyl-biphenylenide solutions were added. Improvements in this technique were made by Slates and Szwarc.[74] Their data are presented in Table IV.

Table IV. Potentiometric Titration with Biphenyl-Biphenylenide[a]

Aromatic Hydrocarbon	Potential V
Biphenyl	(0.0)
Naphthalene	0.043 ± 0.02
Triphenylene	0.132 ± 0.01
Phenanthrene	0.142 ± 0.01
Pyrene	0.592 ± 0.01
Anthracene	0.642 ± 0.01
Benzo (a) pyrene	0.760 ± 0.02
Perylene	0.965 ± 0.01
Naphthacene	1.058 ± 0.02

[a]In THF solvent. Taken from reference 74.

2. Structure and Solvation of Ion Pairs

The equilibrium constant for the reaction of an alkali metal with an aromatic hydrocarbon

$$M + Ar \longrightarrow Ar^{\cdot-} M^{+} \qquad (18)$$

depends upon the nature of the metal, the hydrocarbon, the solvent, and the temperature. These same factors also determine whether the cation radical anion interaction will be as solvent separated ("free") ions, solvent separated (loose) ion pairs, or contact (tight) ion pairs.

Much of our understanding of the equilibria between alkali metals and aromatic hydrocarbons in ether solvents is attributable to Szwarc[10a,b] and Shatenshtein.[75-77] The equilibrium constant for the electron-transfer

reaction from alkali metal to aromatic hydrocarbons is often too large to permit quantitative studies. However, with naphthalene and particularly biphenyl the reduction potentials are sufficiently high that under proper conditions conversion to radical anions is only partial. Shatenstein's results[75-77] show that steric factors in the coordinating solvent are more important than differences in basicity. The highest yield of radical anions is obtained for ethylene glycol ethers because of the ability of these solvents to form comparatively stable five-membered chelate rings. The influence of the identity of the metal on the equilibrium may be summarized by indicating that the highest equilibrium constant in a particular solvent is usually obtained for the smallest cation because of the higher heat of solvation (Li^+, Na^+, K^+, Cs^+).

The relationship between the identity of the alkali metal and the tendency to form ion pairs is highly dependent upon the solvent and anion. In situations where all the cations form contact ion pairs, lithium binds most strongly with the anions. But there are other cases where Li^+ compounds are solvent separated ion pairs while their Na^+, K^+ or Cs^+ counterparts form contact ion pairs.

Ion pairing is favored in the smaller hydrocarbons where the charge is more concentrated,[71] and therefore the interaction with the counter-ion becomes more important.[78] Hence there is a greater tendency for ion pairing in naphthalenide than there is for anthracenide or perylenide.

The sodium salts of naphthalene, biphenyl, anthracene, and perylene have nearly identical dissociation (10^{-6}- 10^{-7}) constants at -70° in THF. As the temperature increases ion-pairing becomes more extensive; this reflects the observation that all of these dissociation processes are exothermic. The smaller radical anions show greater attraction for the

counter ion than larger anions, so the sodium cation is more extensively solvated in the presence of the large perylenide anion and therefore dissociation is less exothermic.

The interaction leading to the separation of ions by a solvent molecule (or molecules) was clearly visualized by Winstein[79] and elaborated by Grunwald.[80] The potential energy of two ions increases as they are pulled away from their contact position. Initially, their attraction for each other is not attenuated by the solvent because the gap between them is too small to accommodate a solvent molecule.[81,82] However, at some critical distance a polar solvent molecule may be accommodated and then the energy of the system decreases as the solvent fills up the vacant space.

The solvent separated ion-pairs exist only in those media in which at least one of the ions, when free, is coordinated with solvent molecules. The association of such ions proceeds smoothly until the solvation shell touches the counterion. At this stage a solvent-separated pair is formed. Further approach requires expulsion of the solvation shell (a discontinuous process) and yields a contact-pair.

The effects of solvent and metal ion can be rationalized as follows: free ions are preponderant only in highly polar solvents (HMPA), in DME loose ion pairs are more typical, and in solvents of low polarity and coordinating ability (THF, dioxane) contact ion pairs are found to exist.

Anions have different cation affinities, i.e. differing abilities to attract cations. The cation affinity can be identified with the standard free energy change accompanying dissociation of a gas-phase ion pair. Anions with large, concentrated, sterically accessible charges have high cation affinities. Those with small, highly dispersed, or sterically inaccessible charges have low cation affinities.

On the other hand, in solution solvation effects on alkali metal cations will modify the cation affinities. Since the smaller the cation, the greater the solvation, the cation affinities may be completely reversed in solution compared to the gas phase.

A further complexity arises in that the alkali metal-radical anions aggregate to form dimers and n mers in solution. The result is that a theoretical analysis of the physical data does not lead to clear, simple correlations of cation affinities with alkali metal atom size or solvation energies. Some aromatic radical anions (naphthalene, phenanthrene) are stable in solvents of widely ranging dielectric constant (2-Me THF, HMPTA) while others such as Perylene do not form stable radical anions in solution. Disproportionation occurs to dianion (see below) and neutral hydrocarbon.

Metal ion effects have been observed to cause disproportionation to go in either direction. For example, in 2-methyl THF (ϵ=6.92)Li^+ favors the disproportionation of stilbene radical anion to dianion over Na^+ while in tetrahydrofuran (ϵ=8.23) the opposite is true.[83,84,85] Whatever else may be concluded in terms of cation affinities in relation to polarity of solvent, it suffices for our purposes to say that solvent effects to cations of aromatic radical anions are far more important than to the anions because the solvent must coordinate to the metal cation in order to solubilize (or even form at all) the radical anion.

3. Dianion Formation

Metal salts of the dianions can be prepared for all of the hydrocarbons which we have considered. Of the three most commonly employed hydrocarbons, anthracene, having the lowest reduction potential, most easily forms the dianion. The lithium, sodium, potassium and rubidium compounds have been prepared.[86] Biphenyl forms the dianion with lithium[87] sodium[88],

and potassium.[89,90] The lithium salt is most stable, a consequence of its binding strength. The potassium salt decomposes in DME so that after 4 hours (apparently at room temperature) 90% of the initial concentration is destroyed.

Formation of the dianion of naphthalene was first recorded by Shatenstein, et al., Buschow and Hoijtink, and later by Smid.[90] Only the dilithium salt has been prepared in appreciable concentration.[91] Treating potassium naphthalenide with metallic potassium in DME is reported to yield 1,4-dihydronaphthalene.[92] Presumably naphthalenide is reduced by potassium to the dianion which is then protonated by DME. An explanation of why biphenyl forms the dianion with more alkali metals than naphthalene is not known, but this undoubtedly has its origin in the strength of the metal-dianion interaction. From X-ray studies on the crystalline complex, bis (tetramethylene diamine) lithium naphthalene dianion, it is known the dianion is situated between the cations with one cation positioned over one ring and the remaining cation positioned under the other ring.[93] The dianion is not planar with four atoms 0.15Å off the mean plane of the group.[93]

A characteristic of the radical anions which must be evaluated when one is interpreting the results of a reaction is the tendency of many radical anions to disproportionate. Hence, a "radical anion" solution may contain dianion which could account for a significant portion of the chemical activity.

$$2Ar^{\cdot-}\ M^{+} \rightleftharpoons Ar^{2-}\ 2M^{+} + Ar \qquad (19)$$

The hydrocarbons discussed here do form dianions under favorable conditions, such as use of excess metal so their presence in radical anion solution and their effects upon ensuing reaction must be evaluated. Even in situations where the dianion is not formed in detectable concentrations, there may be present tiny quantities of the dianion in equilibrium with the

radical anion. In principle, reactions of even these solutions may proceed, in part, through the dianion.

The most complete study of disproportionation is on tetraphenylethylene (T).[71] Studies on the disproportionation equilibria of alkali metal aromatic dianions such as dilithium, disodium, and dipotassium biphenyl and dilithium naphthalene have either not been performed or have received only cursory attention.

Szwarc and associates have recently elucidated the mechanism of electron transfer in the tetraphenylethylene disproportionation.[94] They conclude that electron transfer occurs most rapidly from the free radical anion to the ion pair.

$$T^{\cdot-} + T^{\cdot-}\,Na^+ \rightleftharpoons T + T^{2-}\,2Na^+ \qquad (20)$$

The process indicated by eq. 21 is slightly slower, and that by eq. 22 is too slow to contribute significantly to the disproportionation process.

$$2T^{\cdot-}\,Na^+ \rightleftharpoons T + T^{2-}\,2Na^+ \qquad (21)$$

$$2T^{\cdot-} \rightleftharpoons T^{2-} + T \qquad (22)$$

The solvent is an important factor in these equilibria. Solvents which form strong associations with the cations, such as DME or HMPA, favor formation of the free radical anions, which do not disproportionate.[85] The reduction potential of the free radical anion is higher than the ion pair. Less polar solvents such as dioxane do not bind strongly with the cation, so dianion formation is correspondingly more favorable.

4. Kinetics of Electron Transfer

Electron exchange between aromatic radical anions and their parent hydrocarbons is extremely rapid. Exchange rates[98-102] are determined from

line broadening in esr spectra and are found to be on the order of $10^{8}M^{-1}sec^{-1}$. This rate depends upon whether the cation-radical anion combination is "free" or an ion pair. Electron transfer in the exchange reaction between $Na^{+}Naph^{\cdot-}$ was observed to be nearly two orders of magnitude slower for ion pairs than for the free ions.[121] Electron transfer from the ion pair must be accompanied by migration of the counter ion, the net effect is that atom transfer occurs from ion pairs, and this is slower than simple transfer of an electron.[103]

It should be pointed out that the solvent separated (free) radical anion may not prove to be the most reactive species in all electron transfer (or other) reactions. Some electron transfers proceed more rapidly through ion pairs. There are many examples in the inorganic literature where "bridging" groups are involved. It is likely that the first example from organic chemistry was noted by Garst and associates.[104] They observed that the air oxidation of the carbanion related to Koelsch's radical (2-phenyl bis (biphenylene) allyl) proceeded more rapidly for ion pairs than the free anion. This result was interpreted as being consistent with a transition state in which the charge is more concentrated than in the reactant anion.

$$R:^{-} + O_2 \longrightarrow R^{\cdot} + O_2^{\cdot-} \qquad (23)$$

In this reaction the electron receptor is much smaller than in the exchange of an electron between naphthalene rings, so it should be anticipated that ion pairing would be more important in the transition state.

The factors involved in the rate of electron transfer from aromatic dianions are even less well defined. From disproportionation studies of

radical anions it is known that this must also be fast.[92]

There is also a fast rate of electron transfer from hydrocarbon radical anions to a variety of molecules bearing functional groups. The rates vary from 10^6 to 10^{10} $mol^{-1}sec^{-1}$. The rate difference has a significant impact on the course of chemical reactions; there are a number of examples in which either proton abstraction or electron transfer is inherently possible on the basis of acidity and reduction potential. Because of the rate difference, electron transfer from naphthalenide, for example, is significant even for some compounds having pKa's as low as 20-23.

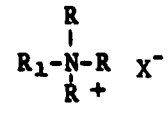
Since lithium naphthalenide was known to react with 5-hexenyl fluoride at a rate 100 times faster than sodium naphthalenide (see Table I, page 7), it was decided that radical generation with lithium naphthalenide in THF would probably be faster than sodium naphthalenide in reactions of benzylic halides or other functional groups such as quaternary ammonium salts. In addition, with lithium as the counter ion rather than sodium, any carbanions generated in following processes would be less reactive toward reaction with the solvent (THF) than carbanions of organosodium compounds which are known to cleave ethers instantly on the laboratory time scale.

STATEMENT OF THE PROBLEM

Interest in the reactions of aromatic radical anions arose when it was discovered that sodium naphthalenide reacts with alkyl[11,13,14,26] and aryl[57,60] halides to produce alkyl and aryl radicals. Although intermediate halogen containing radical anions are hypothesized to form, no experimental evidence for them has ever been obtained because they eliminate halide to form radicals very rapidly. In the preparation of resonance stabilized benzylic radicals, elimination of halogen appears to be almost instantaneous.[40]

Few functional groups other than halogen have been studied. Tosylates[105] are cleaved by naphthalenide to give alcohols, sulfonamides[106] are cleaved to give amines, and polyphenylethanes[107] are cleaved to give methanes.

Variation of the oxidation state of nitrogen does not appear to have been considered as a means for cleaving carbon-X bonds through reduction with naphthalenide ion. Consequently, we began a study of the reactions of naphthalenide ion with quaternary ammonium salts 1.



1

It seems reasonable to assume that the radical anion could reduce the salt by transferring an electron to create an unstable radical analogous to the supposed alkyl-chloride radical anion intermediate. Such radical intermediates for 1 should decompose to produce neutral molecules (3°amines)

and radicals. These radicals should behave like the ones formed from alkyl and aryl halides. Obviously, the relative power of different radical anions could be tested against model quaternary salts such as benzhydryl, anilinium and tetramethylammonium salts.

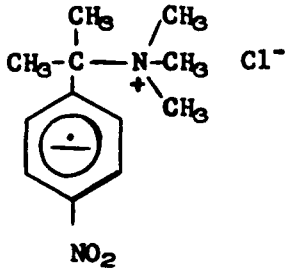
A comparison of reductive cleavages by lithium naphthalenide with displacement reactions of benzylic carbanions was planned for reactions with quaternary ammonium salts and their halogen counterparts. The reason for making this comparison is that radicals formed in the reductive cleavage by an aromatic radical anion might conceivably form dimeric products either by coupling of the radicals, or by an alternative pathway involving radical reduction to a carbanion which then displaces a 3° amine from the original salt or halide from the starting halide.

In order to determine whether these displacements occurred with inversion of configuration at carbon, displacement reactions with R (+) and S (-) - α - phenylethyltrimethylammonium iodide were planned. In addition, an alternative synthesis of 1,1,2-triphenylpropane from S (+) hydratropic acid was planned in order to establish the absolute configuration of the optically active hydrocarbon and, thereby, the stereochemistry of the process by which it forms.

It was expected that all of these quaternary ammonium salts would react to give alkyl or aryl radicals when reacted with the radical anion. It was hoped that the reactions of quaternary ammonium salts would give tertiary amines when cleaved, and this would be a new method for removing nitrogen from carbon.

It is known that p-nitrobenzyl halides[108] react with the 2-nitropropane anion to give carbon alkylation via a radical anion chain

mechanism. Similarly, the reaction of p-nitrocumyl chloride[110] with amines has been proposed to proceed via intermediate 2, a radical anion:



2

Such a radical anion has not been prepared directly, but it would be expected to form if lithium naphthalenide were to transfer an electron to the quaternary ammonium salt.

In the study of quaternary ammonium compounds, we sought to learn whether the radical anion can transfer a ninth electron into the valence shell of N to form an unstable intermediate which decomposes with elimination of the radical. Another question that occurs is whether the quaternary ammonium salt must contain an aryl ring in order for reaction to occur.[108]

Throughout reductive cleavage work with lithium naphthalenide on trimethyl alkyl and aryl substituted quaternary salts, the question arose whether the precursors to radical possessed any selectivity at all with respect to which radical and which 3° amine would form. Consequently, competition studies were planned with quaternary ammonium salts which possessed two different organic groupings and two methyl groups in order to see whether the more stable radical would be formed from the ammonium salt radical precursor. Such intramolecular competition studies were planned for reactions of lithium naphthalenide with

N-benzhydryl-N-benzyl-N,N-dimethylammonium bromide, and N-benzyl-N,N-dimethyl-N-phenylammonium bromide, not only to establish that the cleavage would proceed so as to produce the more stable radical, but also to ascertain whether the initial electron transfer step required the presence of an aromatic nucleus in the original salt in order for reductive cleavage with naphthalene radical anion to be successful.

During the past nine years in study of halide reactions with aromatic radical anions a controversy has developed as to whether the dimer of the original halide forms by <u>alpha</u> coupling (Path A in eq. 1)[40] of two radicals or by an alternative sequence[41] (Path B) involving electron transfer reduction of radical to a carbanion followed by a displacement reaction on the original halide. In order to secure evidence on this point, intermolecular competition studies using equimolar mixtures of benzylic halides reacting with one equivalent of naphthalenide were designed to ascertain whether or not mixtures of freely diffusing radicals could be formed so as to give a statistical array of predictable coupling products.[40]

$$2R\cdot \xrightarrow{A} R\text{-}R \longleftarrow R\text{-}X \quad + \quad R:^{-} \xleftarrow{B} R\cdot \quad + \quad C_{10}H_8^{\cdot -} \qquad (1)$$

Since earlier workers often have tacitly assumed that halide anion is rapidly cleaved by naphthalenide ion with radical formation, a study of three benzylic halides having fluorine, chlorine, or bromine as the departing halide ion was planned in order to establish whether the rate of radical formation was the same in each case. It was believed that a division of radical fates between path A and path B could be achieved that would be reflected in the reduction product: coupling ratio.

RESULTS AND DISCUSSION

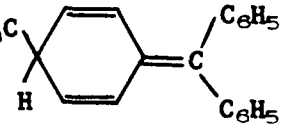
I. REACTIONS OF LITHIUM NAPHTHALENIDE WITH BENZYLIC CHLORIDES AND BROMIDES.

During naphthalenide ion reduction experiments on benzylic halides, stoichiometric formation of triphenylmethyl radicals from trityl chloride and lithium naphthalenide was observed, regardless of the order of mixing the reagents. This independence of the order of addition during titrations suggested that trityl chloride oxidizes trityl carbanion to a radical in a single electron transfer process.

Titrimetric addition of trityl chloride (0.2171 g/ml) to one equivalent of lithium naphthalenide (0.039 mole) in THF (100 ml) produces one equivalent of triphenylmethyl radicals, which dimerize to form 1-diphenylmethylene-4-triphenylmethyl-2 ,5-cyclohexadiene 1. See eq. 1 and 2.

$$(C_6H_5)_3C\text{-}Cl + Li^+Naph^{\cdot -} \longrightarrow (C_6H_5)_3C^{\cdot} + Naph \qquad (1)$$

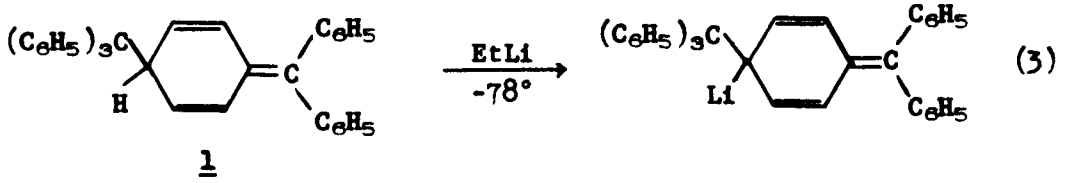
$$2\ (C_6H_5)_3C^{\cdot} \rightleftharpoons \qquad (2)$$



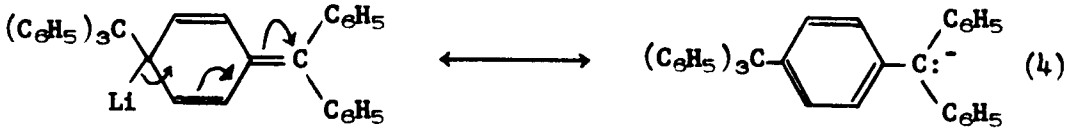
1

The end point can be observed upon the disappearance of the green colored naphthalenide ion whereupon the yellow color of the trityl radical is detected.

After cooling to -78°, the equilibrium of eq. 2 is shifted strongly towards the dimer 1. Isomerization of 1 to p-benzhydryltetraphenylmethane 2 was accomplished in 98.5% yield with ethyllithium and then water. See eq. 3, 4, and 5.



1 (3)



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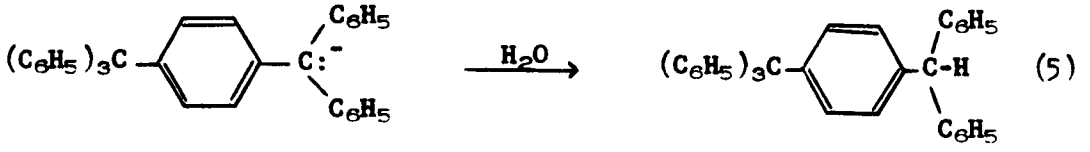
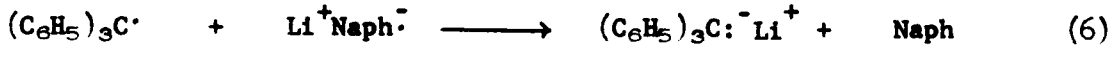


2 (5)

When trityl chloride was added to an excess of naphthalenide (> 2 equivalents / equivalent R-Cl), stirred for 30 minutes and treated with water, the only products detected were triphenylmethane and naphthalene. This may be explained by rapid reduction of the radicals to carbanion before they can couple. See Table 1. and eq. 6 and 7.



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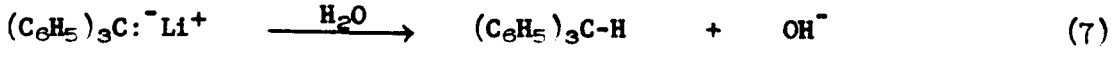


(7)

Table 1. Lithium naphthalenide[a] reduction of benzylic chlorides and bromides.

Compound[b]	Mol ratio $ArH^{\cdot-}$ / R-X	% R-R	% R-H
Ph_3C-Cl	1	100[c]	0
Ph_3C-Cl	3	0	100[c]
Ph_3C-Br	1	100[c]	0
Ph_2CH-Cl	1	78[c]	18[d]
Ph_2CH-Cl	2.27	41.7[c]	51.2[d]
Ph_2CH-Cl	3	19[d]	71[d]
Ph_2CH-Br	1	75[c]	17[d]
$PhCH_2$-Cl	1	72[d]	16[d]
$PhCH_2$-Cl	3	22[d]	70[d]

a. 0.39 M in THF. b. 0.7 - 1.34 M in THF; halide is added slowly to $ArH^{\cdot-}$ c. By isolation. d. By quantitative gas chromatography.

In titrations of equivalent quantities of lithium naphthalenide with benzhydryl chloride or bromide, sym - tetraphenylethane (3, 70-78%) was produced. See eq. 8.

$$Li^{+}Naph^{\cdot-} + (C_6H_5)_2CH\text{-}Cl \longrightarrow (C_6H_5)_2\dot{C}H + Naph$$

$$\downarrow$$

$$(C_6H_5)_2C(H)\text{—}C(H)(C_6H_5)_2 \quad (3) \qquad (8)$$

The formation of 3 may occur either by coupling of benzhydryl radicals (Eq. 8) or by S_N2 displacement between diphenylmethyllithium and benzhydryl chloride. This second pathway arises by reduction of the benzhydryl radicals to benzhydryl carbanion (Eq. 9) followed by reaction with the halide to produce 3.

$$(C_6H_5)_2\dot{C}H + Li^+Naph^- \longrightarrow (C_6H_5)_2CH:^-Li^+ + Naph$$

$$(C_6H_5)_2CH:^-Li^+ \xrightarrow{(C_6H_5)_2CH\text{-}Cl} (C_6H_5)_2CH-CH(C_6H_5)_2 \qquad (9)$$

3

However, the slow inverse addition of one equivalent of naphthalenide ion to benzhydryl chloride also produces 3 (75%) under conditions where halide is in excess and no carbanion formation can be detected visually. Under these conditions, Zieger, Angres, and Maresca assumed that radical coupling must be the predominant pathway for the formation of 3.[40] This view was challenged in 1974 by Closson[41] who used mixtures of naphthalenide ion and t-butanol in reactions with benzylic halides and found diminished yields of ethane coupling products and enhanced yields of reduction products (phenylated methanes). However, these experiments had higher mole ratios (10:1) of naphthalenide ion to halide because of the slow reaction of the radical anion with the t-butanol trapping agent. Comparison of Closson's results with those for a 3:1 mole ratio of radical anion to halide shown in Table 1 show no significant differences. Therefore, the problem of finding a good trapping agent for radical intermediates generated

in aromatic radical anion systems remains unsolved, together with the question of whether the ethane coupling products arise by alpha coupling of two benzylic radicals or by the two step carbanion mechanism.

In his criticism of my original work Closson ignored the competition experiments (described below, see sections III and IV) as well as the known cleavage reaction of ethanes by aromatic radical anions. In 1963 Eisch[107] showed that sodium biphenylenide cleaves polyphenylethanes, and Szwarc has measured the rates of cleavage of 1,2-di-α-naphthylethane with sodium naphthalenide.[108] Our own rate studies on the cleavage of sym-tetraphenylethane (3) in which equivalent quantities of lithium naphthalenide and 3 had reacted for one hour, showed 42% of 3 unchanged. (See Table 2.).

Table 2. Cleavage of sym-tetraphenylethane (TPE) by lithium naphthalenide.

sym- TPE g	Reaction time	Ratio $Naph^{\bullet}$ / sym TPE	Unreacted sym - TPE	%unreacted
3.34 g	1 hr.	1	1.40 g	42%
1.67 g	1 hr.	2	0.44 g	26%
1.10 g	1 hr.	3	0.15 g	14%

Thus, in systems having a ten-fold molar excess of naphthalenide ion, the product methanes would also be formed by cleavage of first-formed ethanes. Since that is unquestionably true, Closson's conclusion that ethane dimers can not be formed by α-coupling of benzylic radicals generated in the absence of excess radical anion (i.e., by slow dropwise addition of naphthalenide ion to halide) is somewhat less than compelling, if not completely vitiated.

Similar titrations of one equivalent of lithium naphthalenide with one equivalent of benzyl chloride gave 72% of bibenzyl 4, in agreement with a previous report.[113] See eq. 10.

$$C_6H_5\text{-}CH_2\text{-}Cl + Li^+Naph^- \longrightarrow C_6H_5\text{-}CH_2\cdot + Naph \qquad (10)$$

$$\downarrow$$

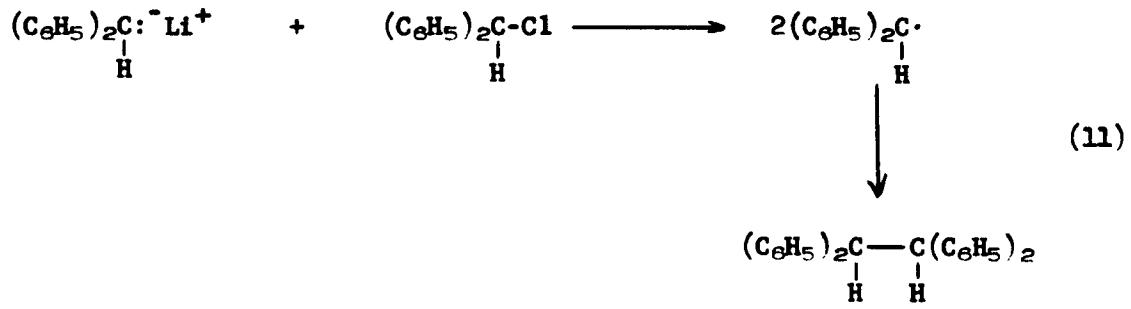
$$C_6H_5\text{-}CH_2\text{-}CH_2\text{-}C_6H_5$$

4

Experiments in which an excess of naphthalenide is present clearly reduced but did not eliminate completely the formation of ethane dimers (see Table 1). This may be explained in terms of a fast reaction between the radical and lithium naphthalenide to produce a carbanion which can displace halide from starting material, forming a polyphenylethane or abstracting a proton from the solvent to give a phenylated methane.

A surprising result in Table 1 is that a three-fold molar excess of lithium naphthalenide reacting with benzhydryl halide does not completely suppress the formation of sym-tetraphenylethane either by reducing benzhydryl radicals to carbanions faster than they can couple or by cleaving sym-tetraphenylethane after it is formed. An analysis of the results would suggest either that benzhydryl radical is not reduced by naphthalenide at diffusion-controlled rates or that benzhydryl anion reacts with benzhydryl halide via displacement at a rate competitive with that of lithium naphthalenide. It is hard to imagine an S_N2 displacement by benzhydryl anion on benzhydryl halide which can operate at a rate competitive with the rates of reduction estimated for electron transfer from naphthalenide.[11b] Perhaps oxidation

of benzhydryl anion by the halide can produce two radicals with the same speed as naphthalenide ion reduction of a radical; see equation below.



(11)

II. REACTIONS OF LITHIUM NAPHTHALENIDE WITH BENZYLIC FLUORIDES.

The reactions of benzylic fluorides with naphthalenide ion exhibited an unusual departure from those results secured for benzylic chlorides and bromides. For example, during naphthalenide ion reduction of trityl fluoride, regardless of the order of the addition, only 4% (fluoride added to naphthalenide) and 2% (naphthalenide added to fluoride) of p-benzhydryltetraphenylmethane was isolated.

From the rate studies of Garst on 5-hexenyl fluorides it is known that fluoride ion is cleaved much more slowly than chloride or bromide ($k_F \approx 5 \times 10^{-4} M^{-1} sec^{-1}$, $k_{Cl} \approx 2 \times 10^2\ M^{-1}\ sec^{-1}$, and $k_{Br} \approx 7.2 \times 10^4\ M^{-1}\ sec^{-1}$). [14b] Therefore, in the trityl fluoride system the trityl radical is formed much more slowly than for trityl

$$Naph^{\cdot -} + Ph_3C\text{-}F \rightleftharpoons Naph + \left[Ph_3C\text{-}F\right]^{\cdot -} \longrightarrow Ph_3C\cdot + F^- \qquad (12)$$

chloride or trityl bromide and the self coupling reaction for $Ph_3C\cdot$ cannot compete effectively with electron transfer reduction to trityl carbanion.

By far the most significant result, however, was the discovery that the trityl carbanion is not oxidized by trityl fluoride to produce two trityl radicals. Consequently, once the trityl carbanion is formed from its radical precursor, it does not revert to trityl radical by a one-electron oxidation with trityl fluoride as was found for trityl chloride and bromide.

The formulation in equation (12) of a pre-equilibrium of trityl fluoride radical anion with naphthalenide suggests a new area of research in that electron spin resonance spectroscopy ought to be able to detect such an intermediate.

For the benzyl and benzhydryl fluoride system it was found that these two fluorides parallel the reaction of the chloride and bromide. The results are summarized in Tables 3 and 4.

Table 3. Addition of benzylic fluorides to lithium naphthalenide.

Compound	Mole ratio $ArH^{\cdot-}$ / R-F	% R-R	% R-H
Ph_3C-F	1	4[a]	90[b]
Ph_2CH-F	1	70[a]	22[b]
$PhCH_2$-F	1	61[b]	30[b]

a. By isolation. b. By quantitative gas chromatography.

Table 4. Addition of lithium naphthalenide to benzylic fluorides.

Compound	Mole ratio $ArH^{\cdot-}$ / R-F	% R-R	% R-H
Ph_3C-F	1	2[a]	95[b]
Ph_2CH-F	1	79[a]	15[b]
$PhCH_2$-F	1	71[b]	20[b]

a. By isolation. b. By quantitative gas chromatography.

From the Tables it may be inferred again that under conditions where halide is in excess a portion of the product must be forming by the alpha coupling of radicals as can be seen by an increase in coupling product yields.

In contrast to Garst's original work on fluorides[35] in which he suggests that fluorides do not form dimers at all, a 71-79% yield of dimer from benzhydryl and benzyl fluoride was observed. This finding

leads to the conclusion that benzhydryl and benzyl radicals couple at rates competitive with one electron reduction by naphthalenide ion to carbanion.

At this point two important questions arise: (1) is Garst's mechanism for dimer formation completely general?, (2) how facile is nucleophilic displacement of fluoride?.

