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The Reduction of Carbonyl Compounds by Sodium Naphthalenide

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WESTERN KENTUCKY UNIVERSITY
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THE REDUCTION OF CARBONYL COMPOUNDS
BY SODIUM NAPHTHALENIDE

A Thesis

Presented to

the Faculty of the Department of Chemistry

Western Kentucky University

Bowling Green, Kentucky

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

James W. Stinnett, Jr.

November 1971

THE REDUCTION OF CARBONYL COMPOUNDS
BY SODIUM NAPHTHALENIDE

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CHAPTER I

INTRODUCTION

Object:

The purpose of this investigation was to study the reactions of sodium naphthalenide with various aromatic carbonyl compounds, particularly aromatic aldehydes and ketones. Although sodium naphthalenide was first investigated in 1936 by Scott et al¹, the synthetic utility of this alkali metal adduct in organic chemistry has only recently been explored. It was thought that sodium naphthalenide might provide a synthetic advantage, as compared to sodium metal solutions, in the reduction of carbonyl functions to their respective glycols and/or alcohols.

Sodium Naphthalenide:

The alkali metals react with a large number of aromatic hydrocarbons in dimethyl ether, 1,2-dimethoxyethane or tetrahydrofuran by transferring one or two electrons to one molecule of hydrocarbon yielding intensely colored

radical anions. For example, naphthalene in THF will accept one electron from sodium to form an anion free radical,



the resulting intense green-colored compound being referred to as sodium naphthalenide. This reaction leads to a reversible equilibrium. The value of the equilibrium constant will be determined chiefly by the magnitude of the energy of solvation of the ions. Solvents like methyl ether or 1,2-dimethoxyethane are very favorable for solvation, whereas ethyl ether, for example is rather ineffective. Other alkali metals in the presence of polar solvents will also undergo the above equilibrium with naphthalene.

Reduction of a 0.1M solution of a hydrocarbon with sodium proceeds 99% or more provided

$$(E_0)_H \geq (E_0)_{\text{Na}} = +0.1 \text{ volt}^2$$

From the equilibrium condition in DME

$$(E_0)_{\text{Na}} + (RT/F) \ln(\text{Na}^+) = (E_0)_N + (RT/F) \ln \frac{(\text{naphthalene})}{(\text{naphthalene}^-)}$$

it can be derived that the standard potential of sodium is about +0.16 volt relative to the half wave potential of naphthalene.³ The relative electron affinities of a series of aromatic hydrocarbons in THF are shown in Table 1.⁴

TABLE 1

REDUCTION POTENTIALS FOR AROMATIC HYDROCARBONS IN THF

<u>Aromatic hydrocarbon</u>	<u>Reduction potentials</u>
Biphenyl	(0.0)
Naphthalene	0.066
Triphenylene	0.113
Phenanthrene	0.124
Anthracene	0.624

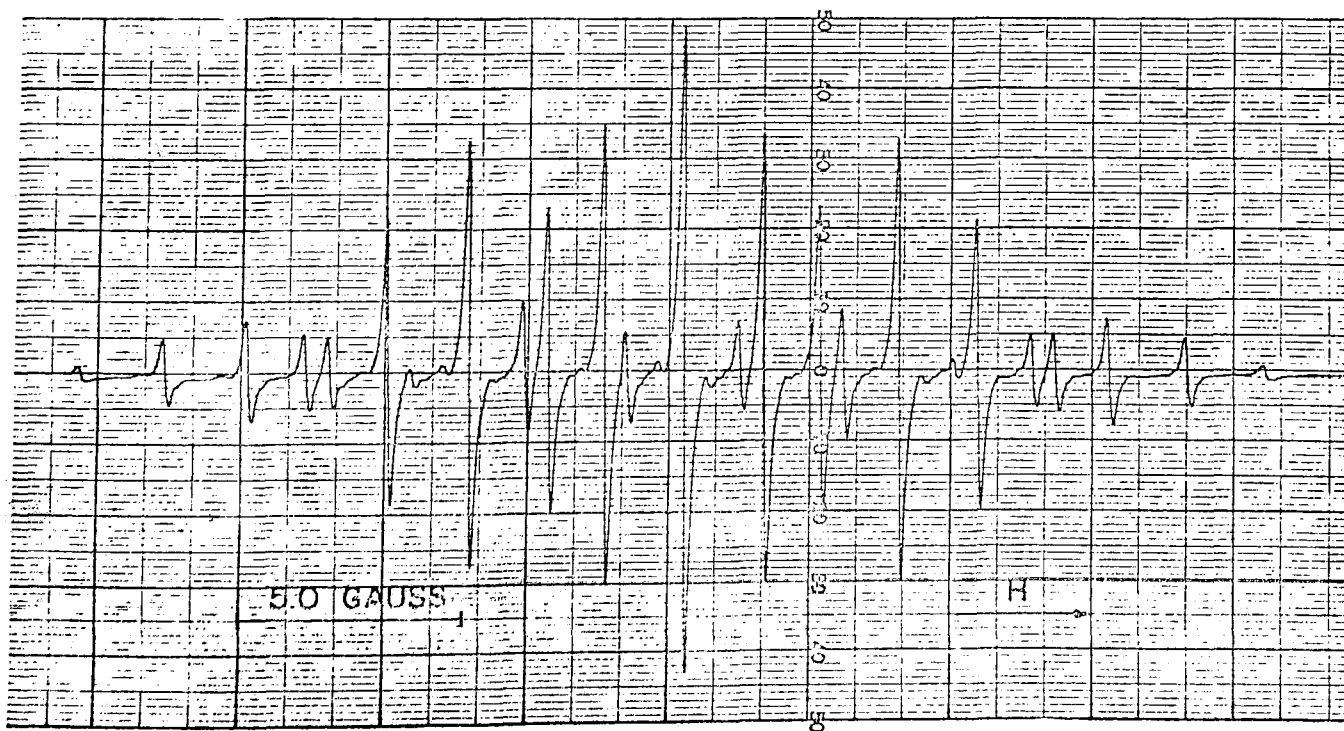
Naphthalene can be reduced to the dinegative ion by sodium when liquid ammonia is used as the solvent but only to the mononegative ion when the solvent is DME or THF.

This reaction arises through transfer of the valence electron of the sodium atom to the lowest energy molecular orbital available in the naphthalene molecule. In terms of the molecular orbital theory, this is the lowest energy antibonding orbital, and the unpaired electron is delocalized over the whole aromatic system. The Huckel molecular orbital approximations can be used to obtain a qualitative interpretation of the properties and electronic spectra of the naphthalenide radical anion.

The rate constants of electron transfer between naphthalene and its radical anion are in the range of 10^6 - 10^8 liter/mole-sec; the rate is dependent upon the solvent, the alkali metal, and most likely the electron affinity of the hydrocarbon and the photoelectric work function of the metal.⁵

Physical evidence for one electron transfer from sodium to naphthalene is provided by polarographic methods, magnetic susceptibility measurements and ESR spectra. The magnetic susceptibility of THF solutions of sodium naphthalenide measured at room temperature by Gouy's method indicate also that the monovalent anion is monomeric in solution with

one unpaired electron.⁶ The ESR spectra of sodium naphthalenide proves unambiguously that the added electron is not localized on a particular carbon atom. The resonance spectrum is not just a single line, but exhibits a remarkable fine structure. The magnitudes of the hyperfine splitting constants observed for the naphthalene radical anion are 4.95 and 1.865 gauss for the alpha and beta protons respectively. This ratio 2.80 is in excellent agreement with the ratio 2.62 of the squares of the coefficients of the alpha and beta protons in the HMO method. The charge density, as determined by the coefficients of the lowest vacant MO of naphthalene, is greatest at the alpha position. The ESR spectrum of sodium naphthalenide is shown in Plate 1.