The first question can be answered by examination of the following equations which constitute Garst's mechanism:

$$\text{Naph}^{\cdot-} + \text{R-X} \longrightarrow \text{R}\cdot \qquad (13)$$

$$\text{R}\cdot + \text{Naph}^{\cdot-} \longrightarrow \text{R}:^{-} \qquad (14)$$

$$\text{R}:^{-} + \text{R-X} \longrightarrow \text{R-X}^{\cdot-} \longrightarrow [\text{R}\cdot\ \text{R}\cdot] \longrightarrow \text{R-R} \qquad (15)$$

Garst's interpretation [11a] does not provide for the possibility of the coupling of initially formed radicals (eq. 13), but instead requires that they be reduced to carbanions at a faster rate (eq. 14). The proposed mechanism further suggests that the carbanion reacts with the halide to produce two radicals in a cage which subsequently couple to produce dimer, (eq. 15). As a test for eq. 15 I chose the reaction of trityllithium with benzhydryl fluoride. This reaction (eq. 16) should produce high yields of pentaphenylethane because trityllithium is an excellent electron donor and a good nucleophile as demonstrated by its ability to displace bromide, chloride and trimethylamine from the corresponding benzhydryl systems.

$$\text{Ph}_3\text{C}:^{-}\text{Li}^{+} + \text{Ph}_2\text{CH-F} \longrightarrow [\text{Ph}_3\text{C}\cdot\ \text{Ph}_2\text{CH}\cdot] \longrightarrow \text{Ph}_3\text{C-CHPh}_2 \qquad (16)$$

However, no pentaphenylethane at all is found, when tritylllithium reacts with benzhydryl fluoride. This result suggests two possible explanations: radical-radical coupling is the predominant pathway for formation of dimers in the reaction of lithium naphthalenide with benzhydryl and benzyl fluorides; or simple nucleophilic displacement of fluoride must be occurring. In the latter case, instead of going through a pair of caged radicals (eq. 15), $R:^-$ performs a simple nucleophilic displacement of X^- from R-X to produce R-R directly.

This last argument brings me to the second question: how easy is nucleophilic displacement of fluoride? During nucleophilic displacement studies on fluorides, it was found that as the group bound to fluorine became larger, through successive additions of phenyl groups, the reaction became slower and slower until it reached the point of no reaction, as in the reaction of tritylllithium with benzhydryl- and trityl- fluorides. (See Table 5.)

Since nucleophilic displacement of fluoride is possible, and the reaction times for displacement are comparable to the reaction of lithium naphthalenide with the fluorides, this leads me to conclude that in the reactions of lithium naphthalenide with benzylic fluorides, intermediate benzylic radicals can be reduced to carbanion and compete in dimer formation with the alpha coupling pathway.

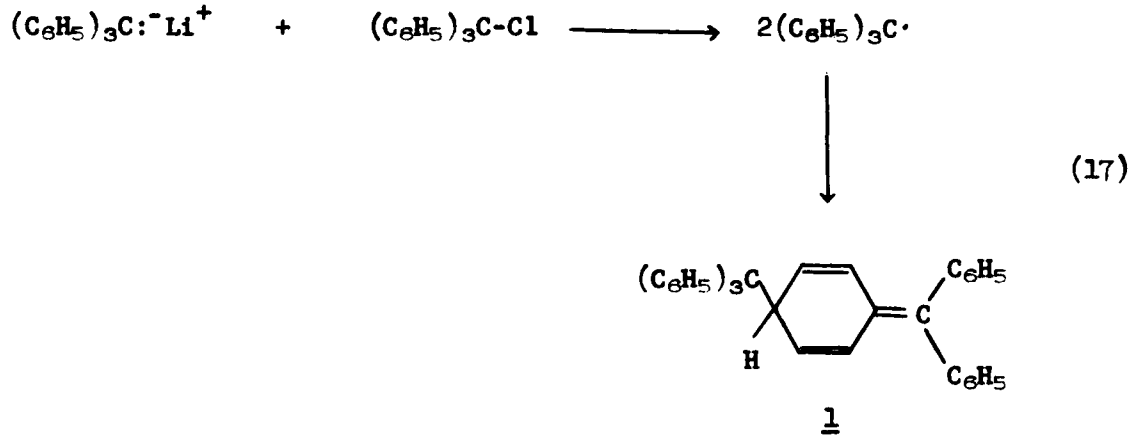
If there is an excess of naphthalenide present then, the initially formed radical is reduced to carbanion faster than it can couple (favoring nucleophilic displacement), while in the cases where naphthalenide is added dropwise to a solution of the fluoride the radical is generated in the absence of naphthalenide, therefore favoring alpha coupling.

Table 5. Reactions of benzylic carbanions with some benzylic fluorides.

Carbanion	Fluoride	Reaction Time	Product	Isolated Yield
$Ph_3C:^-$	Ph_2CH-F	6 days	Ph_3C-$CHPh_2$	0%
$Ph_3C:^-$	$PhCH_2$-F	4.75 hours	Ph_3C-CH_2Ph	91%
$Ph_2CH:^-$	Ph_2CH-F	1 hour	Ph_2CH-$CHPh_2$	96%
$PhCH_2:^-$	$PhCH_2$-F	20 min.	$PhCH_2$-CH_2Ph	95%

III. REACTIONS OF BENZYLIC CHLORIDES AND BROMIDES WITH BENZYLIC CARBANIONS AND SOME COMPETITION EXPERIMENTS.

The question arose as to whether benzylic organolithium reagents could oxidize halides to radicals. During the titration of one equivalent of trityl chloride with one equivalent of lithium naphthalenide, the red color of the triphenylmethyl carbanion could be discerned in the dark naphthalenide solution. The fact that both the red and green color were discharged rapidly with a single drop of halide solution at the end point suggested that trityl chloride rapidly oxidizes triphenylmethyllithium to trityl radicals via electron transfer, (eq. 17).



(17)

1

Verification was secured through preparation of authentic triphenylmethyllithium by metalation of triphenylmethane with n-butyllithium.[114] Titration of trityl carbanion with trityl chloride until discharge of the red color of the carbanion quantitatively produced 1 as judged by isolation of one mole of p-benzhydryltetraphenylmethane for each mole of trityl chloride added. Inverse order of addition experiments, in which trityl carbanion is added to trityl chloride produced one mole of 1 for each mole of added carbanion.

Clearly triphenylmethyl chloride reacts with triphenylmethyl

carbanion *via* a one-electron oxidation process to produce 2 moles of trityl radicals. The best analogy for the present electron transfer oxidation of trityl carbanion by trityl halide is found in the work of Kornblum[115,116] and Russell[43] who have demonstrated that a radical anion chain mechanism operates in oxidation of 2-nitropropane lithium salts by compounds such as p-nitrocumyl chloride and α,p-dinitrocumene.[115]

The question arises whether diphenylmethyl halides react in a similar manner with triphenylmethyl carbanion.

Treatment of triphenylmethyllithium with benzhydryl bromide produced pentaphenylethane, 5 in 95% yield. (See eq. 18.)

$$(C_6H_5)_3C{:}^{-}Li^{+} + (C_6H_5)_2CHBr \longrightarrow (C_6H_5)_3C\text{-}\underset{\underset{H}{|}}{C}(C_6H_5)_2 \qquad (18)$$

5

Use of benzhydryl chloride also produced pentaphenylethane, in 91% yield. These reactions appear to involve either simple nucleophilic displacement[117] or formation of a pair of caged radicals[37] which combine without detectable escape from the cage. Efficient coupling of these radicals would be anticipated, since excess vibrational energy could be readily spread throughout a number of modes of vibration. If any free benzhydryl or trityl radicals were formed, *sym*-tetraphenylethane and 1 would have been produced.

In order to show that cross coupling products would form from mixtures of benzhydryl and trityl radicals, competition experiments using one equivalent of equimolar benzhydryl and trityl halides solution with one equivalent of lithium naphthalenide were run. After discharge

of the aromatic radical anion color, oxygen was bubbled through the mixture to convert residual trityl radicals into bis(triphenylmethyl) peroxide (18%). Pentaphenylethane (36%) and tetraphenylethane (32%) were isolated. See scheme 1.

Scheme 1.

$$\text{Naph}^{\cdot-} + \begin{cases} \text{Ph}_3\text{C-Cl} \\ \text{Ph}_2\text{CH-Cl} \end{cases} \longrightarrow \text{Naph} + \begin{matrix} \text{Ph}_3\text{C}\cdot \\ \text{Ph}_2\text{CH}\cdot \end{matrix}$$

$$\text{Ph}_3\text{C}\cdot + \text{Ph}_2\text{CH}\cdot \longrightarrow \text{Pentaphenylethane (36\%)}$$

$$\text{Ph}_2\text{CH}\cdot + \text{Ph}_2\text{CH}\cdot \longrightarrow \underline{\text{sym}}\text{-tetraphenylethane (32\%)}$$

$$\text{Ph}_3\text{C}\cdot + \text{O}_2 \longrightarrow \text{bis(Triphenylmethyl) peroxide (18\%)}$$

Comparison of the competition experiments with naphthalenide ion with the triphenylmethyllithium-diphenylmethyl-halide reactions leads to the conclusion that diphenylmethyl halides do not oxidize triphenylmethyl carbanion by a single - electron transfer process that produces free trityl and benzhydryl radicals.

The question of whether trityl halides react with diphenylmethyllithium to produce radical intermediates was studied.

Reaction of diphenylmethyllithium and triphenylmethyl chloride was followed by quenching with oxygen and gave predominantly pentaphenylethane (60%), together with sym-tetraphenylethane (6%), bis(triphenylmethyl) peroxide (7%) and benzhydryl and trityl chlorides. These results are

in harmony with rapid establishment of a halogen - metal interconversion equilibrium, as shown in eq. 19.

$$(C_6H_5)_2\underset{\underset{H}{|}}{C}:^-Li^+ \quad + \quad (C_6H_5)_3C\text{-}Cl \rightleftharpoons (C_6H_5)_2CH\text{-}Cl \quad + \quad (C_6H_5)_3C:^-Li^+ \qquad (19)$$

This equilibrium lies well to the right as judged by the low yields of peroxide and sym-tetraphenylethane. If single-electron transfer oxidation of the primary reactants was occurring to any significant extent the yields of pentaphenylethane, sym-tetraphenylethane, and peroxide should be comparable not only in absolute amounts but also to the results from the naphthalenide ion competition experiments. The fact that they are not statistically equivalent leads to the conclusion that coupling of free radical intermediates is not the mechanism for formation of pentaphenylethane and sym-tetraphenylethane from diphenylmethyllithium and trityl chloride reaction. This conclusion finds experimental support in the work of Sommer[117], Sauer and Braig[47], and more conclusively in the work of Angres and Zieger (See section VII) who have shown that benzhydryllithium reacts with (-)-α-phenylethyl chloride or R (+)-α-phenylethyltrimethylammonium iodide with 100% inversion of configuration to give (-) 1,1,2-triphenylpropane and (+) 1,1,2-triphenylpropane.

Whether the reaction of diphenylmethyllithium with benzhydryl chloride involves a polar displacement mechanism or an electron transfer process could not be deduced from the 97.2% yield of sym-tetraphenylethane.

IV. COMPETITION EXPERIMENTS. REACTIONS OF LITHIUM NAPHTHALENIDE WITH EQUIMOLAR MIXTURES OF BENZYLIC CHLORIDES.

Earlier (section III) I described a competition experiment to show that the reaction of trityllithium and benzhydrylbromide did not produce free trityl and benzhydryl radicals, for if they were present they should couple in a random or statistical fashion. The reaction of one equivalent of lithium naphthalenide with one equivalent of an equimolar mixture of trityl chloride and benzhydryl chloride produced after discharge of the aromatic radical anion color and bubbling of oxygen through the system a mixture of bis (triphenylmethyl) peroxide (18%), pentaphenylethane (36%) and tetraphenylethane (32%). This is strong evidence for the formation and coupling of free radicals.

More evidence was obtained during titrations of one equivalent of an equimolar mixture of benzhydryl and benzyl chlorides with one equivalent of lithium naphthalenide to produce the expected statistical array of coupling products, namely 25% bibenzyl, 50% 1,1,2-triphenylethane and 25% sym - tetraphenylethane. This distribution of coupling products was independent of temperature. See Table 6 and Scheme 2. If coupling occurs by radical combination (see Scheme 2), the three ethanes should be formed in a ratio 1:2:1 which reflects only the concentrations of the two radicals formed.[125] This prediction which has received extensive experimental verification, derives from the fact that alpha coupling of radicals requires essentially no activation energy. If coupling occurs by displacement (see Scheme 3) no such statistical product distribution would be expected. In a wide variety of nucleophilic displacement reactions which vary in absolute rate constant over several powers of ten, the rate for displacement on benzyl exceeds that of benzhydryl by at

Table 6. **Relative yields of polyphenylethanes from reaction of lithium naphthalenide with an equimolar mixture of benzhydryl and benzyl chlorides.**

T°	$Ph_2CH-CHPh_2$ 1	Ph_2CH-CH_2Ph 2	$PhCH_2-CH_2Ph$ 3
Ambient	23%	49%	24%
Ambient	24%	49%	24%
-78°	24%	48%	26%

Scheme 2.

$$Naph^{\cdot-} + \begin{cases} Ph_2CH-Cl \\ PhCH_2-Cl \end{cases} \longrightarrow Ph_2CH^{\cdot} + PhCH_2^{\cdot} + Naph$$

$$2Ph_2CH^{\cdot} \xrightarrow{\text{combination}} Ph_2CH-CHPh_2$$

1

$$Ph_2CH^{\cdot} + PhCH_2^{\cdot} \xrightarrow{\text{combination}} Ph_2CH-CH_2Ph$$

2

$$2PhCH_2^{\cdot} \xrightarrow{\text{combination}} PhCH_2-CH_2Ph$$

3

least a factor of twenty. This consideration leads to the conclusion that a carbanion route is not operating during dimer formation in reactions of naphthalenide ion with benzylic halides, for if it were the yields of sym - tetraphenylethane should be considerably lower, while the yields of bibenzyl and 1,1,2-triphenylethane should be substantially

higher because of the lower steric hindrance to their formation.

Scheme 3.

$Ph_2CH:^-$ + $PhCH_2$-Cl ⟶ Ph_2CH-CH_2Ph 2

$Ph_2CH:^-$ + Ph_2CH-Cl ⟶ Ph_2CH-$CHPh_2$ 1

$PhCH_2:^-$ + $PhCH_2$-Cl ⟶ $PhCH_2$-CH_2Ph 3

$PhCH_2:^-$ + Ph_2CH-Cl ⟶ Ph_2CH-CH_2Ph 2

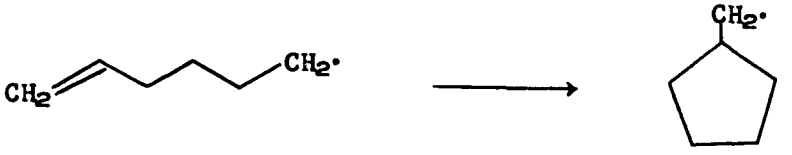
Direct experimental detection of a benzylic radical by electron spin resonance spectroscopy would provide the best physical evidence that radicals are formed from halides upon reaction with naphthalenide ion.

Recently, Shreiner and Zieger have accomplished the esr detection of the bis-(3,5-di-tert-butylphenylmethyl) radical from reaction of sodium naphthalenide with bis-(3,5-di-tertbutylphenylmethyl bromide) in an esr flow system, using mixing chamber experiments. Of special interest was the observation that the radical was unusually long-lived as determined by its detection in the bottom portion of a 6.0 cm long measuring cell.[196]

V. REACTIONS OF LITHIUM NAPHTHALENIDE WITH QUATERNARY AMMONIUM SALTS.

It was found that the reaction of lithium naphthalenide with aliphatic and aromatic trimethylammonium salts occurs selectively with elimination of trimethylamine. The salts listed in Table 7 undergo reductive cleavage with lithium naphthalenide in tetrahydrofuran. The carbon - nitrogen bond to the larger R group is cleaved preferentially to form radicals and trimethylamine.

Evidence for the formation of radicals is inferred from the reaction of 5-hexenyltrimethylammonium iodide, 5, to produce 5-hexenyl radicals which cyclize to cyclopentylmethyl radicals.[66,67] See eq. 20.



(20)

The cyclopentylmethyl radicals react subsequently with lithium naphthalenide to give cyclopentylmethyl carbanion, which undergoes protonation to produce methylcyclopentane in 4% yield. A complete explanation as to why formation of methylcyclopentane serves as evidence for the presence of 5-hexenyl radicals has been given by Garst and his coworkers for reaction of 5-hexenyl halides with sodium naphthalenide.[19]

Analysis of the results on benzhydryltrimethylammonium iodide, 1, to form sym - tetraphenylethane, also suggests that some of the sym-tetraphenylethane is formed by alpha coupling of two benzhydryl radicals (Path A).

(A) $(C_6H_5)_2\underset{H}{C}\cdot \longrightarrow (C_6H_5)_2\underset{H}{C}-\underset{H}{C}(C_6H_5)_2$

Table 7. Reactions of lithium naphthalenide with quaternary ammonium iodide salts in THF.[a]

$RN^+(CH_3)_3I^-$	N°	Reaction time minutes	% R-R	%R-H	%Recovered salt	$\%(CH_3)_3N$:[g]	$\%RN(CH_3)_2$
$(C_6H_5)_2CH$-	1	<5	57[b]	22[c]	22	81-85[b]	5
$(C_6H_5)CH_2$-	2	< 5	6[c]	72[c]	9	87[b]	8[b]
C_6H_5-	3	15	4[c]	39[c]	48	81[b]	10[c]
1-$C_{10}H_7$-[d]	4	90	0.2[c]	45[c]	44	80[b]	17[c]
$CH_2=CH(CH_2)_4$-	5	120		4[e] 35[f]	38	80[b]	....

a. One equivalent of naphthalenide ion per each equivalent of salt; dry salt is added to naphthalenide ion in one portion. b. Trimethylamine was distilled, derivatized with methyl iodide, and tetramethylammonium iodide was isolated. c. Quantitative gas chromatography. d. Lithium biphenylenide was used. e. Methylcyclopentane. f. 1-hexene. g. The values below were calculated according the amount of quaternary salts that reacted.

Radicals formed in the presence of an aromatic radical anion are expected to be reduced to carbanions faster than they can couple to dimer.[118a] Path B summarized in eq. 21, involves two sequential-one-electron reductions during which benzhydryl radical is reduced by a second equivalent of naphthalenide ion to form a diphenylmethyl carbanion which then displaces trimethyl amine from 1 yielding sym-tetraphenylethane.

$$(C_6H_5)_2CH\overset{+}{N}(CH_3)_3\ I^- \xrightarrow{Naph^{\cdot -}} (C_6H_5)_2CH\cdot \xrightarrow{Naph^{\cdot -}} (C_6H_5)_2CH:^- + (C_6H_5)_2CH\overset{+}{N}(CH_3)_3\ I^- \longrightarrow (C_6H_5)_2CH\text{-}CH(C_6H_5)_2 + :N(CH_3)_3 \qquad (21)$$

This reductive cleavage of a carbon - nitrogen bond by naphthalenide ion is analogous to the sodium in liquid ammonia fission of quaternary ammonium salts which has been studied systematically by Grovenstein.[118,119]

This reaction has some analogy to Emde reduction and the electrochemical degradation of aqueous solutions of quaternary ammonium salts.[120] However, the results differed substantially from those reported here, owing to the use of water as solvent (e.g., benzhydryltriethyl ammonium acetate was reduced to diphenylmethane).

The most surprising difference between our results with lithium naphthalenide and those reported earlier is that tetramethyl ammonium iodide did not react with lithium naphthalenide after 3 days at 25°. Sodium in liquid ammonia on the other hand readily cleaved tetramethylammonium bromide completely within 1.0 - 2.0 hours.[118b]

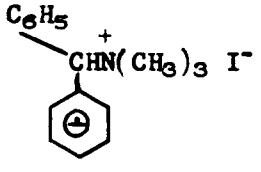
Whereas reductions with sodium in liquid ammonia can be complicated by the presence of strongly basic amide ions, aromatic radical anions are weakly basic and side reactions attributable to Sommelet-Hauser and Stevens

rearrangements are not encountered.

We have carried out Sommelet-Hauser and Stevens rearrangement studies on 1 and 2 using alkyllithium reagents. Use of tritylllithium or benzhydryllithium in THF on 1 and 2 gives yields of > 90% of displacement products, pentaphenylethane, sym - tetraphenylethane, unsym - tetraphenylethane, 1,1,2- triphenylethane. (For further discussion see section VII of results and discussion.)

Normally in reductions with naphthalenide ion one equivalent of naphthalene must be separated from the products. Although it is possible to use α-dimethylaminonaphthalene's radical anion as the reducing agent,[69] we have cleaved 1 to give sym - tetraphenylethane (88-100% yields) using a catalytic amount of naphthalene (1 g) by the portionwise addition of one equivalent of lithium to a suspension of 1 in THF.

The reductive cleavage of a carbon-nitrogen bond by naphthalene ion may form the same type of intermediate (e. g. 6 or 7) as is generated in the synthesis step of the radical anions chain mechanism[121] for substitution at tertiary carbon in p-nitrocumyl chloride and α,p-dinitrocumene by tertiary amine.[110] An alternative possibility is that naphthalenide ion transfers the electron directly into the valence shell of the nitrogen atom to form an unstable intermediate which eliminates the more stable radical and a tertiary amine.



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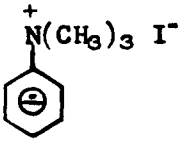

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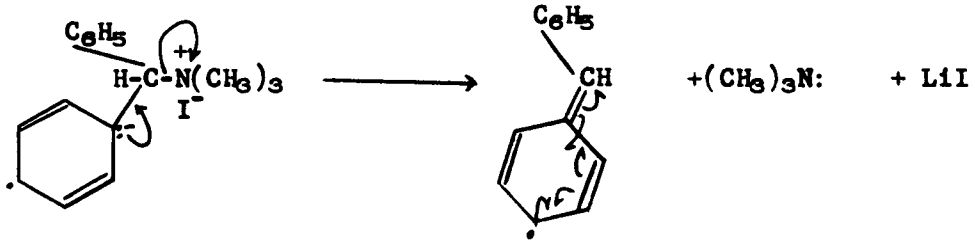
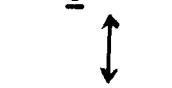
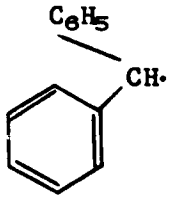
Intermediates 6 or 7 could eliminate tertiary amine as follows:



6 8





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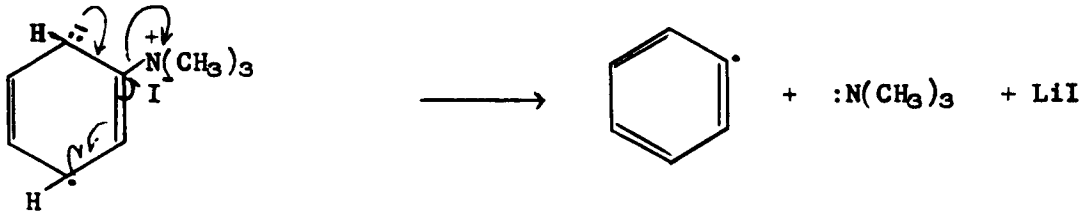
Intermediate 8 is nothing other than a resonance form of the benzhydryl radical 9. Similar elimination of amine from 7 may occur as follows:

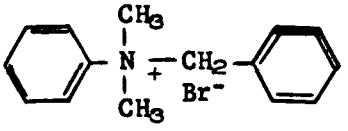


7 10

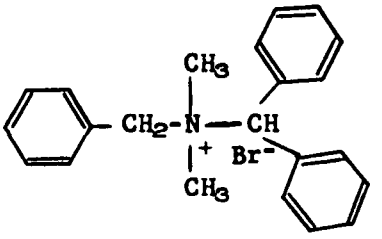
VI. COMPETITION EXPERIMENTS, INTRAMOLECULAR STUDIES INVOLVING LITHIUM NAPHTHALENIDE AND QUATERNARY AMMONIUM SALTS, MECHANISTIC IMPLICATIONS.

Competition experiments with N,N-dimethyl, R,R' - quaternary ammonium salts containing two different potential leaving groups were carried out. The purpose of these experiments was to show whether lithium naphthalenide is selective in its cleavage reactions.

We chose quaternary ammonium salts 1 and 2.



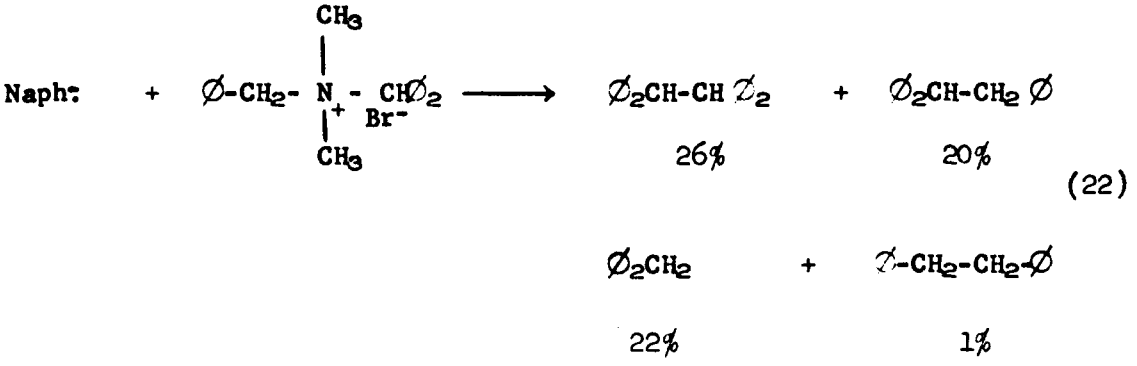
1



2

When one equivalent of 1 was added to one equivalent of lithium naphthalenide the salt cleaved exclusively (100%) to produce the more stable benzyl radical. The products obtained were bibenzyl (66%) and toluene (33%). This experiment suggests that an sp^2 C to N bond is stronger than an sp^3 C to N bond.

Use of salt 2 produced the following: (See eq. 22.)

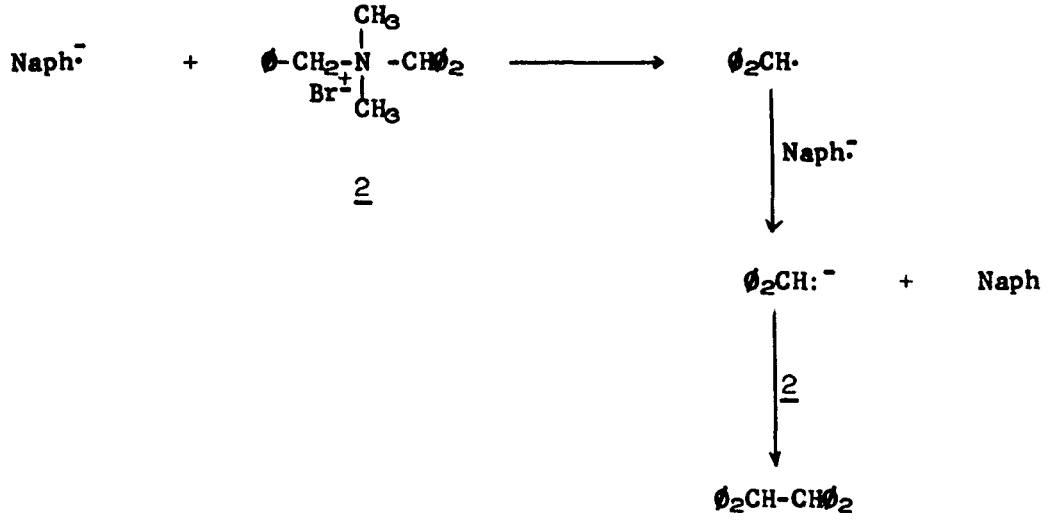


Naph: + $\emptyset$-CH_2- N(+)(Br$^-$)(CH_3)-$CH\emptyset_2$ ⟶ $\emptyset_2$CH-CH $\emptyset_2$ (26%) + $\emptyset_2$CH-CH_2 $\emptyset$ (20%)

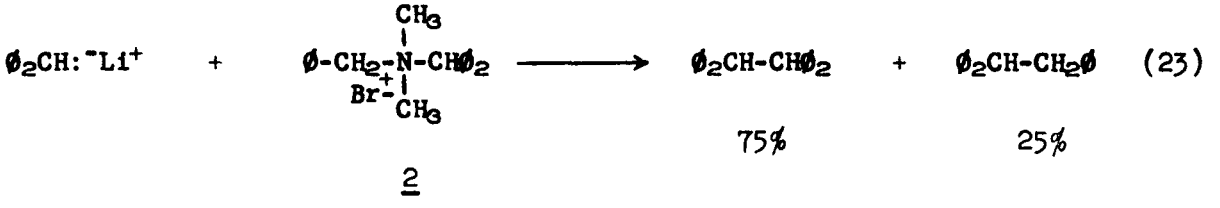
$\emptyset_2CH_2$ (22%) + $\emptyset$-CH_2-CH_2-$\emptyset$ (1%)

(22)

Again, this experiment suggests high selectivity in favor of cleavage of a benzhydryl group over a benzyl moiety. One may ask whether the coupling product ratio in eq. 22 can be explained in terms of a carbanion displacement mechanism as shown in the following scheme or by the alpha coupling of the benzylic radicals.



Displacement studies in which benzhydryl carbanion was permitted to attack the mixed salt 2, gave the results of eq. 23 wherein a 3:1 ratio of sym-tetraphenylethane to 1,1,2- triphenylethane was found.



In the scheme shown above, the benzhydryl radical undergoes reduction to diphenylmethyl carbanion which then attacks the less hindered α-carbon of the benzyl group in 2 rather than the α -carbon of the benzhydryl group in 2. If electron transfer was equal on each side of 2, and free benzhydryl

and benzyl radicals were produced, one should get the same statistical array of coupling products as those reported earlier in section IV.

Since the results of eq. 22 indicate that 1,1,2-triphenylethane is present in appreciable amount, (but not in a 1:3 ratio with sym - tetraphenylethane), it is hard to avoid an interpretation of a carbanionic pathway concomitantly competing with radical-radical coupling. This leads to the conclusion that dimer formation occurs by both pathways.

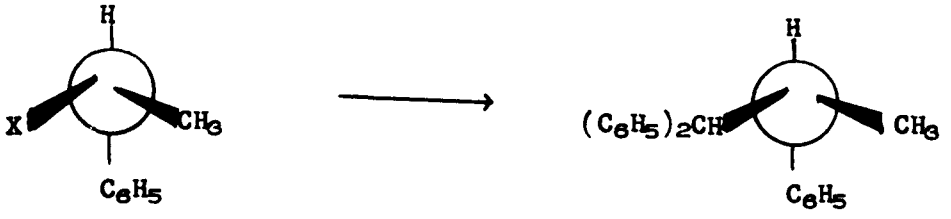
Similarly, if dimer formation in eq. 22 is occurring primarily by a carbanionic pathway, the proportion of sym - tetraphenylethane to 1,1,2- triphenylethane should be the same as in eq. 23. Since the results differ, it would appear that both pathways are operating. The best one can say from the quantitative data from eq. 22 is that 20% of 1,1,2- triphenylethane arises via displacement, or that 20% of benzhydryl radicals suffer conversion to carbanion. Another possible explanation is that salt 2 is cleaved 80% selectively at the benzhydryl moiety.

VII. STEREOCHEMISTRY OF THE REACTION OF BENZYLIC CARBANIONS WITH QUATERNARY AMMONIUM SALTS.

Since one of the pathways by which dimer formation can occur from reactions of lithium naphthalenide with quaternary ammonium salts is displacement of a tertiary amine by a carbanion, a study of the stereochemistry of this reaction seemed appropriate.

S (+) hydratropic acid, 98.2% optically pure 1a, was converted with diazomethane into S (+) methylhydratropate, 95% 1b. Ester 1b reacted with two moles of phenylmagnesium bromide to give 46.4% of S (-) 1,1,2- triphenyl-1-propanol, 1c. Alcohol 1c was reduced with sodium in liquid ammonia to give 50% of R (+) 1,1,2-triphenylpropane, 2. See Scheme 1.

Scheme 1



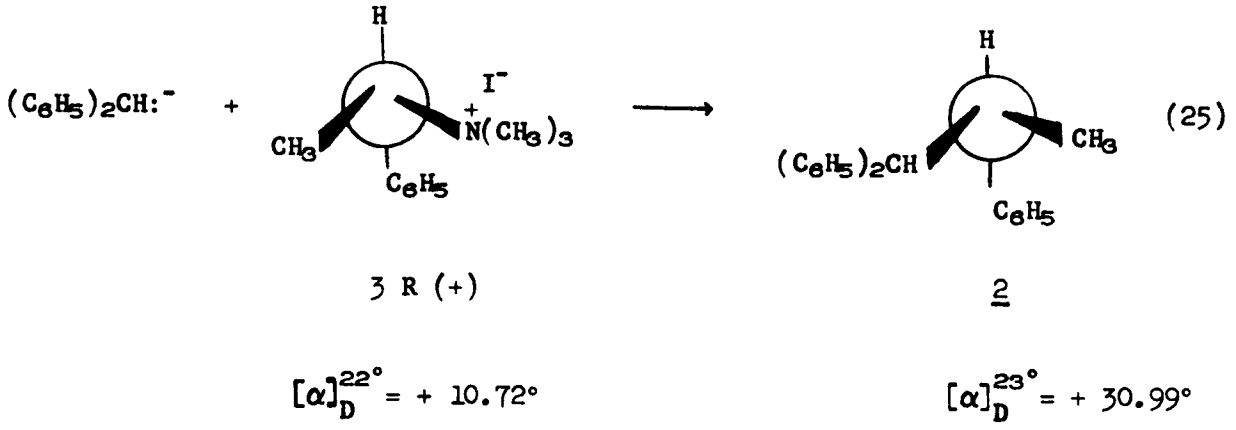
S 1 → R 2

$[\alpha]_D^{22°} = +30.15°$

X	
a =	- COOH
b =	- $COOCH_3$
c =	- $COH(C_6H_5)_2$

That no racemization occurs during the addition of phenylmagnesium bromide to ester 1b has already been demonstrated by Cram and coworkers.[122]

When benzhydryl lithium was reacted with R (+) α -phenylethyltrimethylammonium iodide of 97.5% minimum optical purity, 2 was obtained in 65% yield. See eq. 25.



(25)

3 R (+)

$[\alpha]_D^{22°} = +10.72°$

2

$[\alpha]_D^{23°} = +30.99°$

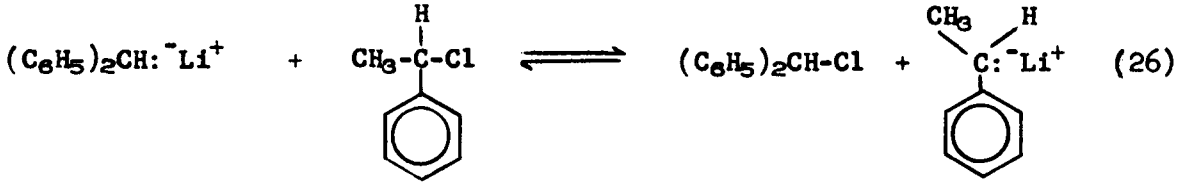
Since the sample of 2 obtained by displacement of trimethylamine from 3 has a slightly higher rotation than the authentic sample of scheme 1, its optical purity is higher indicating that the stereospecificity of reaction (25) is quite high, if not 100%. As the arrangements of groups in R (+) 3 is opposite to that in R (+) 2, reaction (25) occurs stereospecifically with inversion of configuration.[123]

The reactions of trityl-, benzhydryl-, and benzyllithiums with benzhydryl-, 4 and benzyltrimethylammonium iodides, 5, to give polyphenylethane coupling products in greater than 90% yields are summarized in

Table 8. No evidence for Sommelet-Hauser rearrangement products could be detected although such products are the predominant ones in reactions of 4 and 5 with alkyllithium reagents.[124]

Early work reported failure to convert 1b into 1c but described the reaction of (+) α -chloroethylbenzene, $[\alpha]_D$ = +19.5°, to 2, $[\alpha]_D$ = +6.67°, with benzhydrylsodium.[126] That the starting material and product were of low optical purity can be seen from the data on the later conversion of (-) α -chloroethylbenzene, 6 , (47% optically pure, $[\alpha]_D^{25°}$ = -59.3°, neat into (-) 2 ($[\alpha]_D^{24°}$ = -21.7°).[117]

The conclusion[117] that benzhydryllithium reacted with (-) 6 with inversion of configuration is correct, although the % stereospecificity using the rotation value from this work is 70%. No doubt benzhydryllithium reacts with 6 not only by displacement but also to establish a halogen metal interconversion[127] equilibrium forming α-lithioethylbenzene, 7 (eq. 26), which upon reversion to 6 suffers racemization.



6 7

As halogen-metal interconversion is a very fast process in tetrahydrofuran,[128] the coupling reaction must be comparable in speed. An alternate explanation involving electron transfer mechanisms to form redicals[129] would conflict with the general view proposed by Sauer and Braig[47] that organolithiums containing allylic or benzylic groups react with halides by S_N2 mechanisms while alkyllithiums react with halides to form products intelligible only

Table 8

Coupling Reactions of Charge-Delocalized Organolithium Reagents with Trimethylammonium Quaternary Salts

RLi reagent	$R'\overset{+}{N}(CH_3)_3\ I^-$ reactant	R-R' product	% yield[c]
$(C_6H_5)_3\ CLi$[a]	$(C_6H_5)_2\ CH$ - 4	$(C_6H_5)_3C\text{-}CH(C_6H_5)_2$	91
$(C_6H_5)_3\ CLi$[a]	$C_6H_5CH_2$ - 5	$(C_6H_5)_3\ C - CH_2C_6H_5$	93
$(C_6H_5)_2\ CHLi$[a]	$(C_6H_5)_2CH$ - 4	$(C_6H_5)_2\ CH-CH(C_6H_5)_2$	95
$(C_6H_5)_2\ CHLi$[a]	$C_6H_5CH_2$ - 5	$(C_6H_5)_2\ CH\text{-}CH_2C_6H_5$	92
$C_6H_5CH_2Li$[b]	$(C_6H_5)_2CH$ - 4	$(C_6H_5)_2CH - CH_2C_6H_5$	91
$C_6H_5CH_2Li$[b]	$C_6H_5CH_2$ - 5	$C_6H_5CH_2 - CH_2C_6H_5$	90

(a) Prepared by metalation of the hydrocarbon in THF with n-butyllithium.

(b) Prepared by cleavage of benzylmethylether with lithium metal.

(c) Isolated yields. Gas chromatographic analysis of mother liquor indicated additional amounts of material for all compounds except pentaphenylethane which cannot be gas chromatographed.

if radical intermediates were formed.

In the present study, halogen metal interconversion is not a serious possibility and if the coupling product of equation 25 is forming by an electron transfer process, then a geminate radical pair in a cage tight enough to prevent racemization is required. That radical intermediates form in reactions of charge-delocalized organolithiums with halides was shown recently[40] by the electron detachment oxidation of triphenylmethyl carbanion by triphenylmethyl halide which undergoes dissociative electron attachment.[130] Quaternary ammonium halide salts are known to oxidize potassium in liquid ammonia[119] or lithium naphthalenide in THF[131] by an electron transfer process to produce radical species of finite lifetime as judged by trapping products formed through intermolecular processes. If such pathways are being followed during the present coupling reactions, they do not produce radicals of sufficient lifetime to allow diffusion followed by reduction, coupling or disproportionation reactions. Since the quaternary ammonium salts of Table 8 are the same as those which formed radical intermediates upon treatment with lithium naphthalenide[131] (section V of Results and Discussion in this dissertation), the displacement of trimethylamine from salt by a charge delocalized organolithium occurs by a polar process without chemical evidence for an electron transfer component.[132]

Our results should be contrasted with those obtained during a study of the stereochemistry of free radical recombination reactions after thermal decomposition of SS (-) azobis - α - phenylethane to produce α -phenylethyl radicals.[133] The results showed that the principal products were derived from alpha coupling to produce meso and racemic 2,3-diphenylbutanes. Thus a substantial loss of stereochemistry occurs in the loose radical cages which are required for departing nitrogen in such systems.

One of the most important things ascertained from these displacement reactions is that the reactions proceed smoothly to give only one product. While reactions with halogen containing compounds may be complicated by side reactions like halogen-metal interconversion or the formation of cross coupling products, this is not the case with benzylic trimethyl ammonium salts. Therefore, these salts are useful for the high yield preparation of polyphenylethanes which possess the highest possible purity.

SUMMARY AND CONCLUSIONS

The reaction of lithium naphthalenide with benzylic halides and quaternary ammonium salts has been shown to produce benzylic radicals. When these are formed in the absence of naphthalenide ion they have been found to α - couple (Path A) to produce high yields of polyphenylethane dimers.

It has also been found that dimer formation can occur by a two step carbanion mechanism in the presence of excess naphthalenide ion (Path B). When naphthalenide ion is added slowly to the halide solution, the main pathway for dimer formation is α - coupling of two radicals (Path A).

It was found that by replacing chlorine or bromine with fluorine the reaction is much slower in harmony with recently published data.[14b]

The formation of radical intermediates during lithium naphthalenide reduction of quaternary ammonium salts is supported by the reaction of 5-hexenyltrimethylammonium iodide to produce 5-hexenyl-radicals which cyclize to methylcyclopentyl radicals to give methylcyclopentane among other products.

By the use of equimolar mixtures of benzylic halides which were titrated with one equivalent of lithium naphthalenide, it was found that the statistical distribution of coupled products is formed. The formation of a statistical array of coupling products is interpreted as strong evidence for the formation and coupling of free radicals.

Furthermore, it has been shown that although triphenylmethyl chloride (or bromide) oxidize trityllithium to produce two trityl radicals; that triphenylmethyl fluoride undergoes little or no reaction in tetrahydrofuran solvent.

One of the accomplishments of this research is the finding that the

reaction of benzhydryllithium with R (+) - α - phenylethyltrimethyl-ammonium iodide proceeds with 100% inversion of configuration to produce R (+) 1,1,2-triphenylpropane. That 100% inversion of configuration occurs was demonstrated by the stereospecific synthesis of R (+) 1,1,2-triphenylpropane starting from S (+) hydratropic acid.

Similarly, it has been shown that an N,N-dimethyl-N,N,-disubstituted ammonium salt having two different leaving groups where the radicals to be formed are of comparable energy, is cleaved with high selectivity. For example, a benzhydryl group is preferentially eliminated rather than a benzyl group.

Finally, one of the most significant conclusions from this work is that the mechanism of dimer formation in reactions of lithium naphthalenide with benzylic substrates can proceed by α-coupling of two radicals as well as by a carbanion mechanism depending on the mode of operation.

EXPERIMENTAL

REAGENTS

Naphthalene (Eastman Kodak Co., "White Label") was dried in a vacuum desiccator over anhydrous calcium chloride.

Triphenylmethane (Eastman Kodak Co., "White Label") was recrystallized once from hexane and dried in a vacuum desiccator over anhydrous calcium chloride.

Diphenylmethane (Matheson, Coleman and Bell) was vacuum distilled, bp 120°-121° at 9 mm and stored over Linde 4-A molecular sieves.

Amines (Aldrich Chemical Co.) were either distilled at atmospheric pressure or vacuum distilled prior to use.

Lithium wire, 1/16 of an inch in diameter, (Matheson, Coleman and Bell) was stored under light mineral oil and washed twice with THF prior to use.

Tetrahydrofuran (Baker Analyzed) was distilled from fresh lithium aluminum hydride or sodium hydride. Benzophenone and sodium metal were added to the distillate and the resulting ketyl was refluxed for 24 hours. The solvent was distilled from the ketyl before use.

Alkyl lithiums (Alfa Inorganics) were titrated prior to use as follows:[135]

To 20 ml of dry benzene, maintained under an argon atmosphere, was added by means of a syringe 5.0 ml of the solution of the alkyllithium. 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 alkyllithium. This colored solution is titrated with a 1.0 M solution of sec-butanol in dry benzene. The endpoint is indicated by the disappearance of the red-brown complex of

phenanthroline with alkyllithium and the formation of a pale straw-yellow solution. Replicate analyses were accomplished by adding a fresh aliquot of alkyllithium and of phenanthroline to the flask. Titrations were reproducible to within ± 0.01 ml by this technique.

Benzene (J. T. Baker) spectral grade was stored over sodium ribbon and distilled prior to use.

Deuterated solvents: All deuterated solvents were obtained from Stohler isotope chemicals.

D-Tartaric acid (Aldrich Chemical Co., "Gold Label") was dried in a vacuum desiccator prior to use.

Diazald (Aldrich Chemical Co.) of mp 61°-62° was the only precursor for diazomethane.

Argon (Matheson) was used without further purification.

Thionyl chloride (Eastman Kodak Co.) was distilled prior to use. bp 78°-80°.

N-Bromo succinimide (Eastman Kodak Co.) was recrystallized to constant melting point; mp 180°-182°.

Strychnine (Gallard-Schlesinger) was used as obtained without further purification; mp 284°-288°, $[\alpha]_D^{19°}$ = -139.0° (c=1% in chloroform).

2-Phenyl propionaldehyde (Aldrich Chemical Co.) was used as obtained without further purification. There is a 10% impurity which was identified as acetophenone.

Methyl Iodide (Aldrich Chemical Co.) was distilled prior to use. The fraction boiling at 41°-42° was used.

Benzyl Fluoride (Pierce Chemical Co.) was distilled prior to use. bp 140° at atmospheric pressure.

Fluorotriphenylmethane (Cationics Inc.) was used without further purification; mp 103°-104°.

Silver Fluoride (Cationics Inc.) was used without further purification. Formic Acid (90%) from Eastman Kodak Co. was used as obtained. Formaldehyde 37% solution (Baker Analyzed) was used as obtained without further purification.

INSTRUMENTS

Gas chromatography was performed with a Hewlett and Packard Model 5750 B instrument equipped with a flame ionization detector, thermal conductivity detector and disk integrator. Columns are 1/8 of an inch in diameter, and the length is six feet unless otherwise specified. Three different packings were used:

1. 10% SE 30 on Chrom W-DMCS treated.
2. 20% Polyphenylether (5 ring) on Chrom W-DMCS treated.
3. 10% Carbowax 20M on Chrom W DMCS treated.

Conditions for vapor phase chromatography will be given in the following abbreviated form:

(6.0 ft. column, 20% Polyester/Anakrom, 280°/215°, 130 ml/min)

This would indicate that the chromatographic column used was 6.0 ft. in length and was packed with 20% neopentyl glycol sebacate on Anakrom ABS (40/50 mesh). The head temperature of the VPC apparatus was 280°. The furnace was 215° and the helium flow rate was 130 ml/min.

NMR spectra were obtained on a Varian A-60-A and T-60 spectrometer. The former is 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 Model 137; Perkin-Elmer Model 267 or a Perkin-Elmer Model 21 prism infrared spectrophotometer. Spectra were calibrated by means of polystyrene calibration film. Mass spectra were

run on a Varian CH-7 mass spectrometer. All reactions involving alkyllithiums and radical anions were carried out under an argon atmosphere. All melting points and boiling ranges are uncorrected. Solvents were removed in vacuo with a rotary evaporator unless specified otherwise. All solid products were dried overnight in vacuo over calcium chloride before weights and melting points were taken. Analytical samples were dried to constant weight in the same manner.

The infrared spectra of liquid samples were obtained from the neat liquid on sodium chloride plates. Solid samples were prepared as pressed KBr disks. It was necessary to pulverize the mixture of KBr and sample for 5-10 minutes with a Wig-L-Bug amalgamator.[136]

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

QUANTITATIVE ANALYSIS OF REACTION MIXTURES

Vapor phase chromatography was employed as the main method of quantitative analysis unless otherwise specified. The example below (using an internal standard) will show how the calculations were made:

1. A known weight of reaction mixture was taken, 0.1000 g, from the 20.0000 g of the main reaction mixture. A known quantity of an internal standard, (i), 0.0100 g, was added to the reaction mixture aliquot. A gas chromatogram was taken and the area under the curve for i was determined as 150 units and the area for the unknown compound C was 100 units.
2. A response ratio mixture of C and i was composed: For example 0.2000 g of C and 0.2500 g of i. Then another gas chromatogram was run. The areas obtained were C = 400 units and i = 300 units.

2. A response ratio mixture of C and i was composed: For example 0.2000 g of C and 0.2500 g of i. Then another gas chromatogram was run. The areas obtained were C = 400 units and i = 300 units.

3. Solution

$$\text{Response ratio } \frac{C}{i} = \frac{\frac{\text{wt C}}{\text{wt i}}}{\frac{\text{area C}}{\text{area i}}} = \frac{\frac{0.20}{0.25}}{\frac{400}{300}} = 0.60 \left(\frac{C}{i}\right)$$

$$\text{wt of C in aliquot} = \frac{\text{area C}}{\text{area i}} \times \text{response ratio } \left(\frac{C}{i}\right) \times \text{wt of i}$$

$$= \frac{100}{150} \times 0.6000 \times 0.0100$$

$$= 0.0039 \text{ g}$$

From the following proportion the total weight of C in the aliquot was calculated.

$$\frac{0.0039 \text{ g}}{0.1000 \text{ g aliquot}} = \frac{\text{total weight C}}{20.0000 \text{ g reaction mixture}}$$

Total weight of C = 0.78 g

In certain cases NMR spectroscopy was used for quantitative analysis of reaction mixtures. This analysis was performed as outlined by Schaeffer[137].

BENZHYDRYL BROMIDE[138]

A mixture of diphenylmethane 36.96 g (0.22 mol), N-Bromosuccinimide 36.2 g (0.20 mol), benzoyl peroxide (0.48 g, 0.005 mol) and 110 ml of dry carbon tetrachloride was heated under reflux until all of the NBS had been consumed (negative external text with moistened starch-iodide paper), reaction time 45 minutes. The reaction mixture was cooled in an ice-bath and then filtered to remove succinimide. The carbon tetrachloride was removed in the rotary evaporator, and then 50 ml of petroleum ether was added and the solution cooled in an ice-bath. After cool-

ing for 5 hours a quantitative yield (49.4 g) of benzhydryl bromide was obtained, mp 40°-42°; (lit.[140] mp 41°).
nmr ($CDCl_3$) δ 6.3 (s, 1 H), 7.4 (m, 10 H). See nmr spectrum number 1.

BENZHYDRYL CHLORIDE

In a 500 ml round bottomed flask equipped with a reflux condenser and drying tube, were placed 60.0 g (0.21 mol) of benzhydrol and 150 ml of toluene. Then 40 g (0.37 mol) of thionyl chloride was added slowly until all of the benzhydrol went into solution. The mixture was refluxed for two and one-half hours or until no sulfur dioxide or hydrogen chloride evolved. The toluene was removed by simple distillation, and the benzhydryl chloride was distilled in vacuo to afford 37.8 g (90%) of a colorless liquid, bp 135° - 137° at 5 mm; mp 17°; (Lit.[141] mp 18°).
nmr ($CDCl_3$) δ 6.1 (s, 1 H), 7.3 (m, 10 H). See nmr spectrum number 2.

BENZHYDRYL FLUORIDE

Benzhydryl bromide (0.2 mol; 49.4 g) in 100 ml of dry acetonitrile was treated with 38 g (0.3 mol) of silver fluoride in 150 ml of acetonitrile as solvent. The reaction was exothermic and the termperature of the reaction mixture was kept between 20° and 40°. To get a smooth reaction, the solution of the fluoride was added to the benzhydryl bromide in six portions during a period of 20 minutes. After 2 hours, the silver bromide was filtered, the organic layer was washed four times with distilled water and dried over sodium sulfate. Removal of any excess acetonitrile was accomplished by simple distillation. The remaining organic material was distilled in vacuo to give 18.7 g (50%) of benzhydryl fluoride, bp 110° - 113° at 1 mm.

nmr ($CDCl_3$) δ 6.4 (d, 1 H; J_{H-F} = 48 Hz), 7.3 (m, 10 H). See nmr spectrum number 4.

Anal. Calcd. for $C_{13}H_{11}F$: C, 83.87; H, 5.91; F, 10.21

Found: C, 83.72; H, 6.02; F, 10.33.

TRITYL CHLORIDE:[142] A mixture of 250 g of triphenylmethanol and 80 ml of dry benzene was placed in a 1-l round bottomed flask provided with a reflux condenser and a calcium chloride drying tube at the top. The mixture was heated on a steam bath; when it was hot, 50 ml of freshly distilled acetyl chloride was added through the top of the condenser. Heating was continued while the mixture was shaken vigorously. In about 5 minutes all the solid triphenylcarbinol disappeared and a clear solution formed. In the course of 10 minutes, an additional 100 ml of acetyl chloride was added in 10 ml portions. The solution was refluxed for 30 minutes longer.

The solution was cooled by shaking the flask under running water, and during this operation 200 ml of petroleum ether was added through the top of the condenser. The trityl chloride crystallized as cubes. The mixture was cooled in an ice-bath for 1-2 hours, and the product filtered and washed with 100-150 ml of petroleum ether. The colorless solid, after drying in a vacuum desiccator over calcium chloride, weighed 200 g (73%) and had mp 110°-113° with slight previous softening; (Lit.[142] mp 110°-113°). An additional 30 g of colorless material was obtained by concentrating the filtrate to a volume of about 75 ml;total yield is 230 g (87%).

TRITYL BROMIDE

A mixture of triphenylmethane 48.8 g (0.02 mol), NBS 36.2 g (0.20 mol), benzoyl peroxide 0.48 g (0.002 mol) and 200 ml of dry carbon tetrachloride was heated under reflux until all of the NBS had been consumed (negative external test with moistened starch-iodide paper), reaction time 1 1/2 hours. The reaction mixture was cooled in an ice-bath and filtered to remove succinimide. The carbon tetrachloride was removed in the rotary evaporator and then 100 ml of petroleum ether was added and the solution was filtered. The crystals were washed with two 50 ml portions of petroleum ether and had mp 151°-153°. The compound was stored immediately in a desiccator to avoid hydrolysis. (Lit.[147] mp 150°-152°).

TRITYL LITHIUM[143]

To a solution of triphenylmethane, 4.88 g (0.02 mol) in 100 ml of dry THF maintained under argon at 0° was added to 0.021 mol of n-butyl lithium. The solution was allowed to stir for one hour before use.

DIPHENYLMETHYL LITHIUM

To a solution of diphenylmethane, 3.3 g (0.0196 mol) in 75 ml of dry THF maintained under argon at 0° was added 0.02 mol of n-butyl lithium. The solution was allowed to stir for 3 hours before use.

BENZYLLITHIUM[144]

Benzylmethyl ether, (13.3 g, 0.108 mol) was added dropwise to a rapidly stirred mixture of ethyl ether (250 ml) and lithium wire (5 g) which had been cut into small pieces and flattened out. The straw-colored mixture was stirred for 2 hours, after which a straw-colored

material settled, leaving a bright red solution of benzyl lithium which was removed from the solid and the unreacted lithium by means of argon pressure.

TRITYL RADICALS AND GOMBERG'S DIMER (1-DIPHENYLMETHYLENE-4-TRIPHENYLMETHYL -2,5-CYCLOHEXADIENE)

To 0.02 mole of trityl lithium in 100 ml of THF at 0°C, there was added dropwise 5.56 g (0.02 mol) of trityl chloride in 25 ml of THF over a period of 15 minutes. After addition of the last drop of chloride the red color of tritylllithium disappeared after which the yellow color of the trityl radical appeared. The presence of this radical was detected by two chemical methods:

a) Reaction with oxygen: After the tritylchloride had been completely added to the yellow reaction mixture, oxygen was bubbled through the solution for 10 minutes. A large precipitate appeared. This white precipitate was identified as Gomberg's bis-(triphenylmethyl) peroxide mp 183°-185°; (Lit.[145] mp 185°-186°).

b. Isomerization with Ethyllithium to p-Benzhydryltetraphenylmethane

The solution containing trityl radicals (0.04 mol) was cooled to -78°C. Then 0.02 mol of ethyl lithium was added and the reaction mixture immediately turned red. This was allowed to stir for one hour, and then quenched with 5 ml of distilled water. The reaction mixture was poured into 100 ml of saturated ammonium chloride and then thoroughly extracted with (2 x 100 ml) of ether. The organic layer was dried over calcium chloride and the ether removed in the rotary evaporator. The p-benzhydryltetraphenylmethane was washed with hexane and filtered.

mp 226°-227°; (Lit.[146] mp 227°).

nmr ($CDCl_3$) δ 5.46 (S, 1 H), 7.15 (m, 29 H).

PENTAPHENYLETHANE VIA HALIDES

a) To 0.0143 mol of tritylllithium in 100 ml of THF at 0°C, there was added dropwise 3.55 g (0.0143 mol) of benzhydryl bromide in 25 ml of THF. After complete addition of the bromide, the red color of the carbanion disappeared and the final color was yellow. The reaction mixture was poured into 100 ml of saturated ammonium chloride and extracted thoroughly (2 x 500 ml) with ether. Removal of the ether afforded a white solid, which was dissolved in the minimum amount of warm benzene and 100 ml of absolute ethyl alcohol was added leading to the crystallization of a white solid. Two crops of crystals were collected, the first crystallization gave 4.18 g of pentaphenylethane. Concentration of the mother liquor afforded 1.40 g more of pentaphenylethane. Total yield 5.58 g (95%) mp 157°-161°; (Lit.[147] mp 159°-166°).

nmr ($CDCl_3$) δ 7.1 (m, 25 H), 5.8 (S, 1 H). See nmr spectrum number 3.

Anal Calcd. for $C_{32}H_{26}$: C, 93.65; H, 6.35

Found: C 93.37; H 6.44

C 93.33; H 6.48

PENTAPHENYLETHANE VIA DIPHENYLMETHYL TOLUENE p-SULPHONATE

a) Preparation of Diphenylmethyl Toluene p-Sulphonate[148]

Powdered silver tosylate, 8.37 g (0.03 mol) was added to a solution of benzhydryl chloride, 6.06 g (0.03 mol) in dry ether (250 ml). The mixture was heated under reflux for 1 hours, then filtered and concentrated under reduced pressure to 50 ml. On cooling to 0°, diphenylmethyl tosylate 6.5 g (66%) separated, mp 60° (dec.), (Lit.[148] mp 63°) (dec.). Complete solvolysis in aqueous acetone and titration of the liberated acid showed 100% purity.

b) Pentaphenylethane - To a slurry of benzhydryl tosylate 6.48 g (0.02 mol) in dry ether at 0°C was added 0.02 mol of trityl lithium in THF. The trityl lithium lost its color instantly. Addition of 100 ml of water, extraction into 100ml of ether, drying over Na_2SO_4 and removal of the solvent, afforded 7.38 g (90%) of PPE, mp 155°-160°.

c) Using exactly the same procedure as outlined above, but substituting benzhydryl chloride, 2.91 g (0.014 mol) in place of the tosylate, there was obtained 5.31 g (91%) of pentaphenylethane.

UNSYMMETRICAL TETRAPHENYLETHANE VIA HALIDE:

To 0.02 mol of tritylllithium in 100 ml of THF at 0°, there was added 2.52 g (0.02 mol) of benzyl chloride in 50 ml of THF over a period of 15 minutes. After the last drop of the chloride was added, the red color of the carbanion was discharged. The mixture was poured into 100 ml of saturated ammonium chloride solution, and extracted thoroughly with ether (2 x 50 ml). Removal of the ether afforded 6.35 g (95%) of unsymmetrical tetraphenylethane, mp 143°-145°; (Lit[149] mp 144°). nmr ($CDCl_3$) δ 3.95 (S, 2H), 7.3 (m, 20 H). See nmr spectrum number 5.

SYMMETRICAL TETRAPHENYLETHANE VIA HALIDE

a) To 0.0305 mol of diphenylmethyl lithium in 100 ml of THF at 0°C, there was added 6.19 g (0.0305 mol) of benzhydryl chloride in 25 ml of THF over a period of 15 minutes. During the addition of the chloride, the reaction went through green and yellow colors. At the end, the reaction mixture was colorless. Work-up using the method described in the previous preparation gave 10.2 g (100%) of symmetrical tetraphenylethane, which was recrystallized from benzene, mp 218°-219°; (Lit[150] mp 214°-215°). nmr ($CDCl_3$) δ 4.8 (S, 2 H), 7.1 (m, 20H) see spectrum number 6.

b) Following the same procedure as above, but using benzhydryl bromide also afforded a 100% yield of symmetrical-tetraphenylethane.

ADDITION OF BENZYL FLUORIDE TO TRITYL LITHIUM

To 0.02 mol of trityl lithium in 100 ml of THF, there was added dropwise 2.20 g (0.02 mol) of benzyl fluoride in 15 ml of THF for a period of 15 minutes. After addition the reaction was stirred until the red color of the carbanion disappeared (4 3/4 hours). The reaction mixture was added to 100 ml of water, extracted twice with 50 ml portions of ether and dried over sodium sulfate. Removal of the solvent afforded 6.2 g (91%) of unsymmetrical tetraphenylethane, mp 141°-143°. nmr ($CDCl_3$) δ 3.95 (S, 2 H), 7.3 (m, 20 H).

ADDITION OF BENZHYDRYL FLUORIDE TO TRITYLLITHIUM

To 0.02 mol of tritylllithium in 100 ml of THF at 0°C, there was added in one portion 3.72 g (0.02 mol) of benzhydryl fluoride. The reaction was stirred at room temperature after the addition of the fluoride. After 6 days of stirring the red color of tritylllithium still persisted, therefore the mixture was quenched with 10 ml of distilled water, poured into 100 ml of saturated ammonium chloride and extracted into 100 ml of ether. Removal of the solvent afforded a yellow oil. Many attempted recrystallizations of this oil were unsuccessful. Nmr analysis showed it to be a mixture of triphenylmethane, benzhydryl fluoride and solvent related side products such as alcohols.

LITHIUM NAPHTHALENIDE

In a preflamed three-necked flask under an argon atmosphere were placed naphthalene 5.00 g (0.039 mol), dry THF (100 ml) and Li wire 0.270 g (0.039 mol) which had been flattened and cut into thin slices. The green color of the radical anion appeared within 15-30 seconds after lithium contacted the naphthalene solution. This solution was stirred for 1 1/2 hours before use.

ADDITION OF TRITYL CHLORIDE TO LITHIUM NAPHTHALENIDE

To 0.039 mol of lithium naphthalene in 100 ml of THF at 0°C, there was added dropwise 10.87 g (0.039 mol) of trityl chloride which was previously dissolved in 40 ml of THF. The reaction resembled an acid base titration since at the end of the addition the green color of the radical anion was discharged. The reaction mixture was stirred for an additional half hour.