In contrast to the solution of the neutral naphthalene molecule, the naphthalene radical anion is deeply green-colored, giving rise to electronic absorption spectrum in the visible region. Beer's law is obeyed in the concentration range of $0.130 \times 10^{-3}\text{M}$ to $8.67 \times 10^{-3}\text{M}$.

CHAPTER II

REVIEW OF LITERATURE

This chapter presents a review of literature on various aspects of the present investigation.

Reactions of Sodium Naphthalenide:

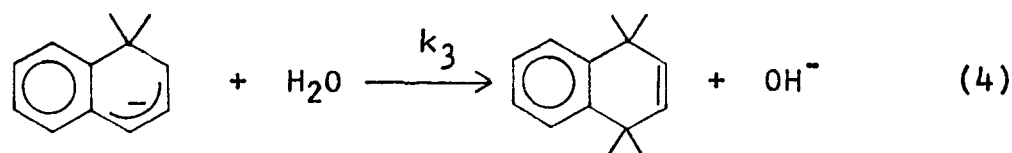
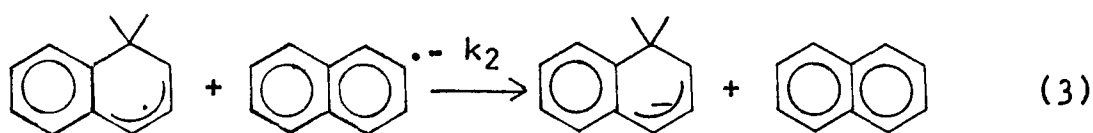
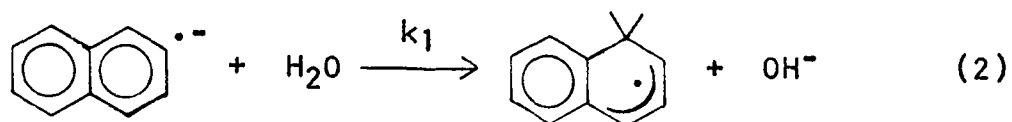
Solutions of sodium naphthalenide have both radical and ionic nature. They undergo a variety of reactions: equilibrium, substitution, oxidation-reduction, and polymerization initiation. Often these processes occur simultaneously. These reactions are the result of proton abstraction (naphthalenide acts as a base), electron transfer (naphthalenide acts as a reducing agent), or radical-radical coupling.

Sodium Naphthalenide as a Base:

In proton active solvents the radical anions become protonated as soon as they are formed. On addition of a proton donor such as water or alcohol to THF solutions of

sodium naphthalenide protonation will occur at the atom having the highest negative charge.

The reaction of sodium naphthalenide with water is one in which the initial step involves sodium naphthalene acting exclusively as a base. A mechanism of this reaction, proposed by Lipkin et al⁷, involves the following steps:



By rapid-mixing stopped flow devices the rate law has been established to be

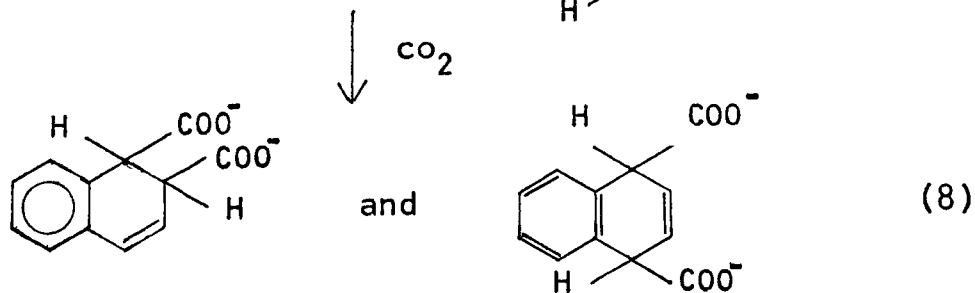
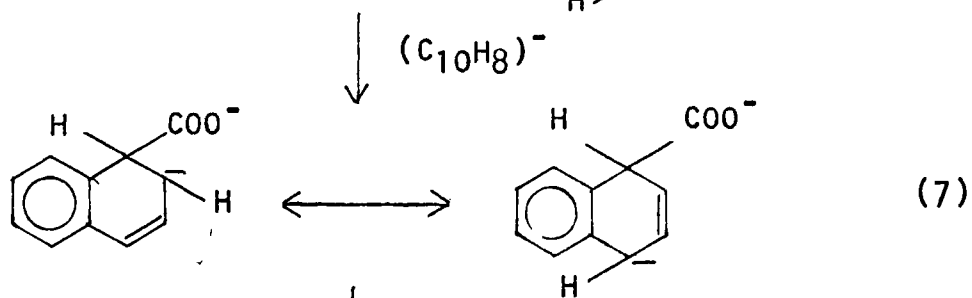
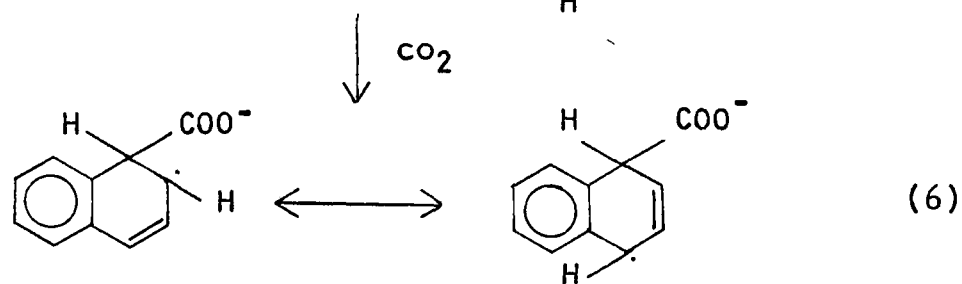
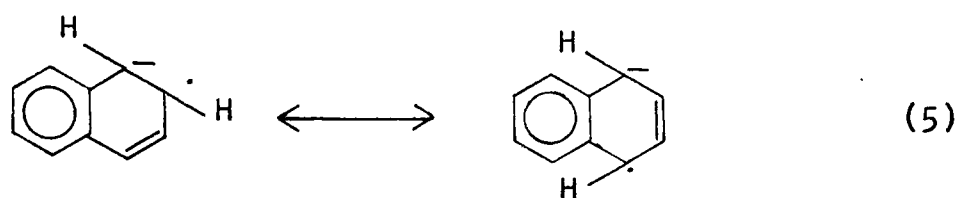
$$-d(\text{Nap}^{\bullet-})/dt = 2k_1(\text{Nap}^{\bullet-})(\text{H}_2\text{O}),$$

with a value of k_1 at 20° of $1.01 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ in THF.⁸

Thus the expected kinetics are overall second order, first order in naphthalenide and first order in water. This is in full agreement with the proposed mechanism of Lipkin.

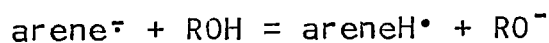
In the reactions of sodium naphthalenide with substances such as water or carbon dioxide two facts are predominate: first, dihydro or substituted dihydro

derivatives of the parent aromatic hydrocarbons are formed; second, in the absence of excess sodium metal, half of the original hydrocarbon is recovered unchanged, while in the presence of excess sodium the original hydrocarbon is completely converted to the dihydro derivative. A mechanism consistent with the above observations is illustrated by the reaction of carbon dioxide with sodium naphthalenide.⁹



Conversion of 5 (two possible resonance structures of the activated naphthalenide radical anion), to 6 is simply a reaction between a Lewis base and acid. The interchange of an electron between 6 and $(C_{10}H_8)^{\cdot -}$ to give 7 is assumed to be very rapid. The final step (7 \rightarrow 8), is assumed to be slow compared to (5 \rightarrow 6).