The temperature of this mixture was brought down to -78°C and (0.039 mol) of ethyl lithium was added slowly over a period of 5 minutes and the temperature was not allowed to rise above -70°. After the first two drops were added the solution turned deep red immediately and was stirred for 1/2 hour and quenched with 50 ml of distilled water. The reaction mixture was poured into 100 ml of saturated ammonium chloride, extracted with 100 ml of ether, and the organic layer dried over sodium sulfate. Removal of the solvent afforded a crude white reaction mixture. The crude product was treated with 50 ml hexane, warmed in the steam bath and then filtered. The insoluble solid was dried and weighed giving 9.28 g (98%). The above solid was identified as p-benzhydryltetraphenylmethane, mp 226°-227°, (Lit[146] mp 227°). nmr ($CDCl_3$, 10% solution), δ 5.46 (S, 1 H), 7.15 (m, 29 H).

ADDITION OF 1 MOL OF TRITYL CHLORIDE TO 3 MOLES OF LITHIUM NAPHTHALENIDE

To 0.039 mol of lithium naphthalenide in 100 ml of THF at 0°C, there was added dropwise 3.62 g (0.013 mol) of trityl chloride previously dissolved in 50 ml of THF. The mixture was stirred for 1/2 hour and at the end of this period the color of the mixture was greenish-red. The reaction was quenched with distilled water and stirred for an additional 1/2 hour.

Quantitative gas chromatography of the mixture (6 ft. column, 10% SE 30/Chrom W; 250/150°, 100 ml/min) showed 3.17 g (100%) of triphenylmethane.

Experiments with trityl bromide showed no appreciable differences in the results.

ADDITION OF BENZHYDRYL CHLORIDE TO LITHIUM NAPHTHALENIDE

To 0.039 mol of lithium naphthalene in 100 ml of THF, there was added 7.89 g (0.0390 mol) of benzhydryl chloride in 25 ml of THF, dropwise over a period of 10 minutes. After the green color of the anion was discharged (3 minutes), the reaction mixture was treated with 100 ml of saturated ammonium chloride solution, and extracted twice (2 x 50 ml) with ether, and dried over sodium sulfate. The ether and THF were removed by simple distillation and the crude product was treated with 20 ml of benzene. The mixture was heated until all of the solid material dissolved, and then allowed to cool to room temperature, whereupon 4.40 g (78% based on reacted benzhydryl chloride) of symmetrical tetraphenylethane crystallized, mp 218-219°; (Lit[150] mp 214-215°), nmr ($CDCl_3$) δ 4.8 (S,2 H), 7.1 (m, 20H). See nmr spectrum number 6.

Quantitative gas chromatography of the remaining liquor (6 ft. column, 10% SE 30/Chrom W; 250/150°, 100 ml/min) showed naphthalene (98%) diphenylmethane 0.99 g (18%), and unreacted benzhydryl chloride 1.2 g (15%).

ADDITION OF BENZHYDRYL FLUORIDE TO LITHIUM NAPHTHALENIDE

To 0.039 mol of lithium naphthalenide in 100 ml of THF, there was added dropwise 5.58 g (0.03 mol) of benzhydryl fluoride in 50 ml of THF. After addition the reaction was stirred until the green color of the naphthalenide disappeared (about 1 1/2 hours). Addition of 100 ml of water, extraction with 100 ml of ether, followed by drying over sodium sulfate and removal of the solvent afforded a white solid which was recrystallized from benzene.

This solid was identified as sym-tetra-phenylethane. Yield 3.51 g (70%), mp 218°-219°. nmr ($CDCl_3$) δ 4.8 (S, 2 H), 7.1 (m, 20 H). Quantitative analysis by gas chromatography (6 ft. column, 10% SE 30/Chrom W, T°, 150°) gave 22% diphenylmethane.

ADDITION OF ONE MOLE OF BENZHYDRYL CHLORIDE TO THREE MOLES OF LITHIUM NAPHTHALENE

To 0.039 mol of lithium naphthalenide in 100 ml of THF, there was added dropwise 3.21 g (0.013 mol) of benzhydryl chloride dissolved in 50 ml of THF. The solution turned reddish-brown and stirred for 1/2 hour. The colored reaction mixture was quenched with 20 ml of distilled water upon which it turned colorless.

Quantitative gas chromatography for the high boiling components (6 ft. column, 10% SE 30 Chrom W, 300°/250°; 150 ml/min) gave 0.40 g (19%) of sym-tetraphenylethane.

Analysis of the low boiling components (6 ft column, 10% SE 30 Chrom W 100°/90°, 100 ml/min) gave 0.58 g (16%) of diphenylmethane.

ADDITION OF BENZYLCHLORIDE TO LITHIUM NAPHTHALENIDE

To 0.039 mol of lithium naphthalenide in 100 ml of THF, there was added dropwise (4.91 g, 0.039 mol) of benzyl chloride dissolved in 50 ml of THF. After the addition the solution turned colorless.

Analysis by gas chromatography of the high boiling components (6 ft. column, 10% SE 30/chrom W 250°/150°, 100 ml/min) gave (2.55 g, 72%) of bibenzyl and naphthalene (92% recovery).

Analysis of low boiling components (6 ft. column, 10% SE 30/chrom W 100°/90°, 100 ml/min) gave (0.58 g, 16%) of toluene.

ADDITION OF BENZYL FLUORIDE TO LITHIUM NAPHTHALENIDE

To 0.039 mol of lithium naphthalenide in 100 ml of THF, there was added dropwise 50 ml (0.039 mol) of a solution that contains 0.044 g/ml of

of benzyl fluoride. After complete addition of the fluoride, it took 30 minutes for complete decoloration of the green naphthalenide solution. Analysis of the reaction mixture by gas chromatography (6 ft. column, 10% SE 30/chrom W, T° 150°) showed bibenzyl 2.18 g (61%). Analysis on the same column but at a column temperature of 90° showed toluene (30%).

ADDITION OF ONE MOL OF BENZYL CHLORIDE TO THREE MOLES OF LITHIUM NAPHTHALENIDE

To 0.039 mol of lithium naphthalenide in 100 ml of THF, there was added dropwise 1.63 g (0.013 mol) of benzylchloride dissolved in 50 ml of THF. After the addition was completed, the solution turned colorless.

Quantitative gas chromatography of the high boiling components, (6 ft. column, 10% SE 30/chrom W, 250°/150°, 150 ml/min) gave 0.51 g (22%) of bibenzyl and naphthalene (93% recovery).

Analysis of low boiling components (6 ft. column, 10%SE 30/chrom W, 100°/90°, 100 ml/min) gave 0.84 g (70%) of toluene.

ADDITION OF AN EQUIMOLAR MIXTURE CONTAINING BENZHYDRYL CHLORIDE AND TRITYL CHLORIDE TO LITHIUM NAPHTHALENIDE

To 0.039 mol of lithium naphthalenide, a solution in 50 ml of THF containing 5.4 g (0.019 mol) of trityl chloride and 3.9 g (0.019 mol) of benzhydryl chloride was added dropwise until the color was discharged. About 30 ml (60%) was required until the color was discharged. Addition of water, extraction with ether (2 x 50 ml) drying over Na_2SO_4 and removal of the solvent gave a faintly yellow solid. Treatment of this solid with 50 ml of chloroform and suction filtration afforded 0.51 g (18%) of Gombergs bis (triphenylmethyl) peroxide, mp 183°-185°.

Evaporation of the chloroform and then recrystallization from benzene afforded 0.66 g (36%) of sym-tetraphenylethane. mp 218°-219°. Evaporation

to dryness again and subsequent recrystallization from benzene (minimum amount required to dissolve it) and alcohol (excess) afforded 1.44 g (32%) of pentaphenylethane; mp 156°-160°.

ADDITION OF TRITYL CHLORIDE TO DIPHENYLMETHYLLITHIUM WITHOUT ISOMERIZING WITH ETHYL LITHIUM

To a stirred solution of diphenylmethyllithium (0.0196 mol) at 0°C, was added 15 ml (60%) of a THF solution of trityl chloride (5.45 g, 25 ml) over a period of five minutes. After the 15 ml were added, the red color of the carbanion was discharged and the reaction mixture was yellowish in color.

Through this reaction mixture an excess of oxygen was bubbled to convert any trityl radical to its peroxide. Subsequent work-up was accomplished by pouring the reaction mixture into 100 ml of saturated ammonium chloride solution. After extraction with ether and removal of it, a white solid was isolated. Treatment with chloroform dissolved all possible hydrocarbons except bis (triphenylmethyl) peroxide, 0.20 g (6.6%) mp 183°-185°.

After separation of the peroxide, the chloroform was removed and on treatment with hot benzene of the white solid and then cooling, another white solid crystallized which was identified as sym-tetraphenylethane 0.20 g (6%); mp 218°-219°. Addition of alcohol to the mother liquor afforded 2.76 g (60%) of pentaphenylethane; mp 157°-161°.

ADDITION OF TRITYL CHLORIDE TO DIPHENYLMETHYL LITHIUM WITH ISOMERIZATION WITH ETHYLLITHIUM

To a stirred solution of diphenylmethyllithium (0.0196 mol) in 100 ml of THF at 0°C, was added 21 ml (84%) of a (5.45 g/25 ml) THF solution of trityl chloride over a period of 5 minutes. After discharge of the

red color, the mixture was yellowish in color. The reaction was cooled to -78° and equilibrated for 1/2 hour, then ethyllithium (0.0196 mol) was added in one portion and the mixture stirred for 1/2 hour. The reaction was quenched at -10°C with 10 ml of distilled water and allowed to warm-up to room temperature. Work-up of the mixture was accomplished by adding 100 ml of ammonium chloride solution, extracting with 100 ml of ether and drying over sodium sulfate. Removal of the ether afforded a white solid which was dissolved in hot benzene and cooled to room temperature to give tetraphenylethane 0.43 g (12%). The remaining solid was identified by nmr to be pentaphenylethane (87%).

ADDITION OF TRITYL FLUORIDE TO DIPHENYLMETHYLLITHIUM

To 0.02 mol of benzhydryllithium in 100 ml of THF at 0°C, there was added 5.24 g (0.02 mol) of tritylfluoride in one portion. The light red color of the mixture changed to dark cherry red indicating halogen-metal interconversion. After one hour of stirring the reaction mixture was poured jetwise into an excess of dry ice in ether. The mixture was treated with 50 ml of water and the layers were separated. The aqueous layer was treated with 5% HCl until acidic and extracted with ether (2 x 50 ml). After evaporation of the ether there were isolated 1.0 g (17%) of triphenylacetic acid; mp 277°-280°.

ADDITION OF LITHIUM NAPHTHALENIDE TO AN EQUIMOLAR MIXTURE OF BENZYL-CHLORIDE AND BENZHYDRYL CHLORIDE

To an equimolar mixture of 0.01 mol of benzyl chloride and 0.01 mol of benzhydryl chloride there was added dropwise 0.02 mol of lithium naphthalenide. The reaction mixture was stirred for an hour before it was quenched with 10 ml of distilled water. Extraction with 100 ml of ether, drying over sodium sulfate and then removal of the solvent

afforded a white reaction mixture. Treatment of this mixture with the minimum amount of hot benzene for dissolution and cooling to room temperature afforded 0.40 g (24%) of sym-tetraphenylethane.

The residue remaining after evaporation of the benzene mother liquor was analyzed by nmr and then by GC. This residue contained bibenzyl (24%) and 1,1,2-triphenylethane (49%).

The above experiment was carried out three times. Twice at ambient temperature and at -60° with no appreciable differences in the yields.

ADDITION OF TRITYL FLUORIDE TO TRITYL LITHIUM

To 0.02 mol of trityl lithium in 100 ml of THF at 0°C, there was added dropwise 5.24 g (0.02 mol) of trityl fluoride in 50 ml of THF over a period of 15 minutes.

After 48 hours of stirring the red color of the carbanion started to fade away at which point the reaction mixture was quenched with 10 ml of distilled water. The mixture was poured into 100 ml of brine, extracted three times with 50 ml portions of ether and dried over sodium sulfate. As the solvent was being removed a white precipitate appeared. This was filtered and was identified as p-benzhydryl tetraphenylethane yield 0.5 g (5%), mp 226°-227°. The remainder of the reaction mixture was identified as a mixture of triphenylmethane and trityl fluoride (95% recovery).

ADDITION OF BENZYL FLUORIDE TO BENZYLLITHIUM

To 0.01 mol of benzyllithium in 100 ml of ether at 0°C, there was added 1.10 g (0.01 mol) of benzylfluoride in one portion, and the reaction mixture stirred until complete decoloration of the carbanion occurred (about 20 minutes). The mixture was poured into 100 ml of saturated

ammonium chloride solution and then extracted into 100 ml of ether. After drying over magnesium sulfate and removal of the solvent there was obtained 1.73 g (95%) of an oil which solidified on standing; mp 50°-51°. This solid was identified as bibenzyl. nmr ($CDCl_3$) δ 2.9 (4 H, S), 7.1 (10 H, S).

ADDITION OF BENZHYDRYL FLUORIDE TO DIPHENYLMETHYLLITHIUM

To 0.02 mol of benzhydryllithium in 100 ml of THF at 0°C, there was added dropwise 3.72 g (0.02 mol) of benzhydrylfluoride dissolved in 50 ml of THF. The reaction mixture was stirred until complete decoloration occurred (one hour). The mixture was poured into 100 ml of ether. After drying over magnesium sulfate and removal of the solvent there was obtained 6.43 g (96%) of sym-tetraphenylethane, mp 218°-219°. nmr ($CDCl_3$) δ 4.8 (s, 2 H), 7.1 (m, 20 H).

ADDITION OF LITHIUM NAPHTHALENIDE TO TRITYL FLUORIDE

To 5.24 g of trityl fluoride (0.02 mol) in 50 ml of THF, there was added dropwise 0.02 mol of lithium naphthalenide. The mixture turned deep red in color and remained that way for 48 hours at which point it was quenched with 20 ml of distilled water.

Analysis by gas chromatography (6 ft. column, 10% SE 30/chrom W, 280/200°, 100 ml/min) gave naphthalene (92%), triphenylmethane (45%), and trityl fluoride (44%), plus 2% p-benzhydryltetraphenylmethane.

ADDITION OF LITHIUM NAPHTHALENIDE TO BENZYL FLUORIDE

To 4.29 g (0.039 mol) of benzyl fluoride in 50 ml of THF, there was added dropwise 0.039 mol of lithium naphthalenide. The mixture was stirred for an additional half an hour and then quenched with 20 ml of distilled water.

Analysis of the high boiling components by quantitative gas chromatography (6 ft. column, 10% SE 30/Chrom W, 250/150°, 100 ml/min) gave 2.51 g (71%) of bibenzyl.

Analysis of the low boiling components but at a column temperature of 90°, gave 0.72 g (30%) of toluene.

ADDITION OF LITHIUM NAPHTHALENIDE TO BENZHYDRYL FLUORIDE

To 5.24 g (0.02 mol) of benzhydryl fluoride in 50 ml of THF, there was added dropwise 0.02 mol of lithium naphthalenide. The mixture was stirred for an additional hour and then quenched with 20 ml of distilled water.

The reaction mixture was treated with 100 ml of saturated ammonium chloride solution, and extracted twice with 50 ml of ether. After drying over sodium sulfate and removal of the solvent there was obtained a crude white mixture. Dissolution with the minimum amount of hot benzene (30 ml), and then cooling to room temperature afforded 2.63 g (79%) of sym-tetraphenylethane.

Analysis by gas chromatography of the remaining organic material (6 ft. column, 10% SE 30/Chrom W, 250/150°, 100 ml/min) gave 15% of diphenylmethane.

CHEMICAL EVIDENCE FOR THE REDUCTION OF TRITYL RADICALS TO TRITYL LITHIUM BY LITHIUM NAPHTHALENIDE

To a solution containing 4.18 g (0.015 mol) of trityl chloride in 50 ml of THF, there was added dropwise 38 ml (0.015 mol) of 0.39M lithium naphthalenide. The solution was yellow in color after the addition. Dropwise addition of another 38 ml aliquot of lithium naphthalenide immediately turned the yellow solution into a bright red color.

After the addition was completed, the bright red solution was stirred for 45 minutes, and then added jetwise to an excess of dry

CO_2 in 100 ml of dry ether. The aqueous layer was extracted 3 times with 50 ml of ether. Addition of 5% HCl to the aqueous layer gave a white precipitate which was identified as triphenylacetic acid 4.14 g (96%). mp 277°-280°.

N,N DIMETHYL BENZHYDRYLAMINE

Benzhydrylamine 36.6 g (0.2 mol) was added with cooling to 51.0 g (1 mol) of 90% formic acid. Then 38 g (0.44 mol) of 37% formaldehyde solution was added and the mixture was heated on the steam bath under reflux for four hours until evolution of gas had ceased. About 17 ml (slightly more than 0.2 mol) of concentrated HCl was added and the formic acid and any excess formaldehyde were evaporated on the steam bath. After evaporation, the reaction mixture was treated (with cooling) with 25% aqueous sodium hydroxide until it was alkaline. A white emulsion appeared which was extracted three times with 50 ml of ether. The ether was removed by simple distillation and a white solid appeared upon cooling. The white solid was recrystallized from the minimum amount of ethanol to yield 30.0 g (71%), mp 69°-70°; (Lit[152] mp 72°-73°), nmr (CD_3CN) δ 2.2 (s, 6 H), 4.1 (s, 1 H), 7.4 (m, 10 H). See nmr spectrum number 8.

N-BENZHYDRYL-N,N,N-TRIMETHYLAMMONIUM IODIDE

N,N-dimethyl benzhydryl amine, 21.1 g (0.1 mol) was dissolved in 150 ml of dry benzene under an atmosphere of argon. Then 21.3 g (0.015 mol) of methyl iodide was added in one portion and the mixture refluxed for 3 hours. After cooling, the white precipitate was filtered and stored immediately in a dark container and dried under vacuum. The weight of this solid was 34.5 g (98%); mp 175° with decomposition; (Lit[153] mp 174°-175° with decomposition). nmr ($CDCl_3$) δ 3.5 (s, 9 H), 6.8 (s, 1 H),

7.4-8.3 (m, 10 H). See nmr spectrum number 9.

N,N-DIMETHYL BENZYLAMINE[151]

Benzyl amine 107 g (1 mol) was added with cooling to 255 g (5 moles) of 90% formic acid. Then 190 g (2.2 mol) of 37% formaldehyde solution was added, and the mixture heated on the steam bath under reflux for four hours or until evolution of gas had ceased. About 85 ml (slightly more than 1 mol) of concentrated HCl was added and the formic acid and any excess formaldehyde was evaporated. The reaction mixture was then made basic with 25% sodium hydroxide and steam distilled. The oil that separated was dried over potassium hydroxide and distilled over sodium to give 108 g (80%) of N,N-dimethyl benzyl amine, bp 176°-180°; (Lit[151] bp 176°-180°). nmr (CD_3CN) δ 2.2 (s, 6 H) 3.4 (s, 2 H), 7.3 (s, 5 H). see nmr spectrum number 10.

N-BENZYL-N,N,N-TRIMETHYLAMMONIUM IODIDE

To 60.0 g (0.44 mol) of N,N-dimethyl benzylamine dissolved in 200 ml of absolute ethyl alcohol were added portionwise and with cooling 85.2 g (0.6 mol) of methyl iodide with vigorous stirring. After all the methyl iodide was added the mixture was stirred for an additional fifteen minutes. Then about 300 ml of diethyl ether was added to fully precipitate the quaternary salt. The amount of benzyl-trimethyl ammonium iodide obtained was 110.8 g (90%); mp 178°-179° with decomposition; (Lit[154]mp 178°-179° with decomposition). nmr in D_2O δ 3.2 (s, 9 H), 4.6 (s, 2 H), 7.7 (m, 5 H). see nmr spectrum number 11.

N-PHENYL-N,N,N-TRIMETHYL AMMONIUM IODIDE

In a 500 ml round bottomed flask, 60.5 g (0.5 mol) of N,N-dimethyl aniline, 200 ml of dry benzene and 99.4 g (0.7 mol) of methyl iodide were

mixed and the reaction stirred for three hours. After three hours most of the iodide had precipitated. Upon filtering and washing with cold benzene, 125 g (95%) of phenyltrimethyl ammonium iodide were obtained. Decomposition point 216°; (Lit[155] 228° dec.) nmr (D_2O) δ 3.8 (s, 9 H), 7.7 (m, 5 H). See spectrum number 12.

N-1-NAPHTHYL-N,N,N-TRIMETHYLAMMONIUM IODIDE

N,N-dimethyl 1-naphthylamine 17.1 g (0.1 mol) was dissolved in 50 ml of dry acetonitrile under an atmosphere of argon. Then, 21.3 g (0.15 mol) of methyl iodide was added in one portion and the mixture was refluxed for two hours. After cooling and addition of 200 ml of ether, the precipitate was filtered and washed twice with 20 ml of diethyl ether. The solid 25 g (80%) was stored immediately in a dark container and maintained and dried under vacuum. mp 173°-175°, (Lit[156] not reported). nmr (D_2O, 10% or DMSO d_6) δ 4.1 (s, 9 H), 8.0 (m, 7 H). See nmr spectrum number 13.

N-METHYLHOMOPIPERIDINE

In a one liter round bottomed flask, 99.18 g (1 mol) of homopiperidine was added with cooling to 255 g (5 moles) of 90% formic acid. Then 190 g (2.2 moles) of 35% formaldehyde was added and the mixture was heated under reflux over night. About 85 ml (slightly more than one mol) of concentrated HCl was added and the formic acid and any excess formaldehyde were distilled. The reaction mixture was made basic with 25% NaOH. The brown oil which separated was dried over KOH. The amine was distilled over sodium to give 91 g (80%) of N-methyl homopiperidine as a clear liquid, bp 140°-141°; (Lit[157] bp 139°-141° at atmospheric pressure $n_D^{23°}$=1.4490). nmr ($CD_3C{\equiv}N$) δ 1.6 (broad singlet, 8 H), 2.3 (s, 3 H), 3.6 (broad singlet, 4 H). See nmr spectrum number 14.

N,N-DIMETHYLHOMOPIPERIDINIUM IODIDE

In a one-liter round bottomed flask was placed 56.6 g (0.5 mol) of N-methylhomopiperidine followed by 300 ml of absolute ethyl alcohol. Then 85.2 g (0.6 mol) of methyl iodide was added slowly and with cooling for a period of fifteen minutes and the reaction was stirred for an additional half hour. Then four hundred ml of diethyl ether was added whereupon complete precipitation of the salt occurred. After filtering and drying, 120 g (95%) of quaternary salt were obtained, mp 270°; (Lit[158] mp 265°). nmr (D_2O) δ 1.8 (broad singlet, 8 H), 3.2 (s, 6 H), 3.5 (m, 4 H). See nmr spectrum number 15.

N,N-DIMETHYL-5-HEXENYLAMINE

In a one hundred ml round bottomed flask was placed 25.5 g (0.1 mol) of N,N-dimethylhomopiperidinium iodide, followed by 50 ml of diethyl ether. The slurry was cooled to 0°C and then (0.1 mol) of n-BuLi in hexane was added and the reaction allowed to warm-up to room temperature.

The reaction was stirred for forty eight hours and quenched carefully with 10 ml of distilled water; 50 ml of ether was added and the layers separated. The aqueous layer was extracted (2 x 30 ml) with ether and the combined ether extracts dried over KOH. Removal of ether by simple distillation at atmospheric pressure was followed by distillation of the amine and afforded 7.6 g (60%) of N,N dimethyl 5-hexenyl amine bp 141°-143°; (Lit[157] bp 142°-144°). nmr ($CD_3C{\equiv}N$) δ 1.4 (m, 4 H), 2.2 (m, 10 H), 4.8-6.2 (m, 3 H). ir 3080 cm^{-1} (medium, terminal olefin). 900 cm^{-1} (monosubstituted). See spectrum nmr number 16.

N,N,N-TRIMETHYL-5- HEXENYL AMMONIUM IODIDE

To 7.0 g (0.055 mol) of N,N-dimethyl 5-hexenylamine in 30 ml of benzene, was added 8.52 g (0.06 mol) of methyl iodide and the reaction

was stirred for one hour. The globules that appeared sank and were taken up in chloroform. To the chloroform solution 100 ml of ether was added and the solution was chilled to 0°. The crystals that formed were filtered and washed with ether. Yield 13.2 g (90%), mp 125°-128°. nmr ($CDCl_3$) δ 1.8 (m, 4 H), 3.5 (m, 13 H), 4.8-6.1 (m, 3 H). See nmr spectrum number 17.

N-BENZYL-N,N-DIMETHYL-N-PHENYLAMMONIUM BROMIDE

In a 500 ml round bottomed flask were placed 100 ml of nitromethane, 34.2 g (0.2 mol) of benzyl bromide and 24.2 g (0.2 mol) of freshly distilled N,N dimethyl aniline. The reaction mixture was stirred for three hours after which 250 ml of diethylether was added to precipitate the ammonium salt. The white solid was collected by suction filtration and washed with two 50 ml portions of ether. The solid was dried in a vacuum desiccator for 24 hours. Yield 58.3 g (100%); mp 144°-146°. nmr (D_2O) δ 3.8 (6 H, s), 5,2 (2 H, s), 7.4 (5 H, m), 7.8 (5 H, s). See nmr spectrum number 18.

N-BENZHYDRYL-N-BENZYL-N,N-DIMETHYLAMMONIUM BROMIDE

In a 500 ml round bottomed flask, was placed 50 ml of nitromethane, 49.4 g (0.2 mol) of benzhydryl bromide and 27.0 g (0.2 mol) of N,N-dimethylbenzyl amine. The mixture was stirred for two hours and 100 ml of diethylether was added to precipitate the salt. After adding the ether a semi-solid appeared which was cooled until it solidified completely. The white solid was recrystallized from acetone, mp 127°-130°, (Lit[159] 125°). Yield 76.4 g (100%).
nmr ($CDCl_3$) δ 3.25 (6 H, s), 5.0 (2 H, s), 8.0 (16 H, m). See nmr spectrum number 19.

N-METHYL-1,2,3,4-TETRAHYDROISOQUINOLINE

To 26.6 g (0.2 mol) of 1,2,3,4-tetrahydroisoquinoline was added with cooling 26 g (0.5 mol) of 90% formic acid. Then 19 g (0.22 mol) of 35% formaldehyde solution was added, and the mixture was heated on the steam bath overnight. About 18 ml (slightly more than 0.2 mol) of concentrated HCl was added and the formic acid and any excess formaldehyde was evaporated. After evaporation the reaction mixture was treated (with cooling) with 25% aqueous sodium hydroxide. The aqueous layer was extracted with (3 x 15 ml) of ether and the ether extracts dried over KOH. Removal of the ether by simple distillation afforded 23.50 g (80%) of the amine; bp 98°-100° at 12mm.

nmr (CD_3CN), δ 2.2 (s, 3 H), 2.5 (t, 2 H), 2.8 (t, 2 H), 3.4 (s, 2 H), 7.1 (m, 4 H). See nmr spectrum number 20.

N,N-DIMETHYL-1,2,3,4-TETRAHYDROISOQUINOLINIUM IODIDE

To 62.8 g (0.40 mol) of N-methyl 1,2,3,4-tetrahydroisoquinoline dissolved in 200 ml of absolute ethyl alcohol was added portionwise with cooling and vigorous stirring 85.2 g (0.6 mol) of methyl iodide. After all the methyl iodide was added the mixture was stirred for an additional fifteen minutes: About 300 ml of diethyl ether was added to fully precipitate the quaternary salt; the yield was 113 g (95%), mp 187°-188°.

nmr (DMSO, 10%), δ 3.4 (m, 8 H), 4.0 (t, 2 H), 4.9 (s, 2 H), 7.5 (m, 4 H). See nmr spectrum number 21.

N,N-DIMETHYL-1,2,3,4-TETRAHYDROQUINOLINIUM IODIDE

A mixture of 26.6 g (0.2 mol) of 1,2,3,4-tetrahydroquinoline 33.6 g (0.4 mol) of sodium bicarbonate, 56.8 g (0.4 mol) of methyl iodide and 200 ml of methanol were heated under reflux with vigorous stirring for

75 hours. After 24 and 48 hours additional portions of methyl iodide were added until a total of approximately 42.6 g (0.3 mole) of methyl iodide had been used. The reaction mixture was then evaporated to dryness under reduced pressure. The residual solid was extracted three times with 150 ml portions of boiling chloroform. The combined extracts were cooled, filtered and evaporated to dryness. The residual crude methiodide was recrystallized once from a mixture of acetone and pentane or dissolved in chloroform and then precipitated with ether;
Yield 52.0 g (90% of theory) mp 182°-184°; (Lit[160] mp 174°).
nmr ($CDCl_3$) δ 2.4 (m, 2 H), 3.1 (t, 2 H), 3.6 (s, 6 H), 4.0 (t, 2 H), 7.8 (m, 4 H). See nmr spectrum number 22.

N,N-DIMETHYLINDOLINIUM IODIDE

A mixture of 35.75 g (0.3 mol) of indoline, 50.4 g (0.6 mol) of sodium bicarbonate 85.20 g (0.6 mol) of methyl iodide and 300 ml of methanol were heated under reflux with vigorous stirring for 75 hours. After 24 to 48 hours additional portions of methyl iodide were added until a total of approximately 106.5 g (0.75 mol) of methyl iodide had been used. The reaction mixture was then evaporated to dryness under reduced pressure. The residual solid was extracted three times with 150 ml portions of boiling chloroform. The combined extracts were cooled, filtered and evaporated to dryness. The residual crude methiodide was recrystallized once from a mixture of acetone-pentane. Yield 70 g (85%), mp 200°-202°; (Lit[161] mp 196°-197°).
nmr (D_2O) δ 3.6 (m, 8 H), 4.3 (t, 2 H), 7.7 (m, 4 H). See nmr spectrum number 23.

ADDITION OF N-BENZHYDRYL-N,N,N-TRIMETHYL AMMONIUM IODIDE TO LITHIUM NAPHTHALENIDE

To 0.039 mol of lithium naphthalenide in 100 ml of THF at 0°C, was added as a slurry in THF 13.76 g (0.039 mol) of N-benzhydryl-N,N,N-trimethyl-ammonium iodide. The green color of the radical anion disappeared almost instantaneously. The reaction mixture was stirred for an additional 15 minutes and then filtered, to give 2.6 g (22%) of unreacted N-benzhydryl-N,N,N- trimethylammonium iodide, mp 175° with decomposition.

The reaction mixture was poured into a saturated sodium chloride solution to which 50 ml of ether was added. The organic layer was extracted with 5% HCl. Upon removal of the ether and THF by simple distillation, a white solid appeared, which was a mixture of naphthalene, sym-tetraphenylethane and diphenylmethane. The above solid was treated with 30 ml of benzene and then heated until the entire product went into solution. Upon cooling 3.77 g (57%) of sym-tetraphenylethane separated mp 218°-219°.

The remainder of the mixture was analyzed by gas chromatography (6 ft. column, 10% SE 30/Chrom W, 250°/150°, 100 ml/min) to give 1.44 g (22%) of diphenylmethane and naphthalene (95%) recovery. There was also N,N dimethylbenzhydryl amine (5%), due to methyl cleavage.

ADDITION OF N-BENZHYDRYL-N,N,N-TRIMETHYLAMMONIUM IODIDE TO LITHIUM NAPTHTHALENIDE WITH DISTILLATION OF THE TRIMETHYLAMINE

The same procedure as outlined above was followed, except that a distillation apparatus was attached to the reaction flask. Methyl iodide 7.1 g (0.05 mol) was placed in the receiving flask which was cooled to -5°C.

After all of the quaternary salt was added, the trimethylamine and THF were distilled from the reaction mixture. The trimethylamine reacted immediately with methyl iodide, and after complete reaction there

was isolated (0.026 mol) 85% based on cleaved salt, of tetramethylammonium iodide, decomposition point > 300°.

ADDITION OF N-BENZYL-N,N,N-TRIMETHYLAMMONIUM IODIDE TO LITHIUM NAPHTHALENIDE

To 0.039 mol of lithium naphthalenide in 100 ml of THF, was added as a slurry 10.80 g (0.039 mol) of N-benzyl-N,N,N-trimethylammonium iodide in THF. The reaction mixture turned colorless in fifteen minutes, and it was stirred for an additional fifteen minutes. The mixture was filtered to remove unreacted N-benzyl-N,N,N-trimethylammonium iodide, 1.0 g (9%). The filtrate was first analyzed for high boiling components (6 ft. column, 10% SE 30/Chrom W, 250°/150°, 100 ml/min) and gave bibenzyl 0.21 g (6%).

Analysis of the low boiling components on the same column (column T°, 85°) gave toluene 2.5 g (72%) and N,N dimethylbenzyl amine (major) plus other minor amine products in a total yield of 8%.

An experiment in which the trimethylamine was distilled and derivatized with methyl iodide afforded (0.03 mol 87%, based on cleaved salt) of tetramethylammonium iodide.

ADDITION OF N-PHENYL-N,N,N-TRIMETHYLAMMONIUM IODIDE TO LITHIUM NAPHTHALENIDE

To 0.039 mol of lithium naphthalenide in 100 ml of THF at 0°C, was added 10.25 g (0.039 mol) of N-phenyl-N,N,N-trimethylammonium iodide. The reaction mixture turned dark brown and it took about 90 minutes for complete decoloration. It was stirred for an additional 30 minutes and then filtered to remove unreacted N-phenyl-N,N,N-trimethylammonium iodide 4.92 g (48%).

The filtrate was analyzed by gas chromatography for the high boiling components first (6 ft. column, 10% SE 30/Chrom W, 50°/150°, 100 ml/min) to give biphenyl 0.12 g (4%).

Analysis of the low boiling components on the same column (column T°-40°) gave benzene 1.17 g (39%).

The reaction mixture was extracted with 5% HCl (2 x 10 ml) and the amine was regenerated using 5% NaOH. The amine was extracted with ether (15 ml). The ether layer was dried over potassium hydroxide and was removed by simple distillation. The amine so obtained weighed 0.184 g (8%) and was identical in all respects to an authentic sample of N,N-dimethyl aniline.

nmr (C_6D_6), δ 2.6 (s, 6 H), 6.9 (m, 5 H).

Experiments in which the trimethyl amine was distilled and derivatized with methyl iodide afforded 0.019 mol (81% based on reacted salt) of tetramethylammonium iodide.

ADDITION OF N-1-NAPHTHYL-N,N,N-TRIMETHYLAMMONIUMIODIDE TO LITHIUM BIPHENYLENIDE

To 0.01 mol of lithium biphenylenide (prepared in the same way as lithium naphthalenide) in 50 ml of THF at 0°C, was added 3.13 g (0.01 mol) of N-1-naphthyl-N,N,N-trimethylammonium iodide.

The mixture turned dark brown and in 90 minutes it became colorless. It was filtered to remove unreacted N-1-naphthyl-N,N,N-trimethylammonium iodide 1.40 g (44%).

The filtrate was analyzed by gas chromatography (6 ft. column, 10% SE 30/Chrom W, 250°/150°, 100 ml/min) to give naphthalene 0.57 g (45%), N,N-dimethyl-1-naphthylamine 0.29 g (17%) and 1,1 binaphthyl 0.025 g (0.2%).

Experiments in which the trimethylamine was distilled and derivatized

with methyl iodide afforded 0.004 mol (80% based on reacted salt) of tetramethylammonium iodide.

ADDITION OF N,N,N-TRIMETHYL-5-HEXENYLAMMONIUM IODIDE TO LITHIUM NAPHTHALENIDE

To 0.02 mol of lithium naphthalenide in 50 ml of THF, was added 5.38 g (0.02 mol) of N,N,N-trimethyl-5-hexenylammonium iodide and the mixture stirred until decoloration occured (2 hours). The reaction mixture was filtered to give 2.06 g (38%) of unreacted quaternary salt.

Analysis by gas chromatography (20 ft. column, 20% Polyphenyl ether/ Chrom W, 60°/60°, 100 ml/min) afforded methylcyclopentane (0.067 g, 4%) and 1-hexene 0.58 g (35%).

Experiments in which the trimethylamine was distilled and derivatized with methyl iodide afforded 1.98 g (80%, based on reacted salt) of tetramethylammonium iodide.

ADDITION OF N-BENZYL-N,N-DIMETHYL-N-PHENYLAMMONIUM BROMIDE TO LITHIUM NAPHTHALENIDE

To a solution of 0.039 mol of lithium naphthalenide in 100 ml of THF, was added as a powder, 11.38 g (0.039 mol) of N-benzyl-N,N-dimethyl-N-phenylammonium bromide and the reaction stirred until complete decoloration of the naphthalenide occurred (15 minutes). The reaction mixture was poured into 50 ml of water and extracted with (2 x 50 ml) of ether. The organic layer was extracted thoroughly with 10% HCl and washed with 5% KOH.

The aqueous layer was treated with 10%KOH and the amine that formed was extracted into benzene and derivatized with methyl iodide to give 5.52 g (53%) of N-Phenyl-N,N,N-trimethylammonium iodide.

The ether layer was analyzed by quantitative gas chromatography

(6 ft. column, 10% SE 30/Chrom W, 250°/150°, 100 ml/min) to give bibenzyl 1.20 g (34%). Analysis on the same column, but at a column temperature of 70° gave toluene 0.65 g (18%). No biphenyl was detected in this reaction. The amount of recovered starting material was 5.57 g (48%).

ADDITION OF N-BENZHYDRYL N-BENZYL N,N-DIMETHYLAMMONIUM BROMIDE TO LITHIUM NAPHTHALENIDE

To 0.02 mol of lithium naphthalenide in 100 ml of THF there was added 7.64 g (0.02 mol) of N-benzhydryl-N-benzyl-N,N-dimethylammonium bromide and the reaction stirred until complete decoloration of the anion occurred (30 minutes). The reaction was stirred for an additional hour and quenched with 50 ml of distilled water. The mixture was treated with 200 ml of ether and extracted with 10% HCl until all of the basic material had been removed.

Analysis by gas chromatography of the ether layer (6 ft. column 10% SE 30/Chrom W, 280°/250°, 100ml/min) gave 1.05 g (20%) of 1,1,2-triphenylethane, and 0.86 g (26%) of sym-tetraphenylethane which was also isolated. Analysis of the low boiling components (6 ft. column, 10% SE 30/Chrom W, 250°/150°, 100 ml/min) gave 22% diphenylmethane and 1% bibenzyl.

Upon work-up of the amine layer and then analysis of the amines by nmr spectroscopy there was obtained 52% of N,N-dimethylbenzyl amine, and 14% of N,N-dimethylbenzhydrylamine. The above amines were derivatized with methyl iodide and separated on the basis of their solubility in chloroform. The N-benzhydryl-N,N,N-trimethylammonium iodide was very soluble in $CHCl_3$, while the N-benzyl-N,N,N-trimethylammonium iodide was only sparingly soluble in chloroform.

ADDITION OF N-BENZHYDRYL-N-BENZYL-N,N-DIMETHYLAMMONIUM BROMIDE TO DIPHENYLMETHYLLITHIUM

To (0.015 mol) of diphenylmethyllithium there was added 5.73 g (0.015 mol) of N-benzhydryl-N-benzyl-N,N-dimethylammonium bromide and the reaction stirred until decoloration of the carbanion had occurred (5 minutes). The reaction mixture was poured into 100 ml of water and extracted with 100 ml of diethylether. The ether was extracted with 10% HCl until all of the basic material had been transferred to the aqueous phase. The ether layer was dried over magnesium sulfate, solvent was removed in the rotary evaporator and recrystallization from benzene gave 3.50 g (75%) of sym-tetraphenylethane. The benzene layer was distilled and the residual oil was chromatographed over a short column of alumina to afford 0.90 g (25%) of 1,1,1-triphenylethane. mp 50°-51°C.

After work-up of the amine layer the following amounts of amines were found: N,N-dimethylbenzylamine 1.41 g (75%) and N,N-dimethylbenzhydrylamine 0.73 g (25%). The above amines were derivatized with methyl iodide and separated on the basis of their solubility in chloroform. The N-benzhydryl-N,N,N-trimethylammonium iodide was very soluble in $CHCl_3$, while the N-benzyl-N,N,N-trimethylammonium iodide was only sparingly soluble in chloroform.

RESOLUTION OF d, l- α- PHENYLETHYLAMINE

a. R (+) - α - phenylethylamine.[162] A solution of 100 g (0.75 mol) of l-malic acid in 500 ml of distilled water was mixed with 120 g (1 mol) of dl - α - phenylethylamine. The resulting solution was heated for 15 minutes on the steam bath, filtered into a 1 liter beaker and allowed to cool slowly. After 24 hours, the crude d - α - phenylethylamine - l - malate which crystallized was collected by suction filtration and

washed on the filter with 25 ml of ice water. The filtrate and washings were evaporated on a steam bath to a volume about two-thirds the original filtrate, and a second crop of crystals was obtained on cooling. By repeating the process, it was possible to obtain a third and usually a fourth crop, after which the mother liquor became too viscous to permit satisfactory crystallization.

The successive crops of crystals were systematically recrystallized as follows: About two thirds of the first crop was dissolved in about three parts of water and the hot solution allowed to deposit crystals by slow cooling. The liquor was filtered or decanted, and the remainder of the first crop was dissolved in it, and the process of crystallization was repeated. The remaining crops were similarly recrystallized in succession from the same liquor, the solution being evaporated to the appropriate volume (2/3 each time) before each recrystallization. The final mother liquor was evaporated in stages, and the viscous residue was united with that of the original recrystallization. The various crops were then recrystallized until constant rotation, (after the fifth recrystallization there was no change in rotation; $[\alpha]_D^{23^\circ} = 12.53^\circ$, C = 8 g/100 ml, ℓ = 2 dm). About 60 g of constant rotation salt was obtained (50% of the theoretical).

The pure malate was decomposed by warming with very slightly more than two equivalents of approximately 2 N sodium hydroxide. The amine was extracted, after cooling, with three 25 ml portions of ether, and the solution dried thoroughly over KOH. The ether was removed by simple distillation and the amine was also distilled by simple distillation, bp 184°-185°; $[\alpha]_D^{25^\circ} = 39.60^\circ$ (neat) ℓ = 0.5 dm, optical purity 98.2% using the best literature value[163] $[\alpha]_D^{25^\circ} = +40.60^\circ$ (neat).

nmr (CD_3CN) δ 1.3 (d, 3 H), 1.4 (s, 2 H), 4.0 (q, 1 H), 7,5 (m, 5 H)
See nmr spectrum number 24.

b. S(-) - α - Phenylethylamine.[164] A mixture of 31.25 g (0.208 mol) of (+) tartaric acid and 450 ml of methanol was placed in a 1 liter Erlenmeyer flask and heated to boiling. To the hot solution was added, cautiously to avoid foaming, 25 g (26.2 ml, 0.206 mol) of dl - α - phenylethylamine and the resulting solution was allowed to cool. Since crystallization occurs slowly, the solution was allowed to stand at room temperature for approximately 24 hours. The (-) amine (+) hydrogen tartrate separates as white prismatic crystals. The product (18.1 g) was collected by suction filtration and washed with a small volume (5-10 ml) of cold methanol. A second crop (3.8 g) was obtained by concentrating the combined mother liquor and washings to 225 ml and allowing crystallization to proceed at room temperature for 24 hours. The two crops were redissolved and recrystallized once more. The product 21.9 g was partially dissolved in 90 ml of water, and 12.5 ml of 50% sodium hydroxide was added to convert the amine salt to the free base. The amine was extracted with ether (50 ml), and the extract was dried over anhydrous magnesium sulfate for 0.5 hours. The ether was removed by simple distillation on the steam bath, and the residue was distilled at atmospheric pressure, (considerable foaming) to give S (-) - α - phenylethylamine. Yield 6.9 g (55%); bp 184°-186°. $[\alpha]_D^{22^\circ}$ =-39.30° (neat) ℓ = 0.5 dm, optical purity 98.0% using the best literature value[165] $[\alpha]_D^{22^\circ}$ =-40.30° neat.
nmr (CD_3CN) δ 1.3 (d, 3 H), 1.4 (s, 2 H), 4.0 (q, 1 H), 7.5 (m, 5 H).
See nmr spectrum number 25.

The above procedure was carried out 6 times in order to secure enough material. Total yield 41 g (55%). The literature value

($d_4^{25°}$ = 0.9528)[163] for the density of α-phenylethylamine was used to calculate the specific rotation.

R-(+)-N,N-DIMETHYL-α-PHENYLETHYLAMINE

R (+) -α-phenylethylamine (12.1 g, 0.1 mol) was added with cooling to (25.5 g, 05 mol) of 90% formic acid. Then (19 g, 0.22 mol) of 35% formaldehyde solution was added and the mixture was heated on the steam bath under reflux for four hours. About 9 ml (slightly more than 0.1 mol) of concentrated hydrochloric acid was added, and the formic acid and any excess formaldehyde were evaporated. The reaction mixture was treated (with cooling) with 25% sodium hydroxide until basic. The aqueous layer was extracted with ether (3 x 15 ml) and the organic layer was dried over potassium hydroxide. Removal of the ether by simple distillation followed by vacuum distillation afforded 11.90 g (80%) of R-(+)-N,N-dimethyl-α-phenylethylamine; bp 92°-94° at 30 mm of pressure; $[\alpha]_D^{22°}$ = 60.50° (neat), ℓ = 0.5 dm, using a density value $d_4^{16°}$ = 0.8966; (Lit[166] $[\alpha]_D^{26°}$ = + 61.76°); optical purity was 98%. nmr (CD_3CN) δ 1.0 (d, 3 H), 1.95 (s, 6 H), 2.8 (q, 1 H), 7.1 (m, 5 H).

See nmr spectrum number 26.

S-(-)-N,N-DIMETHYL-α-PHENYLETHYLAMINE

S-(-)-α-phenylethylamine (24.2 g, 0.2 mol) was added with cooling to (51 g, 1 mol) of 90% formic acid. Then (38 g, 0.44 mol) of 35% formaldehyde solution was added and the mixture was refluxed on a steam bath overnight. About 18 ml (slightly more than 0.2 mol) of concentrated hydrochloric acid was added and the formic acid and any excess formaldehyde were evaporated. After evaporation, the reaction mixture was treated (with cooling) with 25% aqueous sodium hydroxide. The aqueous layer was extracted with ether (3 x 20 ml) and the organic layer dried over potassium hydroxide. Removal of the ether by simple

distillation and then vacuum distillation of the amine afforded 23.80 g (80%) of S-(-)-N,N-dimethyl-α-phenylethylamine. bp 92°-94° at 30 mm of pressure. $[\alpha]_D^{22^\circ}$ =-60.48° (neat) ℓ = 0.5 dm, using a density value of $d_4^{16^\circ}$ = 0.8996.

nmr (CD_3CN) δ 1.0 (d, 3 H), 1.95 (s, 6 H), 2.8 (q, 1 H), 7.1 (m, 5 H)

See nmr spectrum number 27

R-(+)-N,N,N-TRIMETHYL-α-PHENYLETHYLAMMONIUM IODIDE

To a solution of R-(+)-N,N-dimethyl-α-phenylethylamine (14.9 g, 0.1 mol) in ether (100 ml) was added slowly 21.3 g (0.15 mol) of methyl iodide. After fifteen minutes, the mixture had solidified. The flask was cooled in an ice bath for two hours and then allowed to stand at room temperature for twelve hours. The white solid was collected by suction filtration and washed with two 100 ml portions of ether. After it had been dried in the vacuum desiccator for twenty four hours, the solid weighed 27.64 g (95%); mp 155°-156°.

$[\alpha]_D^{22^\circ}$ = + 10.72° in water, C = 0.6184 g/25 ml, ℓ = 2 dm.

$[\alpha]_D^{20^\circ}$ = + 23.28° in 95% ethanol, C = 0.9393 g/25 ml, ℓ = 2 dm

(Lit.[167] $[\alpha]_D^{26^\circ}$ = + 19.60° in alcohol C = 2.5%).

nmr ($CDCl_3$) δ 1.8 (d, 3 H), 3.2 (s, 9 H), 4.9 (q, 1 H), 7.8 (s, 5 H).

See nmr spectrum number 28

S-(-)-N,N,N-TRIMETHYL-α-PHENYLETHYLAMMONIUM IODIDE

To a solution of S (-) N,N-dimethyl-α-phenylethylamine (14.9 g, 0.1 mol) in 100 ml of ether was added slowly 21.3 g (0.15 mol) of methyl iodide. After fifteen minutes a white precipitate appeared. The flask was cooled in an ice bath for two hours and allowed to stand at room temperature for 16 hours. The white solid was collected by suction filtration and washed twice with 50 ml portions of ether. After it had

been dried in the air and finally in a vacuum desiccator (continuos pumping for twenty four hours) the solid weighed 27,64 g (95%). mp 155°-156°; (Lit.[167] mp 157.0°-157.5°). $[\alpha]_D^{22^\circ}$ = -12.03° in H_2O, ℓ = 2 dm, C = 0.6749 g/25ml. $[\alpha]_D^{20^\circ}$ = -22.95° in 95% ethanol, C = 0.8568 g/25 ml, ℓ = 2 dm. (Lit. see previous preparation)

See nmr spectrum number 29.

(+) 1,1,2-TRIPHENYLPROPANE FROM REACTION OF BENZHYDRYL LITHIUM WITH R-(+)-N,N,N-TRIMETHYL-α-PHENYLETHYLAMMONIUM IODIDE

To approximately (0.04 mol) of benzhydryllithium in 100 ml of THF at 0°C was added 11.64 g (0.04 mol) of R-(+)-N,N,N-trimethyl-α-phenyl-ethylammonium iodide. The reaction was stirred for 1.0 hour after which the red color of the carbanion had disappeared. After acidification with hydrochloric acid, extraction with ether, drying of the ether ($CaCl_2$) and removal of the solvent, the remaining oil was fractionally distilled in vacuo to give a middle fraction of bp (165°) at 1 mm. Treatment of this oil with cold methanol caused crystallization of 7.02 g (65%) of crude (+) 1,1,2-triphenyl-propane, mp 60°-64°, $[\alpha]_D^{23^\circ}$ = +29.56° in acetone, ℓ = 2 dm. Five recrystallizations from methanol afforded the analytical sample, mp 64°-66°. $[\alpha]_D^{23^\circ}$ = + 30.99° in acetone, ℓ = 2 dm, C = 0.6061/25 ml.

Anal: Calcd for $C_{21}H_{20}$: C, 92.64; H, 7.35

Found: C, 92.51; H, 7.41

nmr ($CDCl_3$) δ 1.20 (d, 3 H), 3.6 (m, 1 H), 4.1 (d, 1 H), 7.3 (m, 15 H)

See nmr spectrum number 30

(-) 1,1,2-TRIPHENYLPROPANE FROM REACTION OF BENZHYDRYLLITHIUM WITH S-(-)-N,N,N-TRIMETHYL-α-PHENYLETHYLAMMONIUM IODIDE

To approximately (0.04 mol) of benzhydryllithium at 0°, was added 11.64 g (0.04 mol) of S (-) N,N,N-trimethyl-α-phenylethylammonium iodide. The reaction was stirred for 1.0 hour after which the red color of the carbanion had disappeared. After acidification with HCl, extraction with ether (100 ml), drying of the ether ($CaCl_2$) and removal of the solvent, the remaining oil was fractionally distilled in vacuo to give a middle fraction of bp 165° at 1 mm. Treatment of this oil with cold methanol caused crystallization of 8.0 g (73%) of crude (-) 1,1,2-triphenylpropane, mp 60°-63°. $[\alpha]_D^{22^\circ}$ = -27.54° in acetone. Five recrystallizations from methanol afforded the analytical sample, mp 65°-67°; $[\alpha]_D^{22^\circ}$ = -28.74° in acetone, ℓ = 2 dm, C = 0.6096 g/25 ml.

Anal: Calcd for $C_{21}H_{20}$: C, 92.64; H, 7.35

Found: C, 92.58; H, 7.23

nmr ($CDCl_3$) δ 1.20 (d, 3 H), 3.6 (m, 1 H), 4.1 (d, 1 H), 7.3 (m, 15 H)

See nmr spectrum number 31

RACEMIC HYDRATROPIC ACID

This acid was prepared by three different procedures listed below as a,[168] b, and c.[169]

a. To a well stirred solution of (24.7 g, 0.184 mol) of dℓ-hydratropaldehyde (90% purity) and 69 g (0.406 mol) of silver nitrate in 110 ml of ethanol and 110 ml of water, a solution of (25.8 g, 0.645 mol) of sodium hydroxide in 520 ml of H_2O was added over a period of 1.5 hours. The suspension was heated on a steam bath with continuous stirring for another hour. The silver and silver oxide were removed by vacuum filtration and washed with water and ether. The filtrate was extracted twice

with ether (200 ml). The aqueous layer was distilled until the organic solvents were removed, then acidified with 10% HCl and extracted with two 100 ml portions of ether. The ether solution was dried over sodium sulfate, concentrated and the residue distilled in vacuo. The hydratropic acid distilled at 144°-147° at 11 mm, and weighed 20.5 g (74%). The neutral fraction upon distillation gave ca 2 g (8%) of acetophenone, bp 80°-82° (11 mm), $\eta_D^{25^\circ}$ = 1.5287.

The nmr of racemic hydratropic was as follows:

nmr ($CDCl_3$) δ 1.4 (d, 3 H), 3.7 (1, 1 H), 7.35 (s, 5 H), 12 (s, 1H).

b. Into a 3 liter flask, fitted with a mechanical stirrer, were placed 1.4 liters of 50:50 acetone-water mixture and 50 g of magnesium sulfate, followed by 200 g (1.5 moles) of dℓ hydratropaldehyde. Then potassium permanganate 170 g (1.07 moles) was added in 15 g portions and the temperature was maintained between 30° and 35° . When the addition of permanganate was completed, the manganese dioxide was filtered by vacuum filtration . The solution was acidified with 10% HCl until slightly acidic. The acid was extracted with 5% sodium bicarbonate and the bicarbonate layer was extracted thoroughly with ether to remove unreacted aldehyde and acetophenone. The acid was then regenerated by using 10% HCl, extracted with ether (200 ml), dried (Na_2SO_4) and then distilled in vacuo, bp 144°-147° (11 mm). Yield 112 g (50%).

nmr ($CDCl_3$) δ 1.4 (d, 3 H), 3.7 (q, 1 H), 7.35 (s, 5 H), 12 (s, 1 H).

c. To a combined solution of racemic hydratropaldehyde (159 g, 1.17 moles) in 480 ml of ethanol and hydroxylamine hydrochloride (99.0 g, 1.41 moles) in 120 ml of water, was added slowly 96 ml of 19 N aqueous sodium hydroxide solution. After the mixture was stirred for three hours, it was cooled by addition of about 600 ml of ice water and allowed to warm to,

and remain overnight at room temperature. The basic reaction mixture was exhaustively extracted with ether, and the combined ether extracts, after drying and evaporation, yielded racemic hydratropaldoxime, 135 g (76%); as a colorless oil, bp 110° (3.5 mm); (Lit.[169] bp 133° at 11 mm). Ir (neat) νmax 3220 and 1500 cm^{-1} (bonded OH) and 1760 cm^{-1} (C=N).

The oxime (135 g, 0.90 mol) was heated with acetic anhydride (200 ml) under reflux during 0.5 hour. After the orange reaction mixture was allowed to cool to room temperature and neutralized with sodium bicarbonate, it was exhaustively extracted with ether. Evaporation of the combined and dried (Na_2SO_4) ether extracts provided racemic hydratroponitrile as a colorless oil: 84 g (71%); bp 74° (0.5 mm); (Lit.[169] bp 106° at 12 mm). Ir (neat) νmax 2245 cm^{-1} (C = N)

Racemic hydratroponitrile (84 g, 0.63 mol) was suspended in concentrated aqueous sodium hydroxide solution and heated under gentle reflux during 18 hours. The reaction mixture was allowed to cool and carefully acidified with 10% HCl, and the resulting acidic solution was extracted with ether. Evaporation of the combined and dried ether extracts provided racemic hydratropic acid: 72 g (76% yield); bp 113° (1 mm); (Lit.[169] 147° at 11 mm and 159° at 25 mm).

Ir (neat) νmax 2960 and 1701 cm^{-1}

nmr ($CDCl_3$) δ 1.4 (d, 3 H), 3.7 (1, 1 H), 7.35 (s, 5 H), 12 (s, 1 H).

RESOLUTION OF HYDRATROPIC ACID

S (+) HYDRATROPIC ACID: Racemic hydratropic acid (48 g, 0.32 mol) and ℓ-strychnine (88 g, -.26 mol) were dissolved in 200 ml of 75% (v/v) aqueous ethanol, and the resulting solution was kept in the refrigerator (ca, 0°C) for three days. The crystallized strychnine hydratropate was collected, redissolved in fresh 75% aqueous ethanol and allowed once

again to crystallize slowly in the refrigerator. This procedure was repeated through the sixth recrystallization since the fifth and sixth recrystallization did not give rise to any improvement in the melting point (176°-177°) of the white crystalline salt. The constant melting strychnine hydratropate was taken up in 6 N HCl, and the liberated acid was extracted into ether (100 ml). Distillation of the oily residue obtained from evaporation of the combined and dried (Na_2SO_4) ether extracts gave S (+) hydratropic acid, 9.0 g, bp 101°-103° (0.4 mm). $[\alpha]_D^{22^\circ}$ = 97.00° neat, ℓ = 0.5 dm; (Lit.[170] $[\alpha]_D^{21^\circ}$ = 98.8° neat); optical purity using the literature value was 97.5%.

nmr ($CDCl_3$) δ 1.4 (d, 3 H), 3.7 (q, 1 H), 7.35 (s, 5 H), 12 (s, 1 H). See nmr spectrum number 32

S (+) METHYL HYDRATROPATE: This reaction was carried out by using the Diazald Kit sold by Aldrich. This experiment should be carried out in a hood with a protective shield, because diazomethane is explosive and very toxic.

a. Diazomethane: A solution of potassium hydroxide (5 g) in 8 ml of water was placed in the distilling flask and 25 ml of 95% ethanol was added (no boiling chips). The flask was heated in a water bath to 65° and a solution of 21.5 g (0.1 mol) of N-methyl N-nitroso-p-toluene sulfonamide in 130 ml of ether was added through the dropping funnel over a period of about 25 minutes. The rate of addition should be about the equal of the rate of distillation. When the dropping funnel was empty, another 20 ml of ether was added slowly and the distillation was continued until the distilling ether was colorless. The combined ethereal distillate contains about 3 g (approx. 0.07 mol) of diazomethane and was approximately 0.5 M.

b. Methyl Ester: The acid (7.5 g, 0.05 mol) was dissolved in ether, and the ethereal diazomethane solution was added in small portions with swirling until the yellow color of the diazomethane persisted and nitrogen gas was no longer evolved. The solution was warmed on a steam bath briefly to expel the excess reagent and the ether was evaporated. The methyl ester was vacuum distilled; bp 60°-65° at 2 mm. Yield 7.80 g (95%). $[\alpha]_D^{22^\circ}$ = + 103.50° neat, ℓ = 0.5 dm; (Lit.[171] bp 71°-75° at 4.5 mm, $[\alpha]_D^{25^\circ}$ = -44.5° neat, ℓ = 1 dm. The available literature data only has this rotation for the levo-isomer).

nmr ($CDCl_3$) δ 1.2 (d, 3 H), 3,5 (s, 3 H), 3.6 (q, 1 H), 7.35(m, 5 H).

See nmr spectrum number 33

S (-) 1,1,2 TRIPHENYL-1-PROPANOL

The phenylmagnesium bromide was prepared by adding a solution of bromobenzene (23.4 g, 0.15 mol) in 50 ml of THF to 3.2 g (0.13 mol) of Mg and keeping a mild reflux through the addition. After the addition was completed the Grignard reagent was refluxed for 0.5 hour. Then 5.0 g (0.03 mol) of S (+) methyl hydratropate was added dropwise, and after the addition the reaction mixture was refluxed for two hours. The mixture was decomposed at 0° by adding carefully 100 ml of 10% ammonium chloride solution. The mixture was extracted thoroughly with ether (3 x 50 ml) and the organic layer dried over magnesium sulfate. After evaporation of the solvent, the oil was distilled in vacuo to give 4.0 g of S (-) 1,1,2-triphenyl-1-propanol, bp 180°-182° (3.0 mm);

$[\alpha]_D^{23^\circ}$ = - 142° in methanol, C = 1.7171 g/25 ml, ℓ = 2 dm.

nmr ($CDCl_3$) δ 1.4 (d, 3 H), 2.4 (s, 1 H), 4.0 (q, 1 H), 7.3 (m, 15 H).

ir (neat) 3600, 3020, 1150, 750, 710 cm^{-1}

REDUCTION OF S (-) 1,1,2-TRIPHENYL-1-PROPANOL TO R (+) 1,1,2-TRIPHENYLPROPANE WITH SODIUM IN LIQUID AMMONIA

The carbinol (5.76 g, 0.02 mol) and ethyl alcohol (2.02 g, 0.044 mol) were dissolved in a mixture of 50 ml of THF and 200 ml of liquid ammonia and sodium (1.01 g, 0.044 mol) was added in small pieces with stirring during 45 minutes. After all the sodium had disappeared most of the ammonia was evaporated, and the residue cautiously decomposed by the addition of crushed ice. The product was extracted with ether; the ether was dried (Na_2SO_4) and evaporated. The residual oil was distilled in vacuo to give R (+) 1,1,2-triphenyl-propane (2.72 g, 50%). Upon addition of cold methanol, the oil solidified, mp 63°-65°. $[\alpha]_D^{22^\circ}$ = + 30.15° in acetone, C = 0.5998 g per 25 ml, ℓ = 2 dm. This material was identical in its nmr and ir spectral properties to the sample described from the reaction of R (+) N,N,N-trimethyl-α-phenylethyl-ammonium iodide with benzhydryllithium.

PENTAPHENYLETHANE FROM TRITYLLITHIUM AND N-BENZHYDRYL-N,N,N-TRIMETHYL-AMMONIUM IODIDE

To a solution of tritylllithium (0.02 mol) in THF at 0° under argon was added 7.06 g (0.02 mol) of solid N-benzhydryl-N,N,N-trimethylammonium iodide. After 25-30 minutes the red color of the lithium reagent disappeared completely. After work-up using ether and water, the ether layer was extracted exhaustively with 5% HCl, neutralized with 5% NaOH and dried over $MgSO_4$. Upon removal of the ether a light yellow powder appeared which was dissolved in the minimum amount of hot benzene and precipitated by adding excess absolute ethanol. Yield 6.54 g (80%); mp 156°-161°. Concentration under reduced pressure gave 1.22 g (10%) additional of pentaphenylethane which was identical to a sample described

previously.[40]

nmr ($CDCl_3$) δ 5.8 (s, 1 H), 7.2(m, 25 H).