The formation and lifetimes of several aromatic anions in irradiated solutions of arenes in the aliphatic alcohols have been investigated by the pulse radiolysis technique.¹⁰ The aromatic anions show a fast decay which follows a first order rate law. The absolute rate constants for this decay, suggested to be a proton transfer from the alcohol,

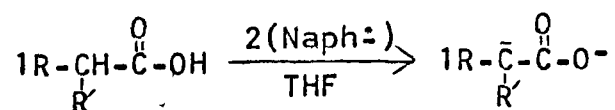


have been determined for four alcohols and three aromatic anions. The rate constants, which are found to be in the order $\text{CH}_3\text{OH} > \text{C}_2\text{H}_5\text{OH} \cong \text{C}_3\text{H}_7\text{OH} > (\text{CH}_3)_2\text{CHOH}$, show a close correlation with the acidity of the alcohols as measured by other means. The absolute rate constant has also been determined for the attachment reaction of the solvated electron in ethanol



H. Normant and B. Angelo¹¹ have studied the action of sodium naphthalenide on a variety of compounds containing active methylene groups or acidic hydrogens. Table 2 gives the products of the reactions between sodium naphthalenide and various compounds containing an acidic hydrogen. Sodium naphthalenide was sufficiently basic to abstract a proton from compounds such as biphenyl methane and fluorene. The carbanion formed by proton abstraction was allowed to condense with CO₂ or a carbonyl group.

Base catalyzed condensation reactions are effected by the action of sodium naphthalenide on several carboxylic acids, aliphatic and aromatic, followed by the addition of the appropriate aldehyde or ketone.¹² Some of these condensation reactions are illustrated in Table 3. The first step of this reaction involves the formation of a stable dianion:



which condenses with the carbonyl compound in the next step:



Hydrolysis of the condensed product gives the beta hydroxy carboxylic acid.

TABLE 2

THE ACTION OF SODIUM NAPHTHALENIDE ON COMPOUNDS
CONTAINING AN ACTIVE HYDROGEN

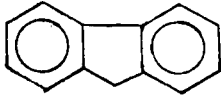
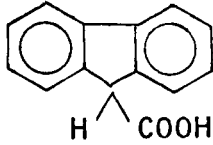
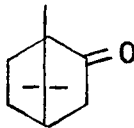
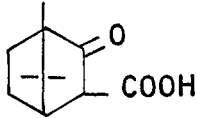
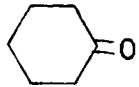
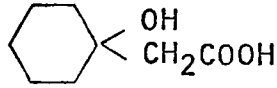
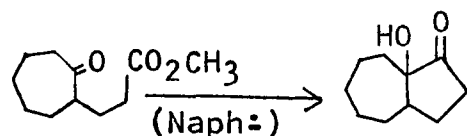
<u>Active Hydrogen Compound</u>	<u>Reactant</u>	<u>Product</u>
	CO_2	
$(\text{C}_6\text{H}_5)_2 \cdot \text{CH}_2$	CO_2	$(\text{C}_6\text{H}_5)_2 \cdot \text{CH} \cdot \text{COOH}$
$\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CN}$	CO_2	$\text{C}_6\text{H}_5 \cdot \underset{\text{COOH}}{\text{CH}} \cdot \text{CN}$
	CO_2	
$\text{CH} \equiv \text{CH}$	CO_2	$\text{CH} \equiv \text{C} \cdot \text{COOH}$
$\text{CH} \equiv \text{CH}$	CH_3CHO	$\text{CH}_3 \cdot \text{CHOH} \cdot \text{C} \equiv \text{H}$