UNSYMMETRICAL TETRAPHENYLETHANE FROM TRIPHENYLMETHYLLITHIUM AND N-BENZYL-N,N,N-TRIMETHYLAMMONIUM IODIDE

To a solution of tritylllithium (0.02 mol) in 100 ml of THF at 0° under argon was added solid N-benzyl-N,N,N-trimethylammonium iodide (5.54 g, 0.02 mol) with stirring for four hours. The mixture was poured into ice water and then extracted twice with 50 ml of ether. The ether layer was washed with 5% HCl, neutralized with 5% NaOH and dried over $MgSO_4$. Removal of the ether afforded crude unsym-tetraphenylethane which was recrystallized from a 50:50 mixture of ether and petroleum ether.
Yield: 6.01 g (90%), mp 143°-145°. (Lit.[172] mp 144°).
nmr ($CDCl_3$) δ 3.95 (s, 2 H), 7.2(m, 20 H).

SYMMETRICAL-TETRAPHENYLETHANE FROM DIPHENYLMETHYLLITHIUM AND N-BENZHYDRYL-N,N,N-TRIMETHYLAMMONIUM IODIDE

To a solution of benzhydryllithium (0.01 mol) in 100 ml of THF was added (3.53 g, 0.01 mol) of solid N-benzhydryl-N,N,N-trimethylammonium iodide with stirring for one hour. After work-up using ether and water, the ether layer was extracted exhaustively with 5% HCl, neutralized with 5% NaOH and dried over $MgSO_4$. Removal of the ether, followed by recrystallization of the crude product from benzene and alcohol (5:1), afforded a 3.01 g (95%) yield of sym-tetraphenylethane; mp 218°-219°; (Lit.[150] mp 214°-215°).

1,1,2 TRIPHENYLETHANE FROM BENZHYDRYLLITHIUM AND N-BENZYL-N,N,N-TRIMETHYLAMMONIUM IODIDE

To (0.04 mol) of benzhydryllithium at 0° was added as a solid (11.08 g. 0.04 mol) of N-benzyl-N,N,N-trimethylammonium iodide in one portion, and the reaction stirred until complete decoloration of the

carbanion occurred. The reaction was poured into 100 ml of 5% HCl and then extracted into 100 ml of ether. After drying over $MgSO_4$ and removal of the solvent there was obtained 9.5 g of crude 1,1,2-triphenylethane (92%), mp 50°-52°. Recrystallization from 95% alcohol gave 9.1 g of the product as needless, mp 53°-54°; (Lit.[173] mp 54°)
nmr ($CDCl_3$) δ 3.5 (d, 3 H), 4.3 (t, 1 H), 7/2 (m, 15 H).
See nmr spectrum number 35.

1,1,2-TRIPHENYLETHANE FROM BENZYLLITHIUM AND N-BENZHYDRYL-N,N,N-TRIMETHYL AMMONIUM IODIDE

To (0.01 mol) of benzyllithium at 0° there was added (3.53 g, 0.01 mol) of N-benzhydryl-N,N,N-trimethylammonium iodide in one portion, and the reaction stirred until complete decoloration of the carbanion occurred. The reaction was poured into 100 ml of 5% HCl and extracted into 100 ml of ether. After drying over $MgSO_4$ and removal of the solvent there was obtained 2.34 g (91%) of crude 1,1,2-triphenylethane, mp 50°-52°; (Lit.[173] mp 54°).
nmr ($CDCl_3$) δ 3.5 (d, 3 H), 4.3 (t, 1 H), 7.2 (m, 15 H).
See nmr spectrum number 35.

1,2-DIPHENYLETHANE FROM BENZYLLITHIUM AND N-BENZYL-N,N,N-TRIMETHYL-AMMONIUM IODIDE

To (0.01 mol) of benzyllithium at 0° there was added (2.77 g, 0.01 mol) of N-benzyl-N,N,N-trimethylammonium iodide in one portion, and the reaction mixture stirred until complete decoloration of the carbanion occurred. The reaction was poured into 100 ml of 5% HCl and then extracted into 100 ml of ether. After drying over $MgSO_4$ and removal of the solvent, there was obtained 1.63 g (90%) of an oil which solidified on standing, mp, 50°-51°; (Lit.[174] mp. 52.0°-52.5°).

nmr ($CDCl_3$) δ 2.9 (s, 4 H), 7.1 (s, 10 H).

ADDITION OF TRITYLBROMIDE TO LITHIUM NAPHTHALENIDE**

In a carbon copy experiment of that just described, in which trityl bromide (12.59 g, 0.039 mol) was substituted for trityl chloride, identical results were secured.

ADDITION OF TRITYL FLUORIDE TO LITHIUM NAPHTHALENIDE**

To 0.02 mol of lithium naphthalenide in 100 ml of THF, there was added dropwise 5.24 g (0.02 mol) of trityl fluoride previously dissolved in THF (50 ml). After complete addition, the reaction turned red and remained red for 48 hours until it was quenched with 10 ml of distilled water. After work up using methods described previously there was obtained 0.45 g (4%) of p-benzhydryltetraphenylmethane, mp 226°-227°. The remainder of the reaction mixture was identified as a mixture of triphenylmethane and trityl fluoride.

SOLUBILITY OF SOME QUATERNARY AMMONIUM SALTS IN THF

The solubility of the salts below was measured by the following method: An accurate weight of the salt was dissolved in 25 ml of THF and the suspension stirred and equilibrated at 20°C for two hours. The suspension was filtered and the THF evaporated until constant weight was achieved. The results are tabulated on the following page in Table 1.

** These experiments should precede the one entitled ADDITION OF ONE MOLE OF TRITYL CHLORIDE TO 3 MOLES OF LITHIUM NAPHTHALENIDE, on page 90.

SOLUBILITY OF QUATERNARY AMMONIUM SALTS IN THF AT 20° C.

SALT	Solubility in g/25 ml	Solubility in mg/ml
$Ph-\overset{+}{N}(CH_3)_3\ I^-$	0.0075	0.30
$Ph-CH_2-\overset{+}{N}(CH_3)_3\ I^-$	0.0030	0.12
$Ph_2CH-\overset{+}{N}(CH_3)_3\ I^-$	0.0918	3.7
$CH_2=CH-(CH_2)_4-\overset{+}{N}(CH_3)_3\ I^-$	0.0108	0.43
Naph - 1 - $\overset{+}{N}(CH_3)_3\ I^-$	0.0277	1.1
$Ph_2CH-\overset{CH_3}{\underset{CH_3}{N}}-CH_2Ph\ ^+Br^-$	0.0330	1.32
$PhCH_2-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{N^+}}}}-Ph\ Br^-$	0.0133	0.53

Table 1.

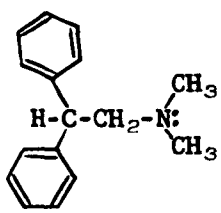
CONTROL EXPERIMENTS

1. THE REACTION OF LITHIUM NAPHTHALENIDE WITH SYM-TETRAPHENYLETHANE.

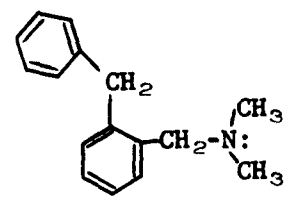
This experiment was carried out by reacting for one hour one equivalent of sym-tetraphenylethane with one, two, and three equivalents of lithium naphthalenide respectively. After decoloration of the radical anion, the mixture was worked-up as described previously in page 93. The results are tabulated on page 48 in Table 2.

2. THE REACTION OF N-BENZHYDRYL-N,N,N -TRIMETHYLAMMONIUMIODIDE WITH ALKYL-LITHIUM REAGENTS.

To a suspension of N-benzhydryl-N,N,N-trimethylammonium iodide, 1.0 g (0.003 mole) in 50 ml of THF, was added 0.006 mole of RLi (R=CH_3, CH_3CH_2, i-C_3H_7, and n-C_4H_9), and the reaction stirred for two hours. The reaction was carefully treated with 10 ml of distilled water, extracted into 50 ml of ether, and then extracted with 5% HCl. Treatment of the aqueous layer with 5% KOH, extraction into ether, followed by removal of the ether afforded 0.3 g of a mixture of amines, which were identified by nmr spectroscopy to be:



N,N-dimethyl-2,2-diphenyl-ethylamine



2-Benzyl-N,N-dimethylbenzyl-amine

The above amines arise from Stevens and Sommelett-Hauser rearrangements. These amines were not found during reactions of benzylic carbanions with benzhydryltrimethylammonium iodide.

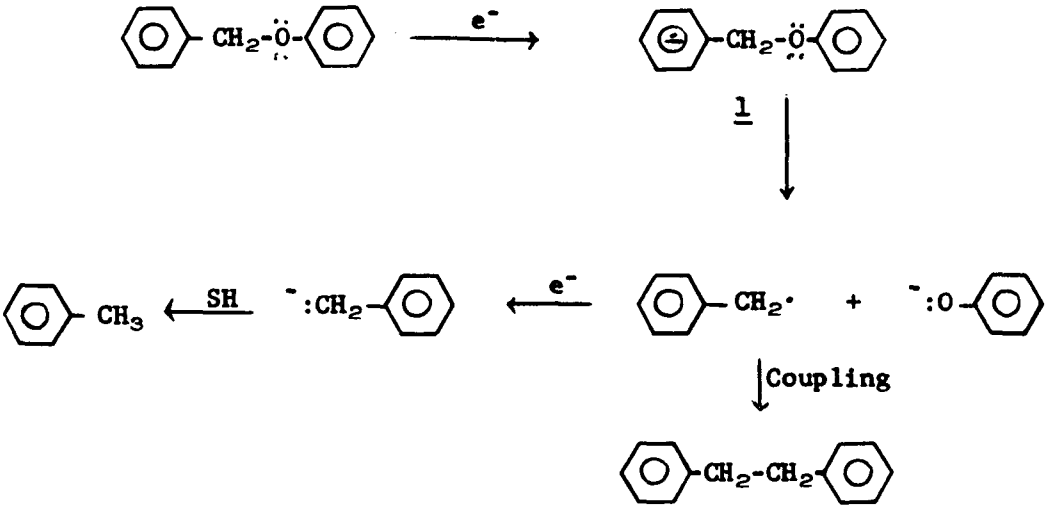
APPENDIX A

A SUMMARY OF REACTIONS OF AROMATIC RADICAL ANIONS WITH SOME ETHERS, SULFUR DIOXIDE, SULFONATE ESTERS, SULFONAMIDES, AND HYDROGEN AND NITROGEN.

1. Ethers.

Angelo[175] investigated the cleavage of several ethers. The most likely mechanistic possibility, using benzylphenylether as a model, is analogous to the radical anion reactions elucidated by Kornblum, et al[176]. (Scheme I)

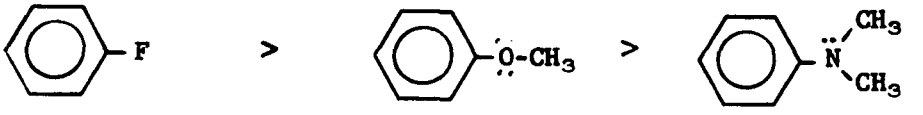
Scheme I



Reduction of the ether would presumably form the radical anion in which the added electron is in the benzyl ring, 1. Ejection of phenoxide would form the benzyl radical, which upon reduction and protonation is converted to toluene. Traces of bibenzyl might result from radical coupling, but this is not certain. The high yields of dimer in many reactions raises considerable doubt about this. For example, biallyl ether forms 50% biallyl

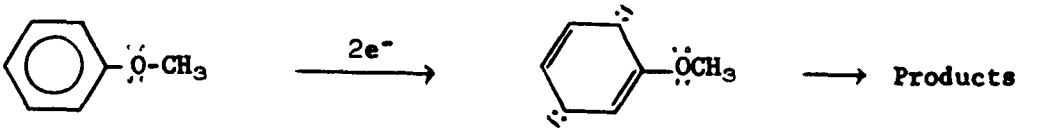
and 30% alkyl alcohol. In view of the facile reduction of alkyl radicals by sodium naphthalenide, a 50% yield of dimer by radical coupling seems much too high. Perhaps dimer formation is actually the product of a displacement reaction between the allyl carbanion and the ether.

Eisch, using dilithium biphenyl, studied the cleavage of a variety of ethers, heterocyclics, and hydrocarbons.[59] The ease of cleavage of molecules of the type Ar-Z, where Z = F, OCH_3, or $N(CH_3)_2$, is consistent with the decrease in σ values of the substituents.[177]



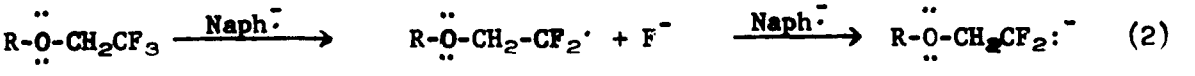
σ_p +0.062 -0.268 -0.0600

These reactions are slow enough that kinetics studies are feasible and the results might best be accounted for by a new scale of radical anion values. These reactions were interpreted by Eisch to be the result of a two electron transfer. (Shown in equation 1 for anisole). In view of more recent developments, a radical anion mechanism is more likely.



(1)

Electron transfer has also been proposed to account for the cleavage of β - trifluoro ethyl ethers as a means of forming alcohols in high yields.[178]



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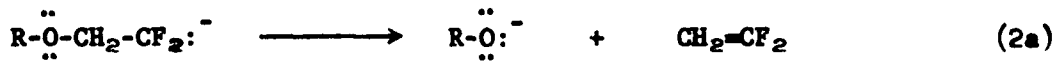
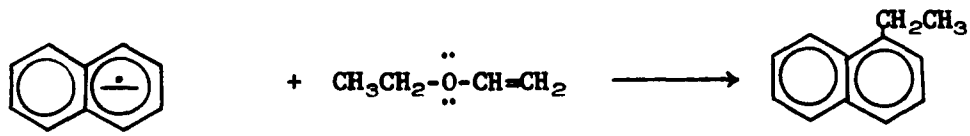


$$R\text{-}\ddot{O}\text{-}CH_2\text{-}CF_2\text{:}^- \longrightarrow R\text{-}\ddot{O}\text{:}^- + CH_2{=}CF_2 \qquad (2a)$$

There are inherent advantages in the use of alkali metal aromatic radical anions compared to the use of the metal in effecting ether cleavage. The homogeneous conditions permit the reactions to proceed faster and generally affords higher yields of the cleavage products. The rapidity of the reactions permits lower reaction temperatures. Use of a metal, especially lithium, usually requires an excess to be present, whereas ethers can be titrated with the highly colored radical anion solutions until the color persists, then quenched; this technique allows for the use of stoichiometric amounts of radical anion. Yet another advantage is that this method is successful for compounds which are inert to a metal.

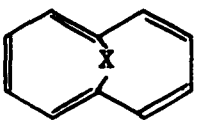
A variety of ether cleavage reactions have been performed with a metal in the absence of an electron carrier such as naphthalene or biphenyl. Mention is made of these reactions simply because mechanistically they appear to be very similar to the reactions already considered. Some leading references are listed.[179]

In another type of reaction, Watanabe and associates report an alkylation reaction with ethyl vinyl ether.[180] No mechanism is specified.



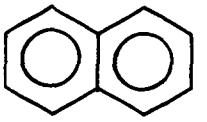
$$+ \; CH_3CH_2\text{-}\ddot{O}\text{-}CH{=}CH_2 \longrightarrow \qquad (3)$$

Reactions of the hydrocarbons 1,6-imino and 1,6-oxido-10-annulenes with sodium and potassium in DME are particularly interesting. Elimination of the heteroatom bride occurs, leading to naphthalene. No mechanism is proposed for this reaction.[181]



X= NH, O

$$\xrightarrow[\text{DME}]{\text{Na or K}}$$



(4)

2. SULFUR DIOXIDE, SULFONATES, AND SULFONAMIDES.

The reactions of alkali metals aromatic radical anions with compounds containing sulfur have been limited in scope to sulfur dioxide, sulfonate, and sulfonamides.

Sulfur dioxide combines with typical organometallic reagents such as Grignard reagents to form salts of sulfinic acids. The difference between the typical organometallic reagent and aromatic radical anions is again demonstrated by the observation that sodium naphthalenide undergoes almost exclusively electron transfer.[182] When electron transfer is favorable, the aromatic radical anions are poor nucleophiles. The sulfur containing products of this reaction are sodium thiosulfate (35%), sodium sulfite (35%), and sodium dithionite (30%), and are accounted for by scheme II. Dithionite 2 is formed by dimerization; this ion is unstable and is known to disproportionate.[183]

Scheme II

$$SO_2 \xrightarrow{Naph^{\cdot}} SO_2^{\cdot -} \xrightarrow{\text{dimerize}} \underset{\underline{2}}{S_2O_4^{2-}} \xrightarrow{2e^-} S_2O_3^{2-} + SO_3^{2-}$$

Not unexpectedly, the extent of electron transfer depends upon comparative electron affinities of the aromatic compound and sulfur dioxide.

N-substituted aryl sulfonamides undergo facile cleavage with sodium naphthalenide to liberate amines.[184] The cleavage method may have some value in the preparation of pure secondary amines[185] and may conceivably have some applications in peptide synthesis. The overall equation is

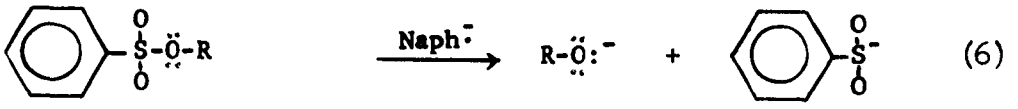
$$Ar\text{-}SO_2\text{-}\overset{H}{\underset{|}{N}}\text{-}R(Ar) \xrightarrow{Naph^{\cdot}} ArSO_2^- + ArH + H_2NR(Ar) \qquad (5)$$

As for so many reactions, only naphthalenide has been investigaged. Several observations are noteworthy. Alkylmethane sulfonamides do not cleave under the normal reaction conditions. For example, even with 20 equivalents of sodium naphthalenide, N-octylmethanesulfonamide shows 2% reaction and was recovered after quenching. This contrasts with the results of N-p-tolyl-p-toluene sulfonamide which forms cleavage products in 87% yield. Such disparity is attributable to the difference in reduction potentials; the dialkyl sulfonates do not as readily accept an electron as their aromatic counterparts. In a later paper it was determined that proton abstraction from N-octylmethanesulfonamide formed the anion, which of course, is even less prone to reduction.[186] Treatment of N-p-tolyl-p-toluene sulfonamide with sodium naphthalenide, followed by quenching in air to prevent formation of dihydronaphthalenes via hydrolysis, is reported to lead to 5 ± 2% dihydronaphthalenes. Thus, electron transfer is clearly the more favorable process even though the amide hydrogen is more acidic than in the N-alkyl analogs.

The reaction is amazingly selective. Conceivably the toluene sulfonamides of dipeptides could cleave at either the peptide or sulfonamide links. But, cleavage is highly specific, occurring at the sulfonamide link to free the dipeptides in yields greater than 89% in every case. Aryl halogens do not remain intact, however N-(m-chlorophenyl) p-toluene-

sulfonamide is cleaved to form aniline.[184] At room temperature 2-6 equivalents of sodium naphthalenide are required for sulfonamide cleavage, but at -60° to -80° exactly 2 equivalents are sufficient.[186] In fact, the end point can be titrated to the persistence of a faint green color. At -70° the only products are the sodium salt of the amine and the sodium arene sulfinate. At higher temperatures the aromatic compound and a number of sulfur containing salts are formed.

Not surprisingly, the cleavage of toluenesulfonates also occurs readily, and alcohols are recovered in high yields (eq. 6).



(6)

These reactions were performed at -80° with 2-6 equivalents of sodium naphthalenide.[187] Sodium phenanthrenide appears to work almost as well, whereas sodium anthracenide reacts more slowly and gives lower yields.

As with sulfonamides, alkyl alkanesulfonates do not give good yields of cleavage alcohol. The sulfonates do react, however; for example, octadecylbutanesulfonate forms 44% octadecylalcohol and 20% pentadecane, and 30% is converted presumably to alkylated dihydronaphthalenes. The product distribution is sensitive to the concentration of sodium naphthalenide, because as the naphthalenide ion concentration increases there is formed an increasing percentage of alcohol. This result is consistent with the mechanism of eq. 7-9,[188] with increasing naphthalenide favoring eq. 9.

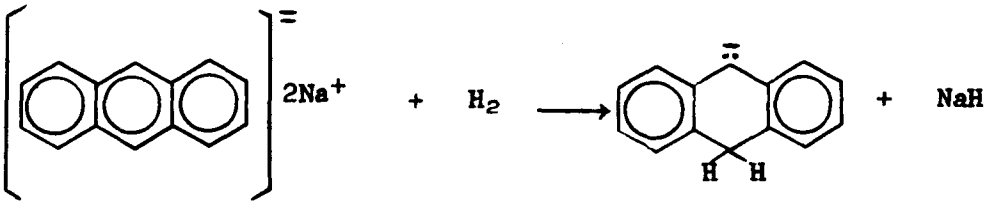
$$R'OSO_2R + Naph^{\cdot-} \longrightarrow R'OSO_2R^{\cdot-} + Naph \quad (7)$$

$$R'OSO_2R^{\cdot-} \longrightarrow R^{\cdot} + RSO_3^{-} \quad (8)$$

$$R'OSO_2R^{\cdot-} + Naph^{\cdot-} \longrightarrow R'\text{-}O^{-} + RSO_2^{-} + Naph \quad (9)$$

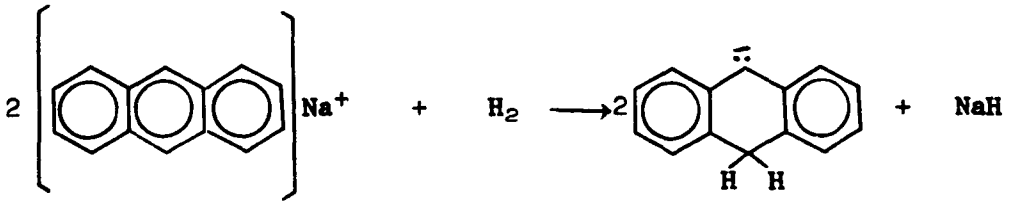
3. HYDROGEN

The radical anion and dianion of anthracene react with molecular hydrogen to form adducts, but they do so by different routes. Heterolytic cleavage of hydrogen occurs in the presence of the dianion.[189]



(10)

The radical anion causes both heterolytic and homolytic fission of hydrogen, the latter process being shown in eq. 11.



(11)

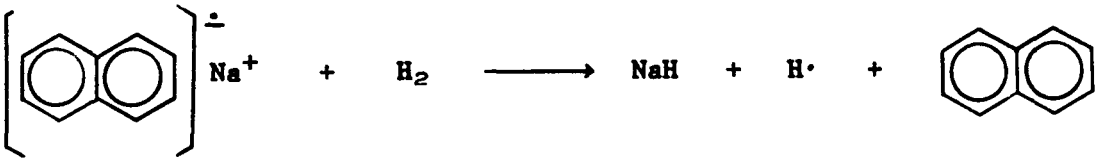
Whether these products are formed by direct combination or initial electron transfer has not been determined.

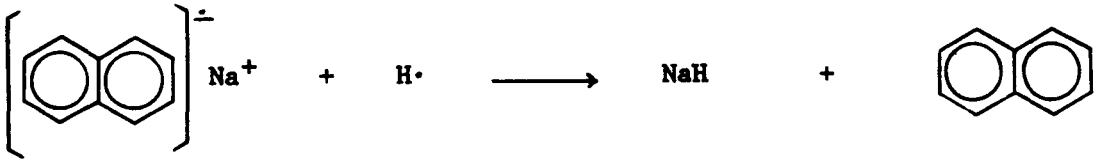
The 9-monohydroanthracene anion, under different conditions, does eliminate hydride.[190] Ejection of the hydride is a step in the hydrogenation of butadiene to 1 and 2-butenes with sodium anthracenide or the corresponding dianion.

With naphthalenide an entirely different process predominates.[191]

Naphthalenide donates an electron to hydrogen to effect its fission; this is shown in scheme III.

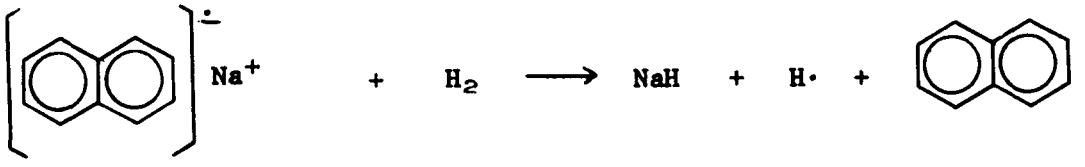
Scheme III

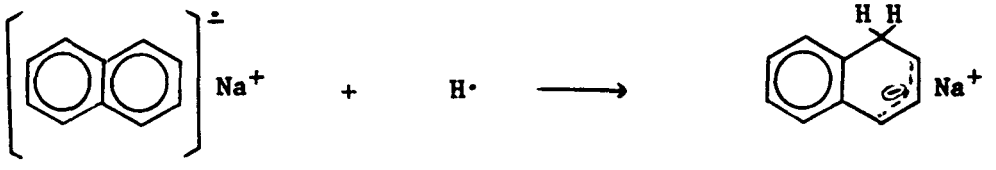




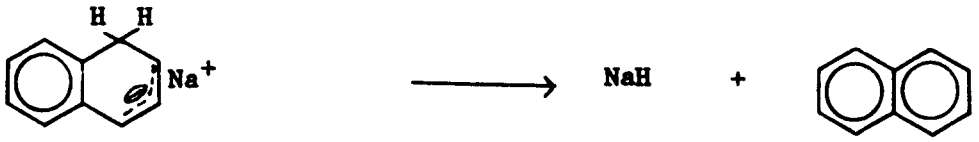
Naphthalenide also combines with atomic hydrogen (Scheme IV). Experiments with deuterium indicate that this route is minor.

Scheme IV





Scheme IV (Continuation)



The rates of reaction for scheme IV have been measured for a number of radical anions and dianions.[192]

NITROGEN

Isolation of the first simple chemical complex of molecular nitrogen was reported in 1965 by Allen and Seroff.[193] The following year Volpin and Shur announced the chemical fixation of nitrogen.[194] Their technique involved treating $CrCl_3$, $MoCl_5$, WCl_6, $FeCl_3$, or $TiCl_4$ with ethylmagnesium bromide in ether solution under 150 atm. of nitrogen. After quenching with acid they were able to recover an average of about 0.12 mole of ammonia per mole of transition metal.

Since this initial discovery, a number of refinements have been made. One of the most important of these has been the use of metal aromatic radical anions as the source of electrons.[195] The advantages of radical anions compared to Grignard reagents include the following: (1) the electron transfer from the Grignard reagent is not as favorable as from the radical anion; (2) Grignard reagents are better bases and nucleophiles than are aromatic radical anions which means they undergo competitive reactions more readily.

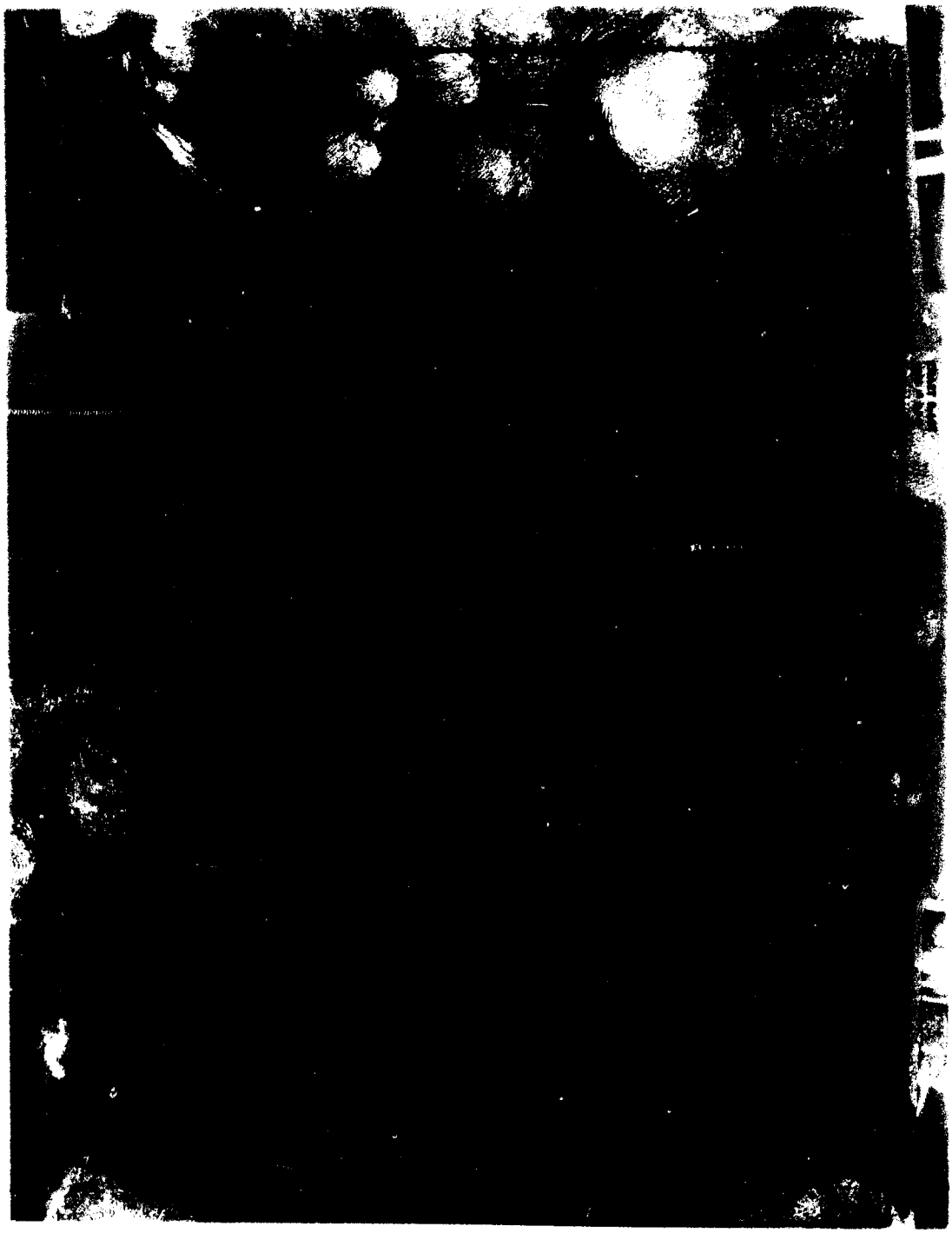
APPENDIX B

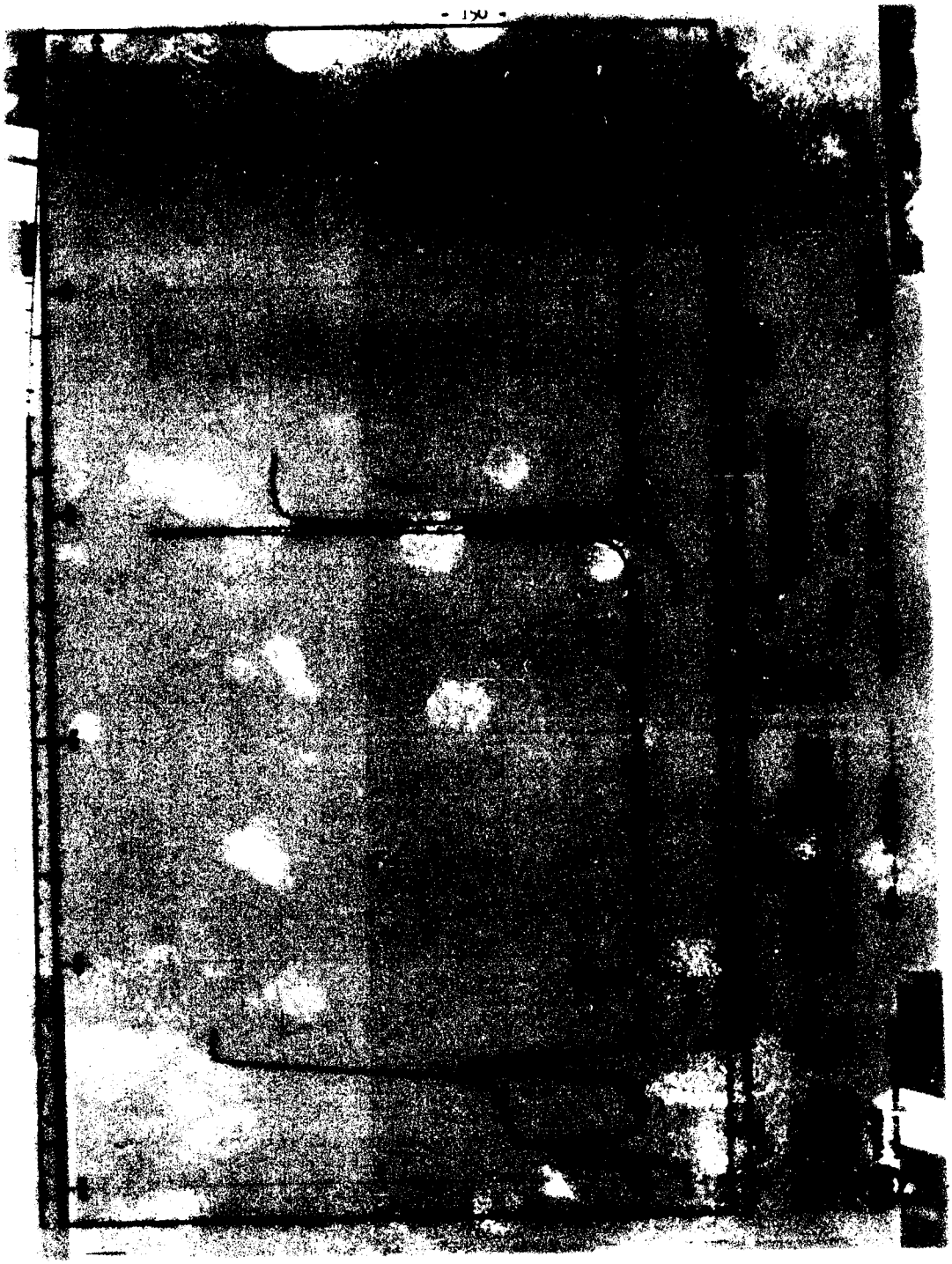
ABBREVIATIONS

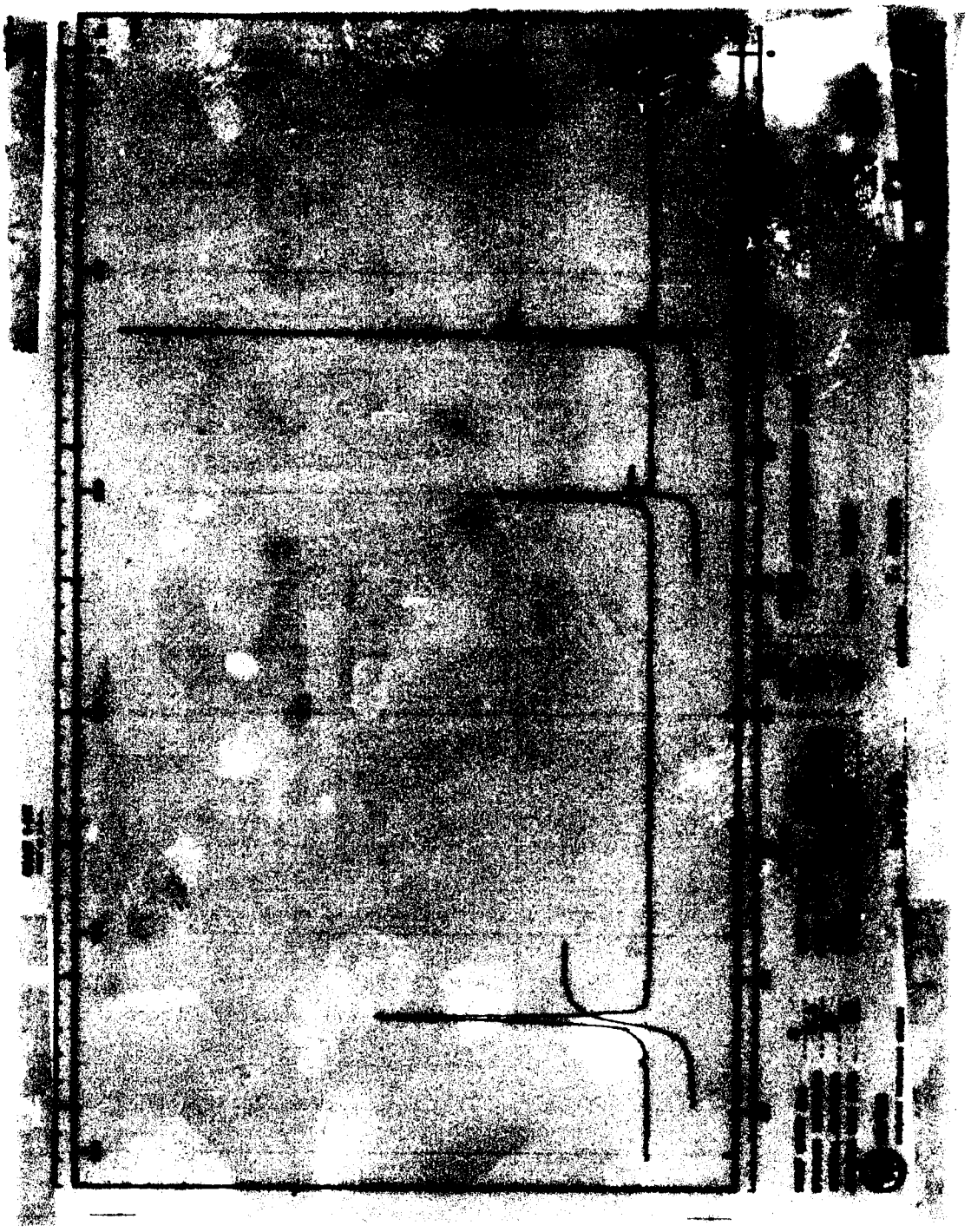
Naphthalene	Naph
Symmetrical-tetraphenylethane	Sym-TPE
Tetrahydrofuran	THF
Dimethoxyethane	DME
Nuclear magnetic resonance	nmr
Infra-red	ir
Pentaphenylethane	PPE
Dielectric constant	ϵ
2-methyltetrahydrofuran	2-MeTHF

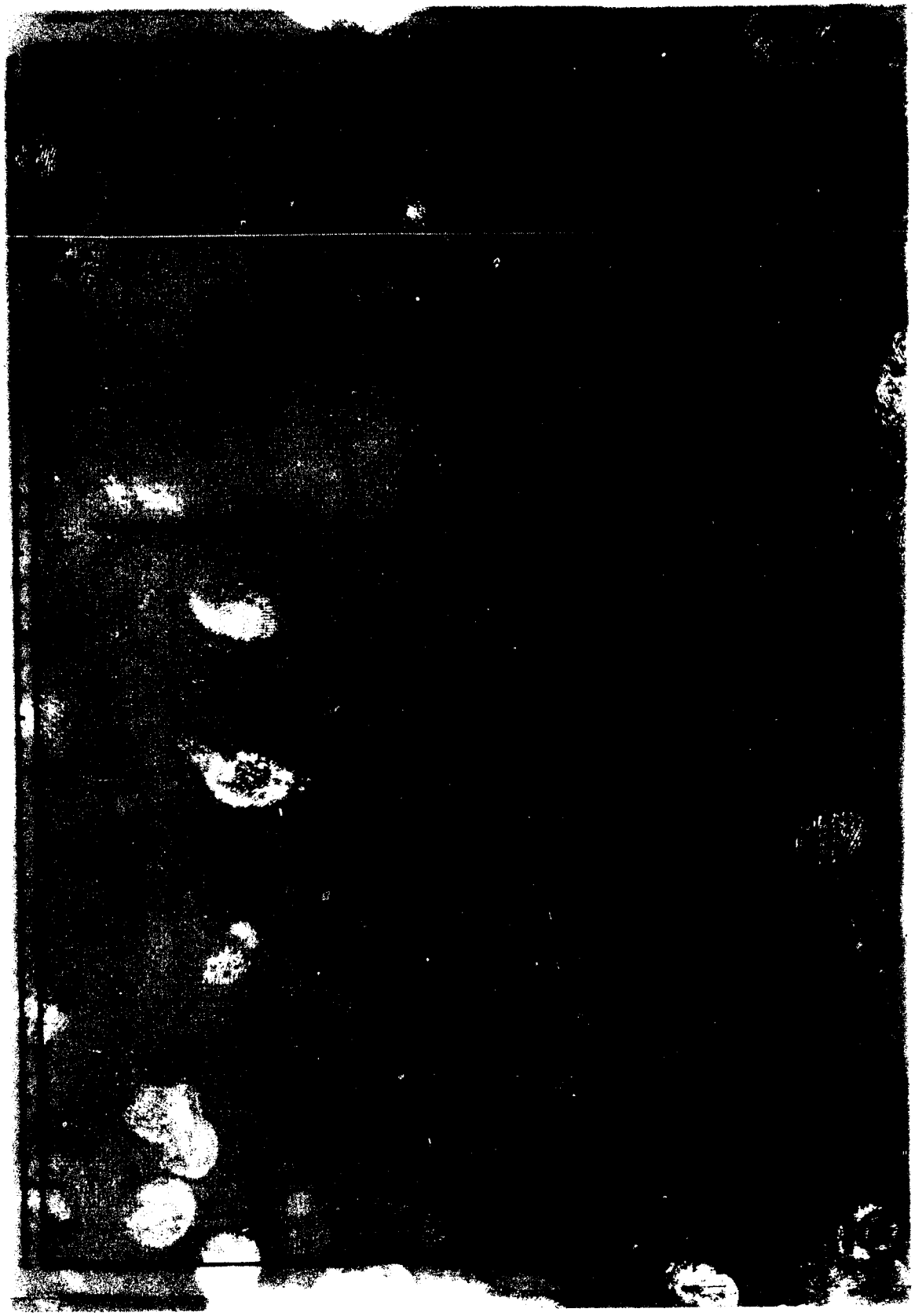
APPENDIX C

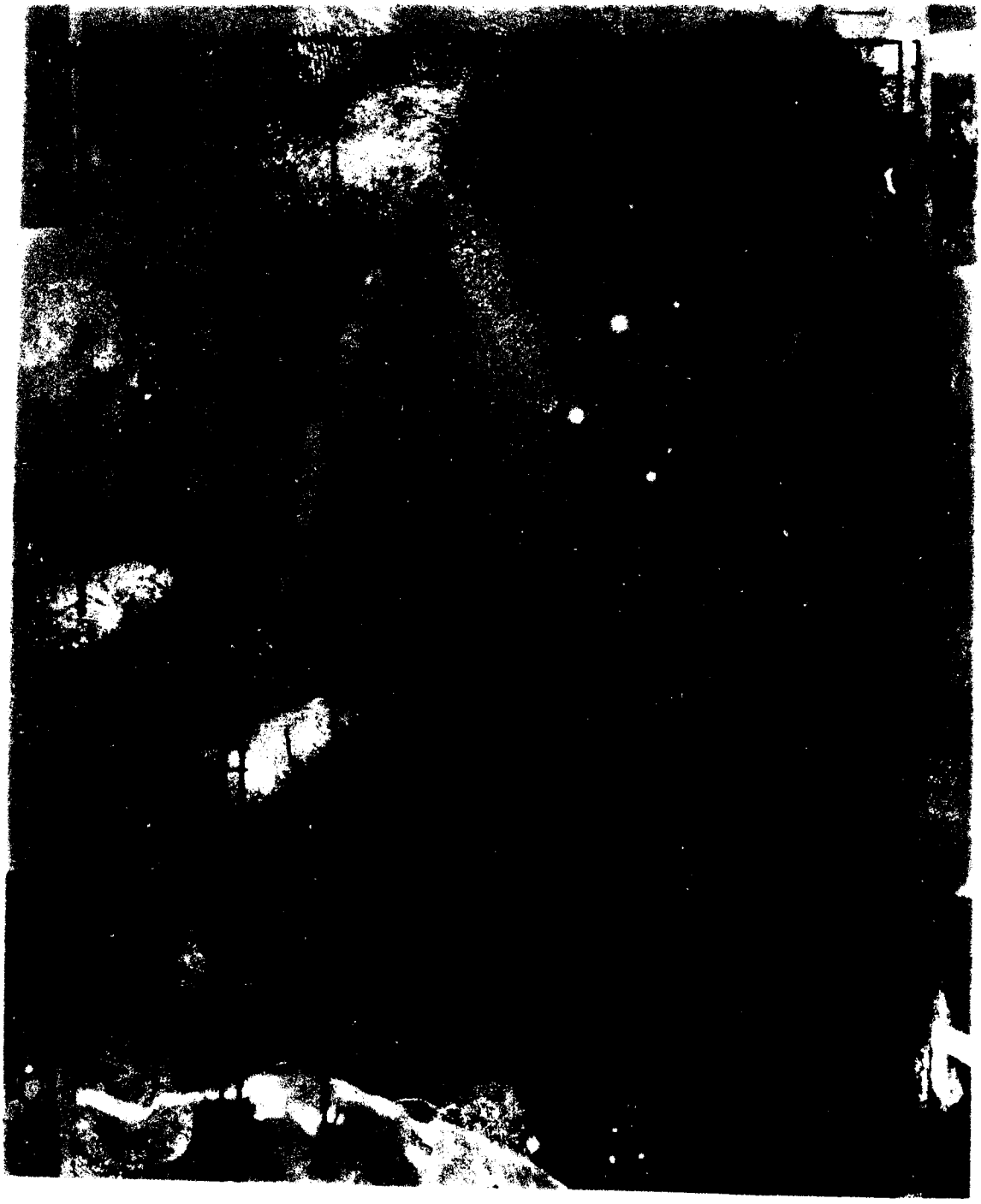
NUCLEAR MAGNETIC RESONANCE

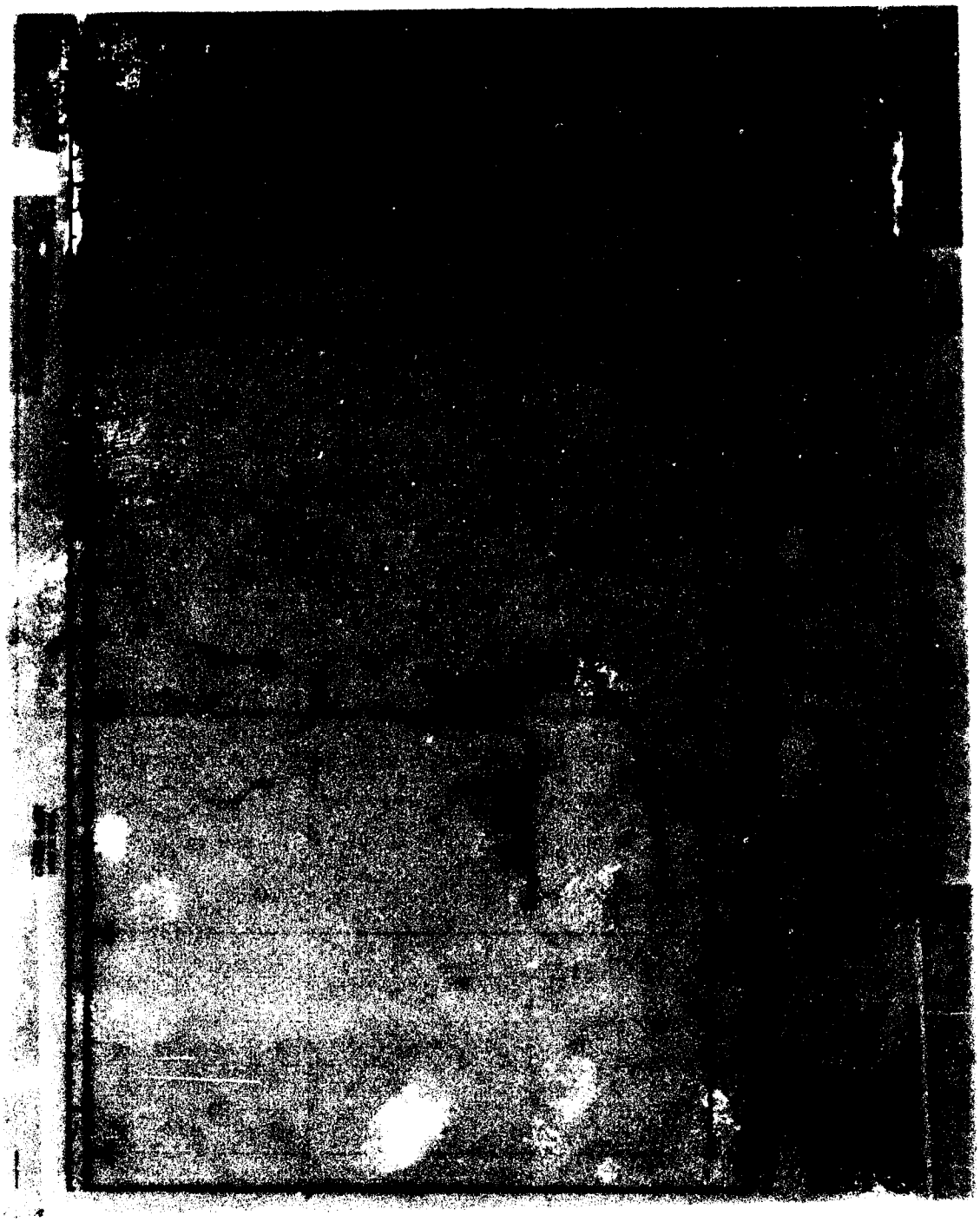


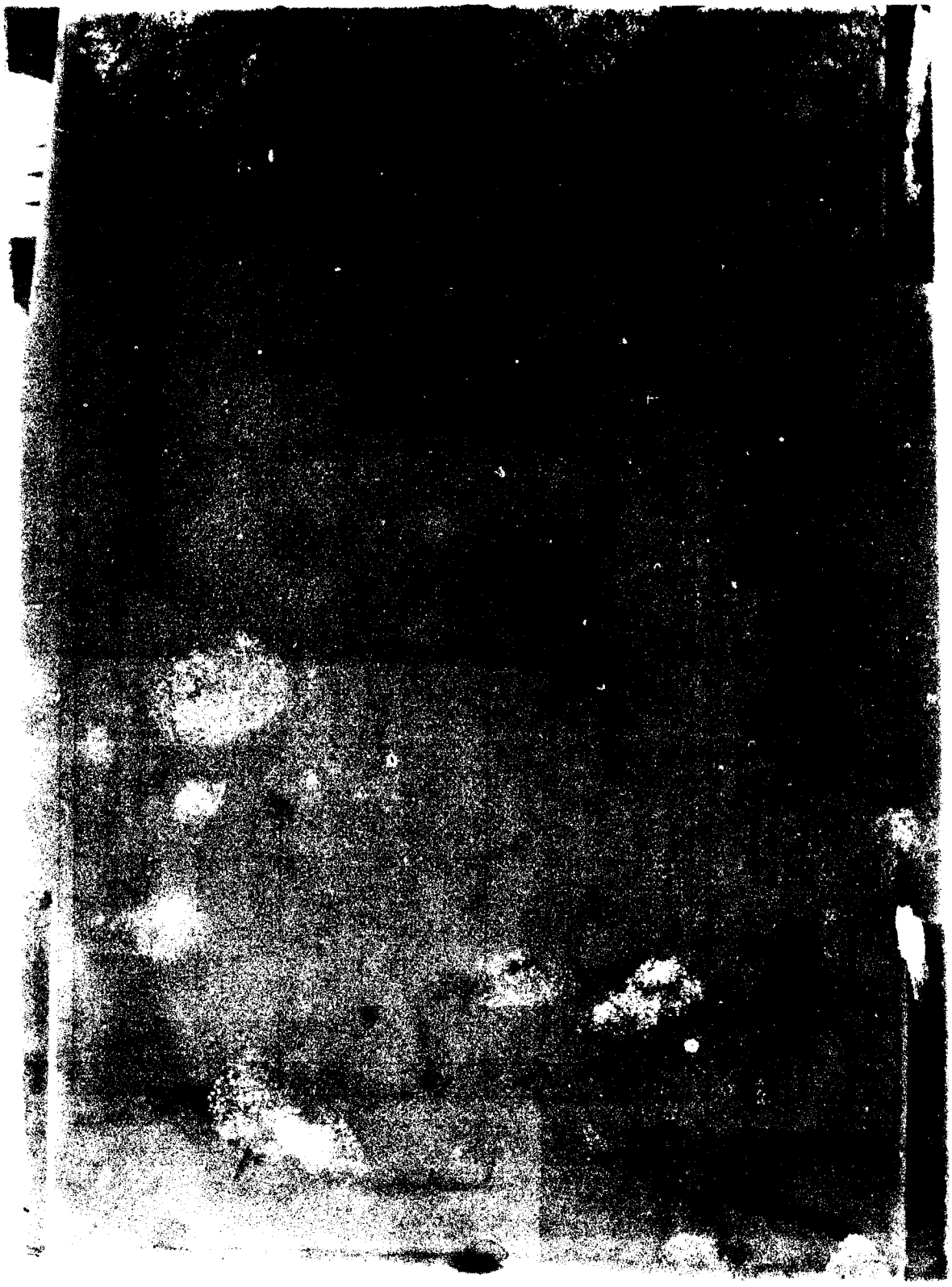


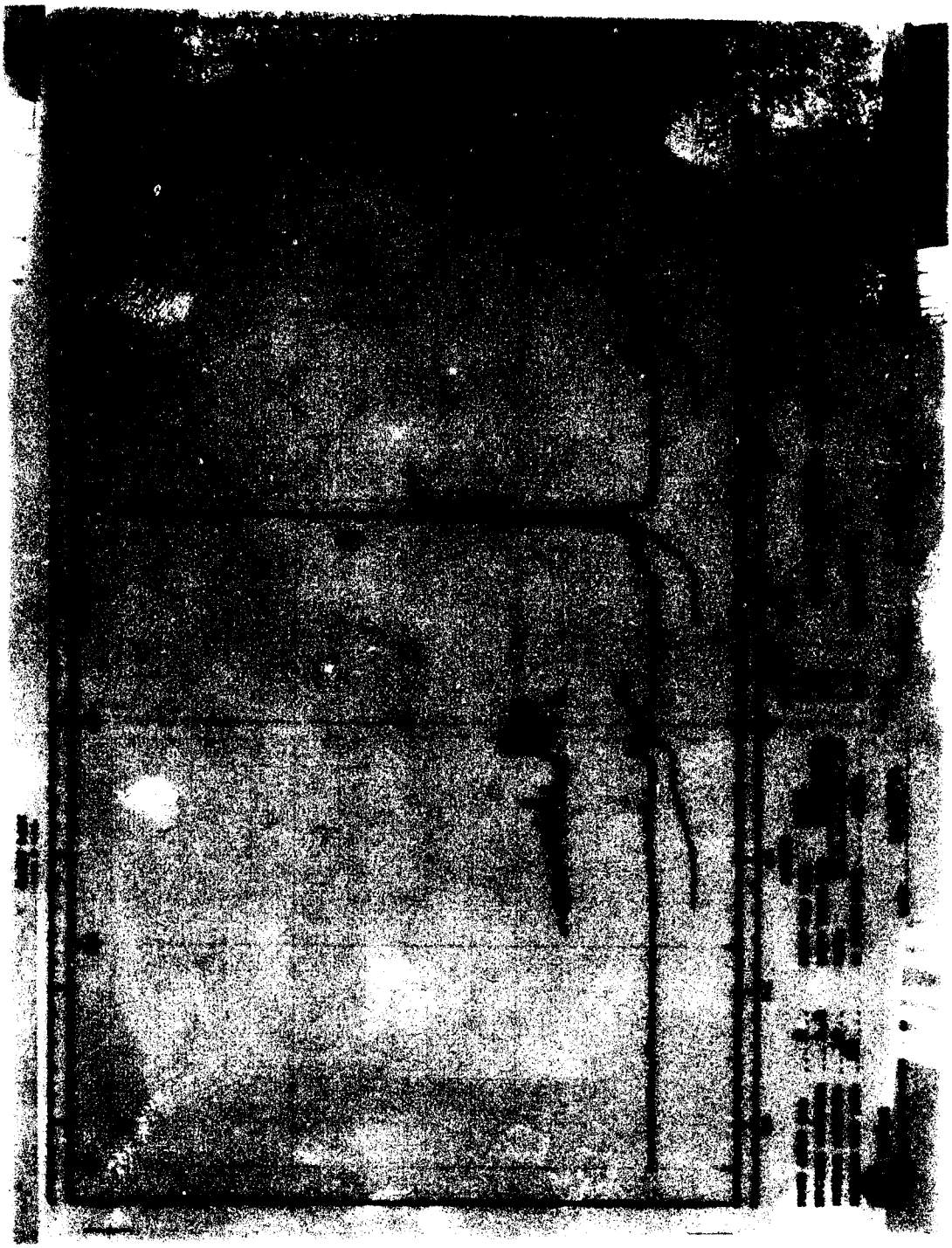










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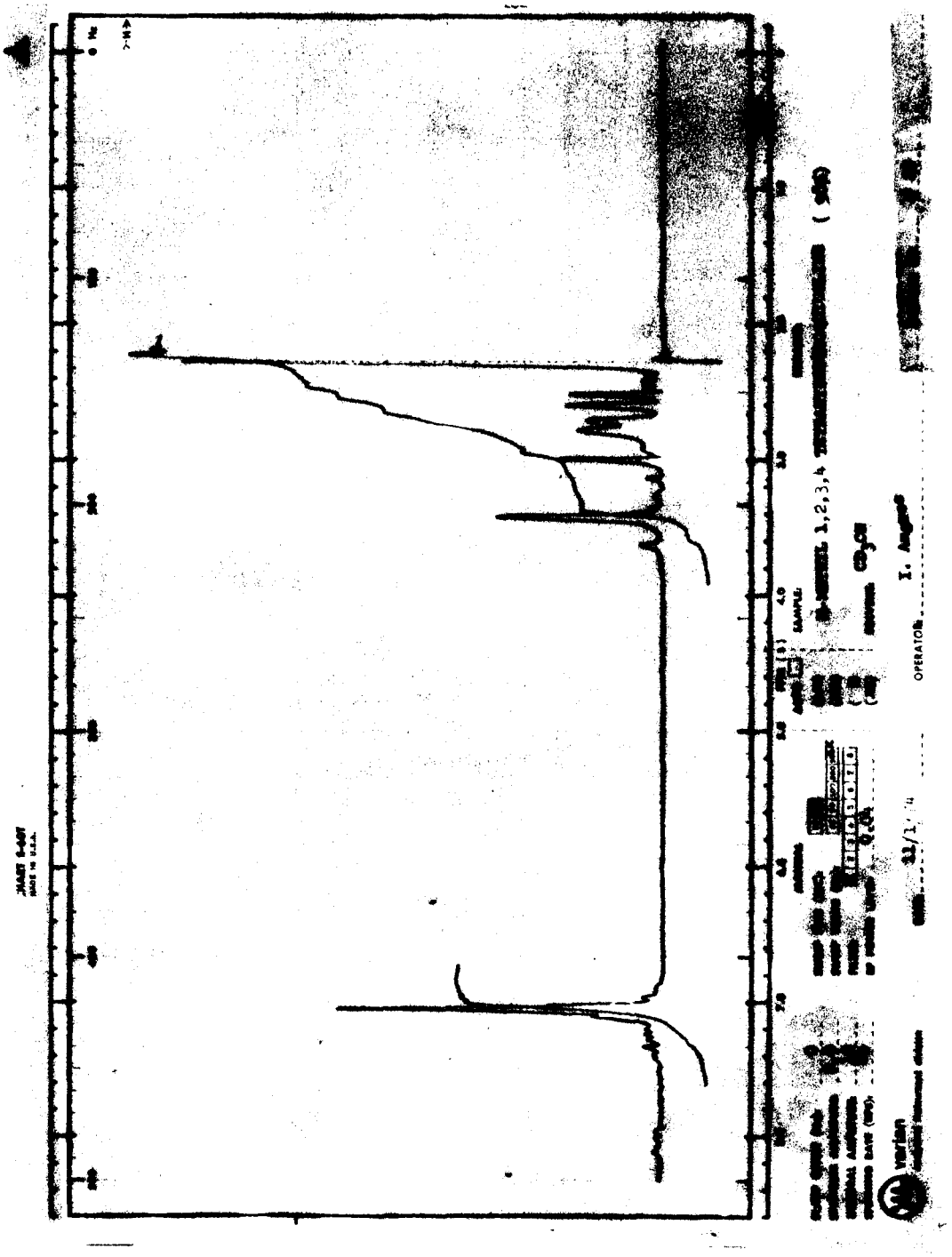