TABLE 3

CONDENSATION OF CARBOXYLIC ACIDS WITH CARBONYL COMPOUNDS
IN THE PRESENCE OF SODIUM NAPHTHALENIDE

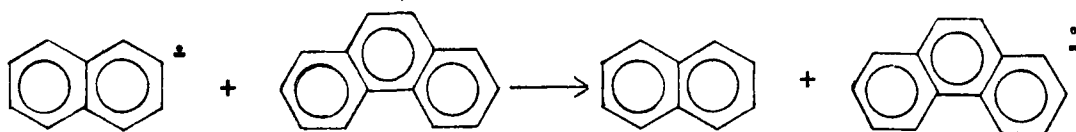
<u>Carboxylic Acid</u>	<u>Carbonyl Derivative</u>	<u>Product</u>	<u>% Reduction</u>
CH_3COOH	$\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$	$\begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_5-\text{C}-\text{CH}_2\text{COOH} \\ \\ \text{C}_6\text{H}_5 \end{array}$	58
CH_3COOH			38
CH_3COOH	$\text{CH}_3\text{CO}(\text{CH}_2)_4\text{CH}_3$	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2-\text{C}-\text{CH}_2\text{COOH} \\ \\ (\text{CH}_2)_4\text{CH}_3 \end{array}$	37.3
CH_3COOH	$\text{CH}_3(\text{CH}_2)_6\text{CHO}$	$\text{CH}_3(\text{CH}_2)_6\text{CHOHCH}_2\text{COOH}$	80
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	$\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$	$\begin{array}{c} \text{HO} \quad \text{C}_2\text{H}_5 \\ \quad \\ \text{C}_6\text{H}_5-\text{C}-\text{CH}-\text{COOH} \\ \\ \text{C}_6\text{H}_5 \end{array}$	60

Synthesis of fused ring bicyclic systems by an acyloin type condensation is accomplished by the action of sodium naphthalenide on keto esters. An example is the addition of methyl- β -(2-ketocycloheptane)propionate to a THF solution of sodium naphthalenide to form 7-hydroxy-8-keto-bicyclo(5.3.0)decane.¹³



Electron Transfer Reactions of Sodium Naphthalenide:

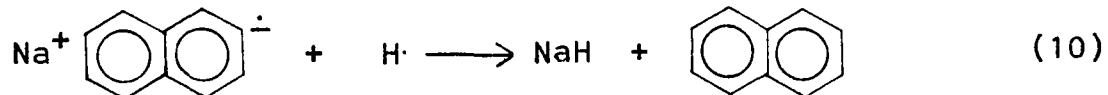
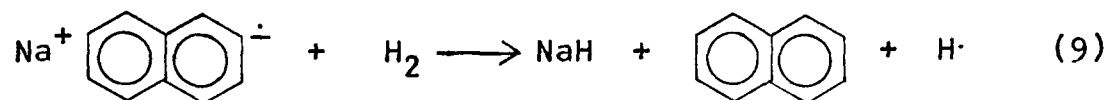
Potentiometric titration experiments of various aromatic hydrocarbons with sodium naphthalenide provide excellent examples of the electron transfer nature of the naphthalenide radical anion. In these reactions sodium naphthalenide transfers an electron to another aromatic hydrocarbon such as phenanthrene.



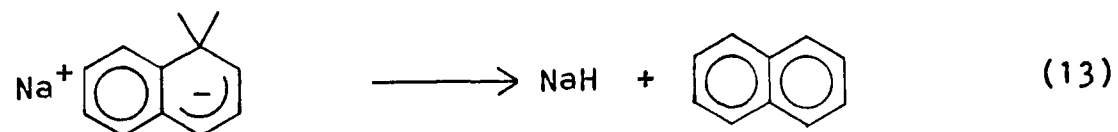
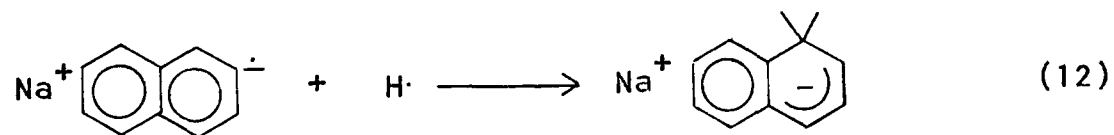
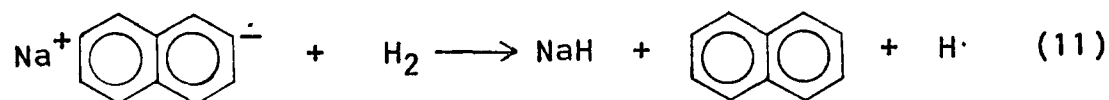
Reduction potentials for the aromatic hydrocarbons with respect to naphthalene are determined in this manner.