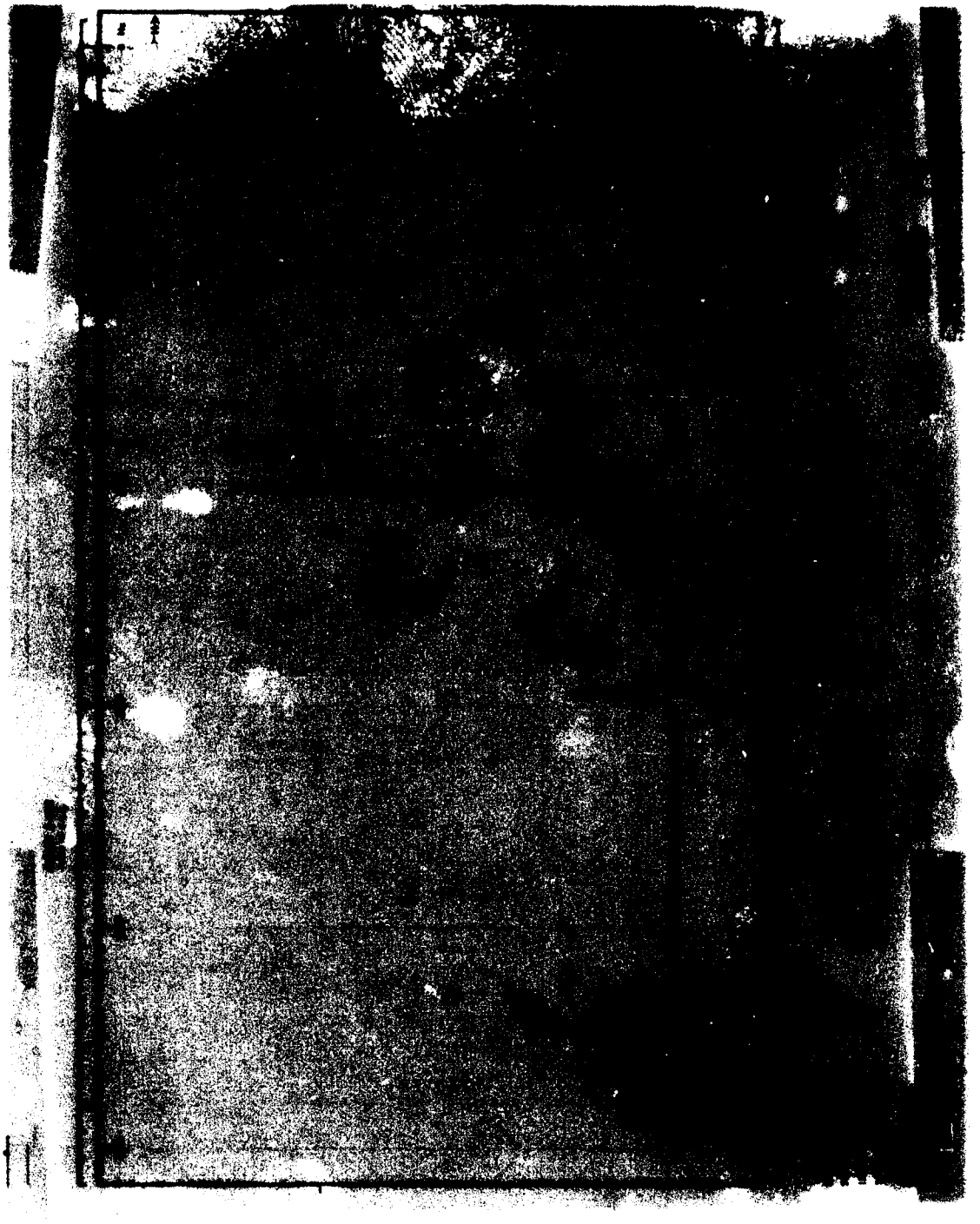


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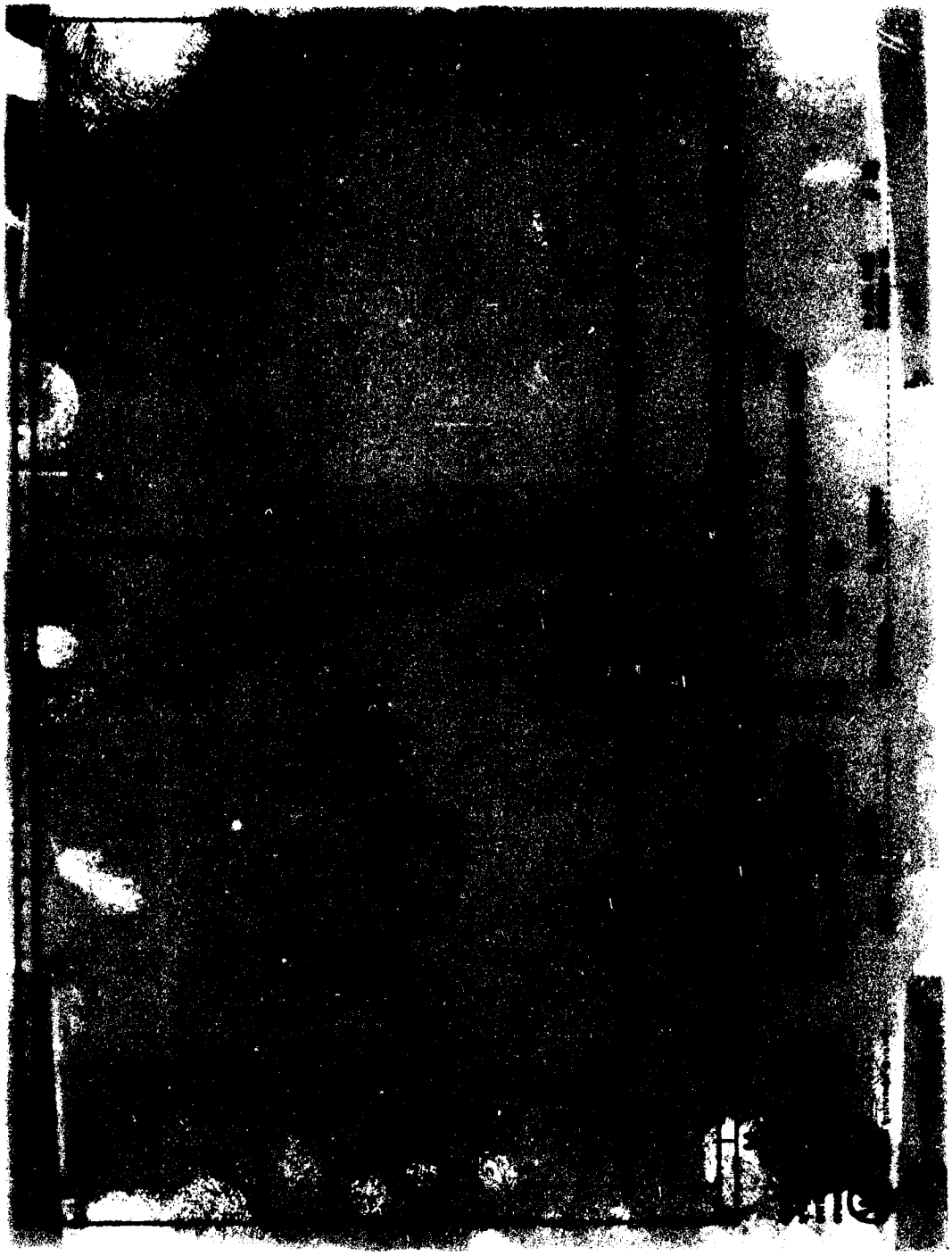

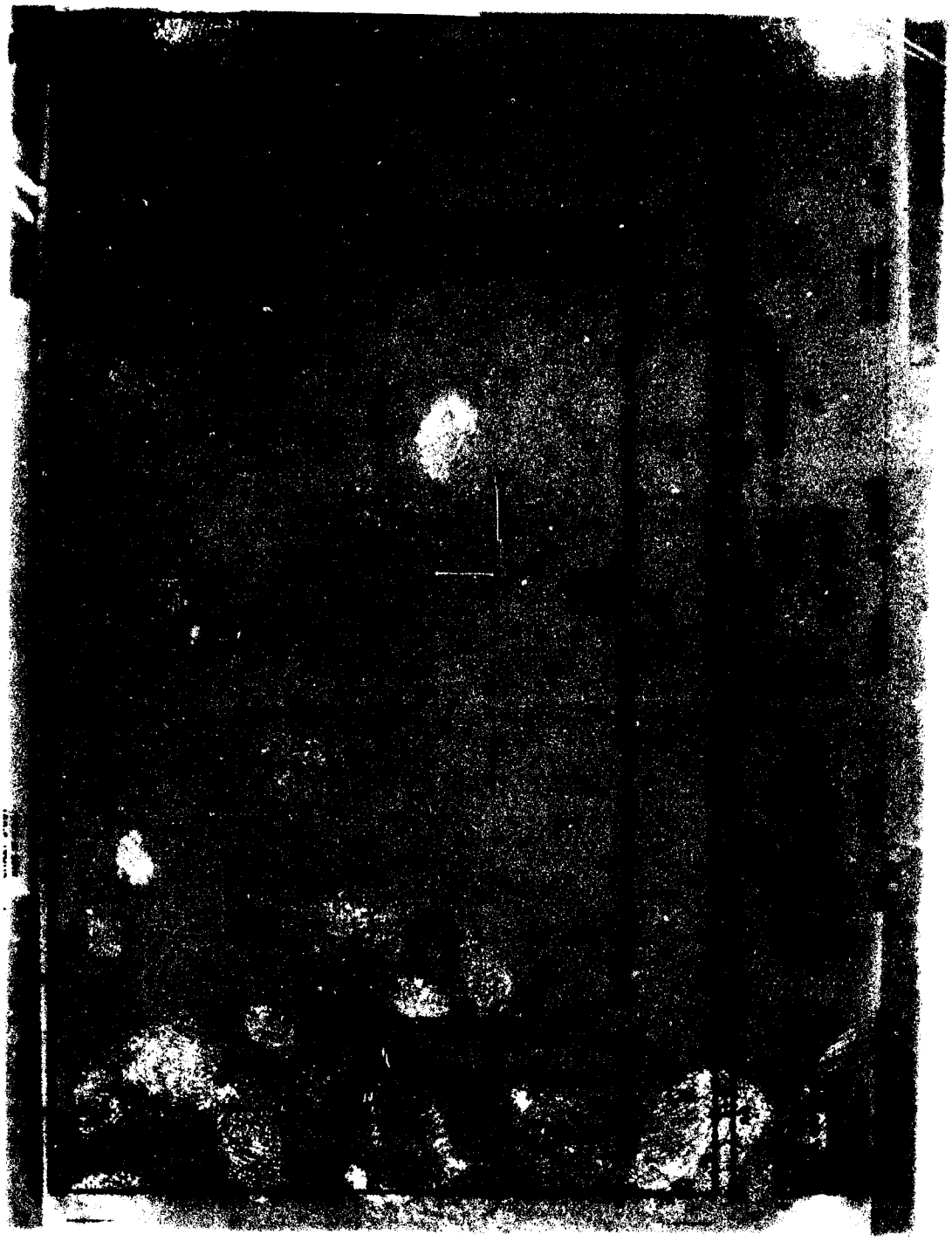

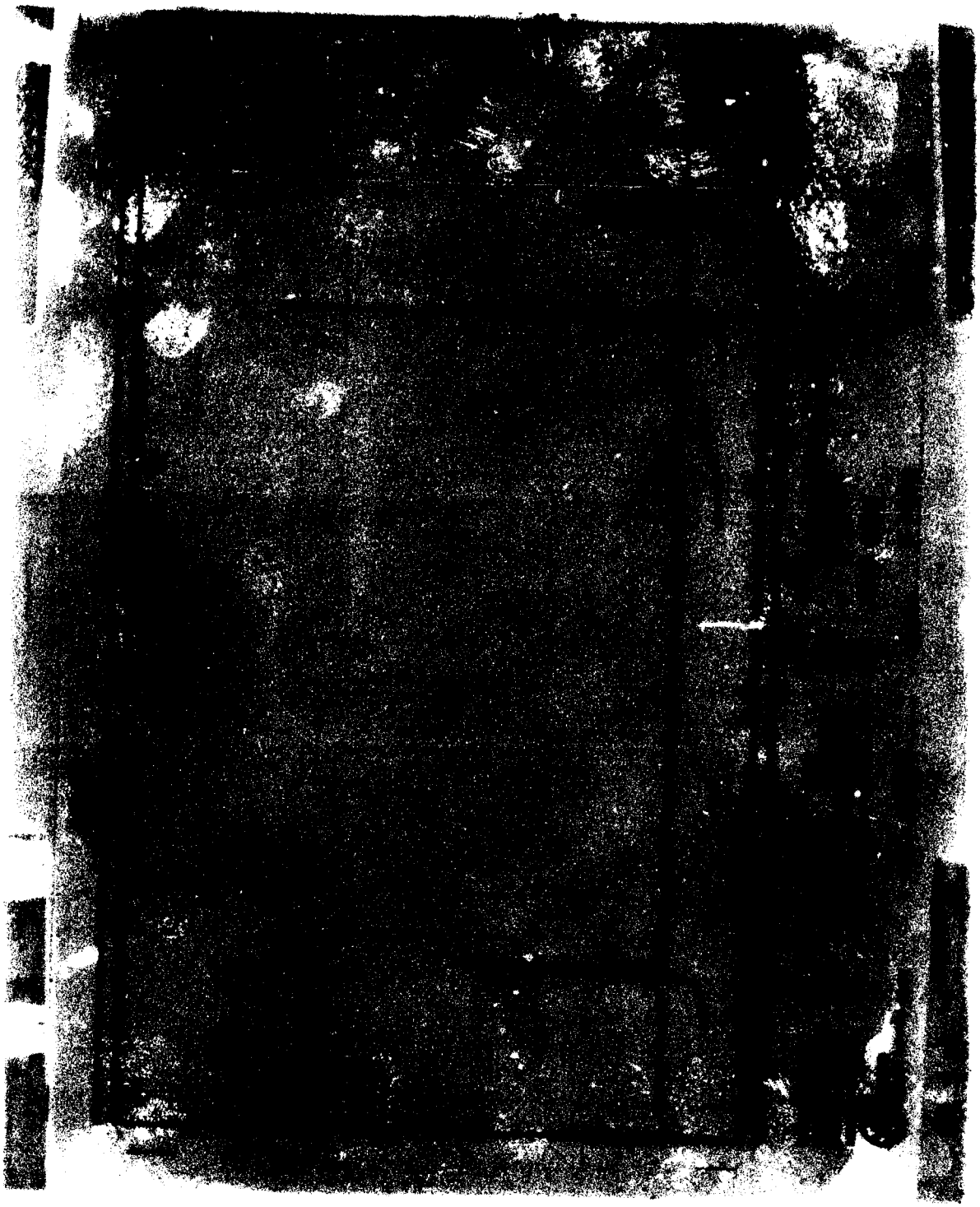

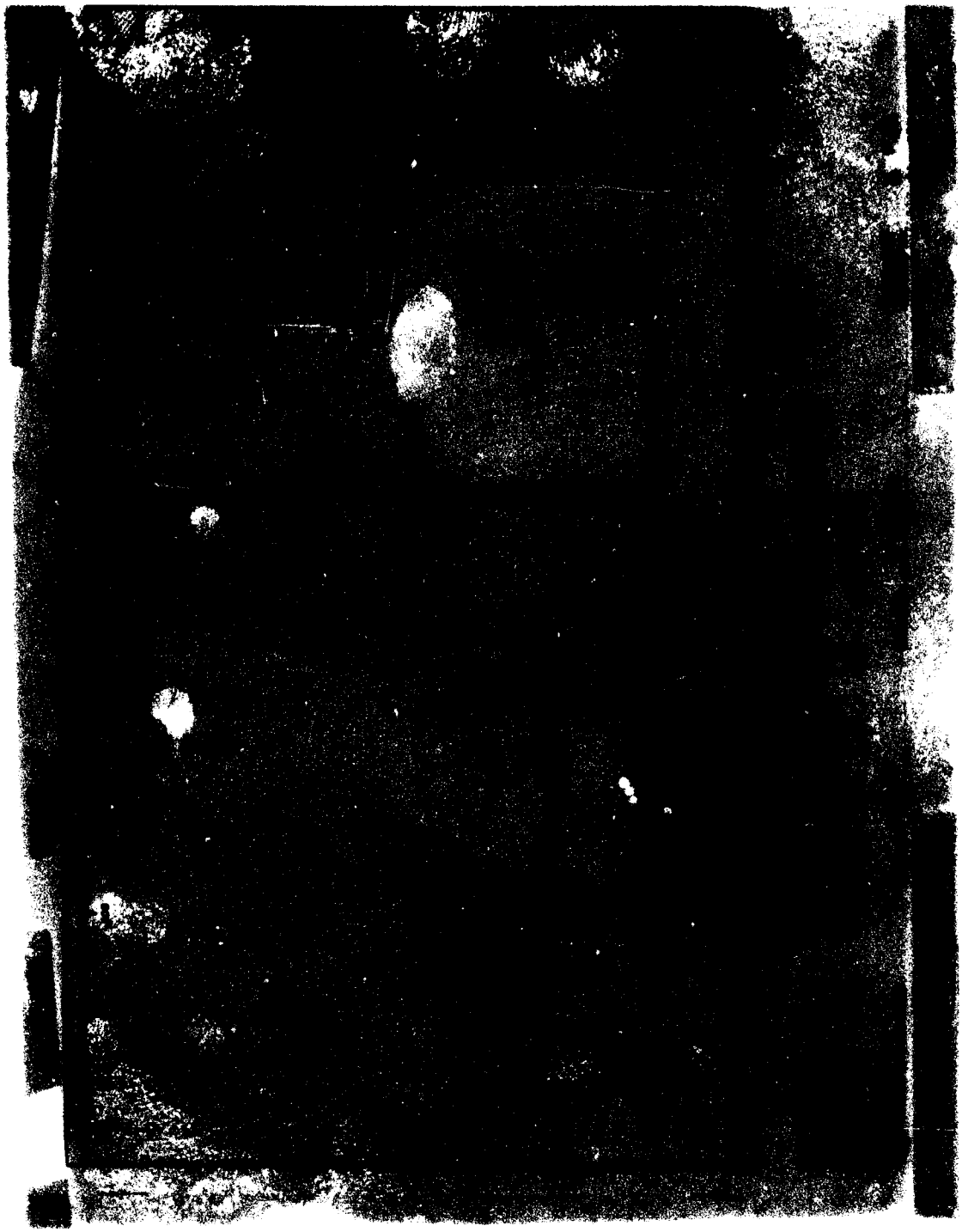

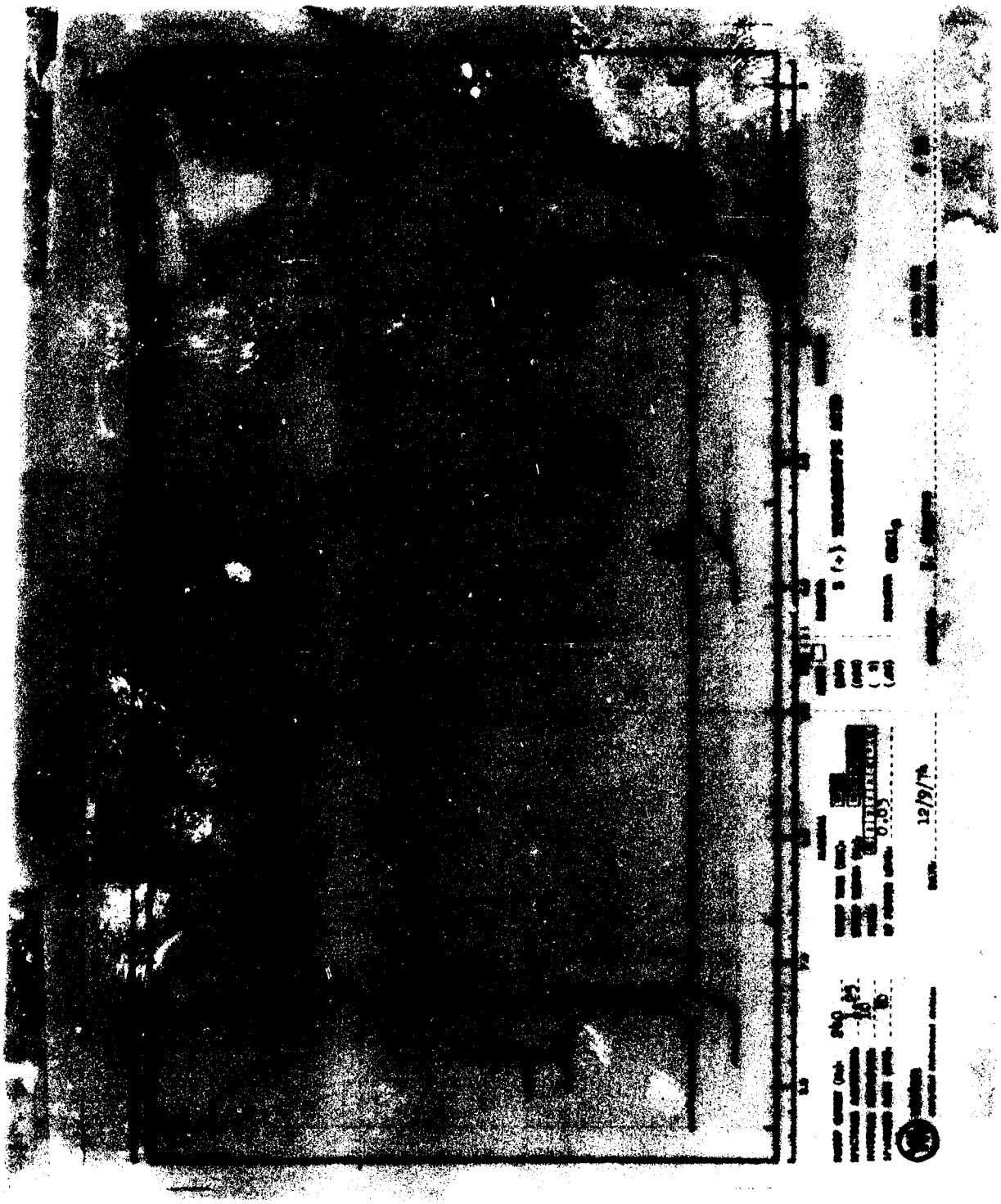

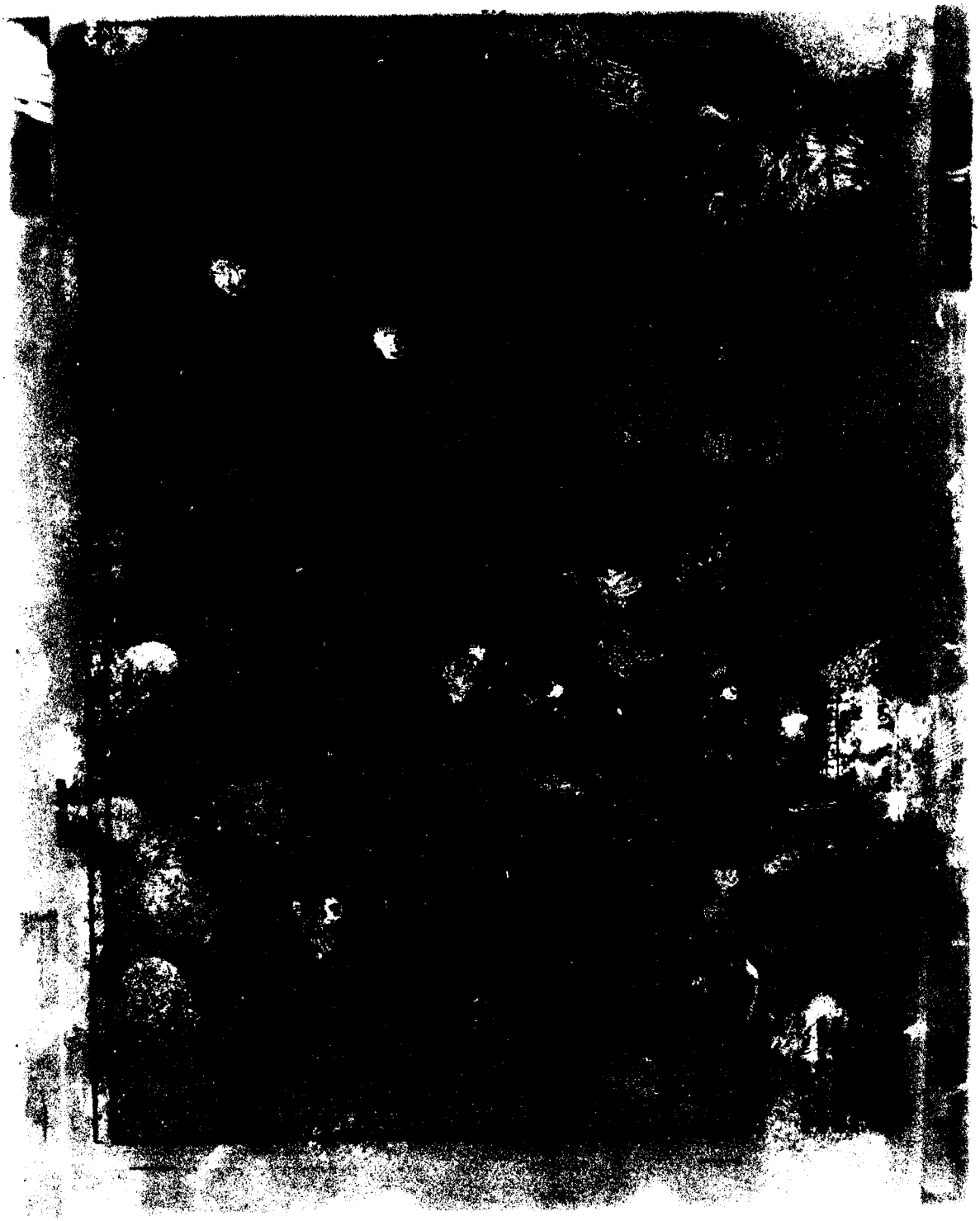

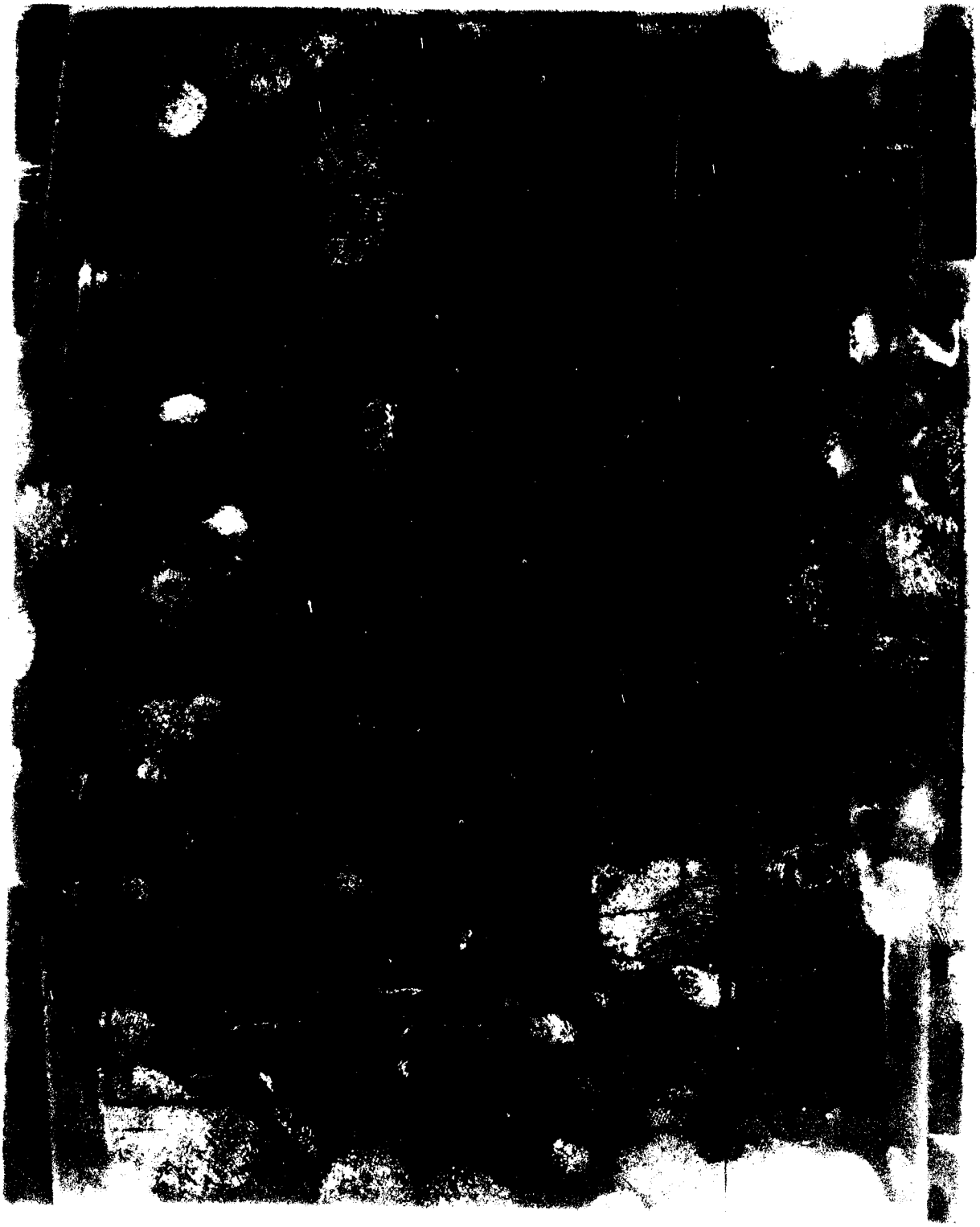

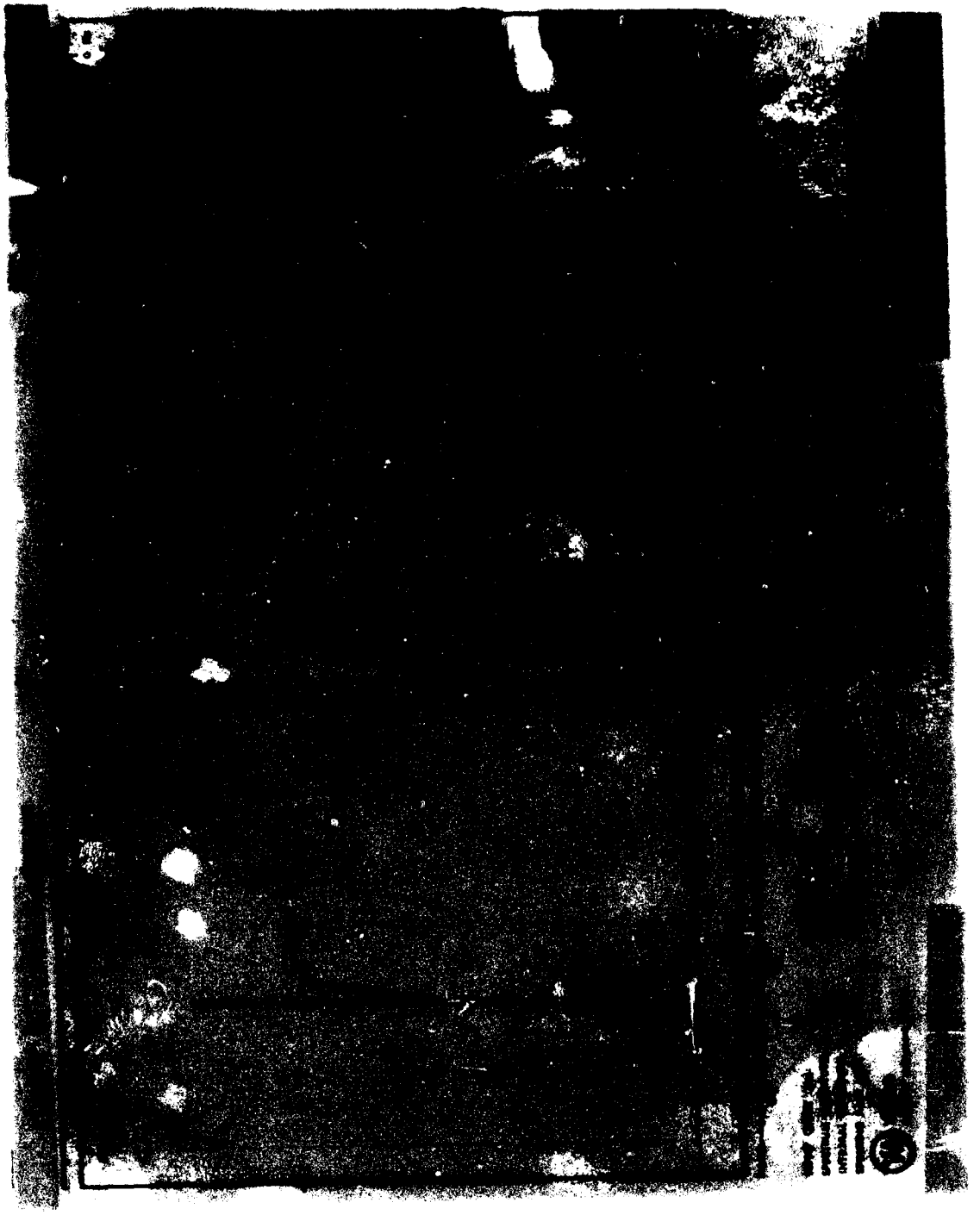

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