THF solutions of sodium naphthalenide absorb molecular hydrogen resulting in the production of sodium hydride and naphthalene in stoichiometric amounts.¹⁴ Two reasonable mechanisms for the reaction have been proposed (9-13).

Mechanism I

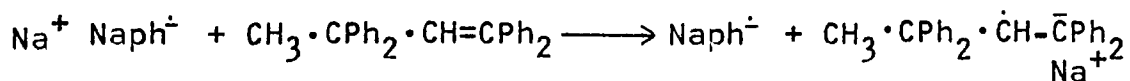


Mechanism II

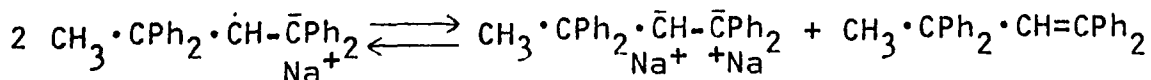


While both schemes involve initial electron transfer to molecular hydrogen to give hydride and a hydrogen atom (9,11), they differ in the subsequent steps. Mechanism I involves reduction of the hydrogen (10) whereas Mechanism II involves addition of the hydrogen radical to the radical anion, followed by loss of hydride to give the observed products. Studies using deuterium D_2 gas indicate that both mechanisms are operative.

On mixing an equimolar solution of sodium naphthalenide with 1,1,3,3-tetraphenylbut-1-ene or tetraphenylethylene rapid electron transfer occurs to form the radical ion.¹⁵

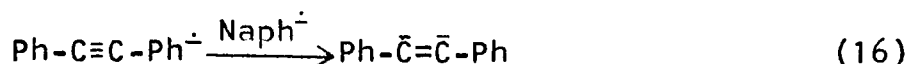
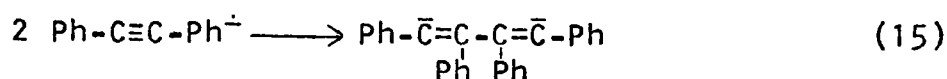
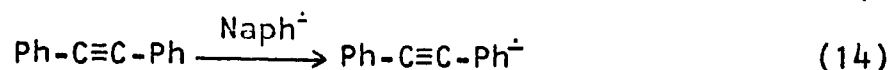


Because of steric hindrance, this radical ion does not dimerize, but disproportionates to give the dianion and the olefin.

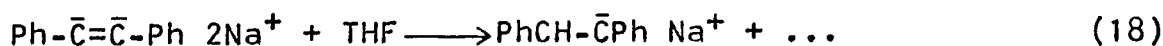
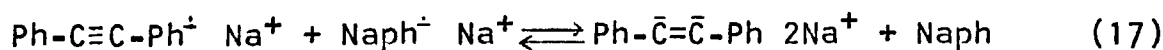


Hydrolysis of the dianion results in 1,1,3,3-tetraphenylbut-1-ene corresponding to 85% of the original olefin; 1,1,3,3-tetraphenylbutane corresponding to 10% of the original olefin; and 1,1-diphenylethane corresponding to 5% of the original olefin.

The reaction of biphenylacetylene with sodium naphthalenide has been reported by A. D. Dadley and A. G. Evans.¹⁶ The mechanism proposed by Evans and Dadley for this reaction involves an initial rapid electron transfer (14) with the formation of either the dimer (15) or the monomer dianion (16).

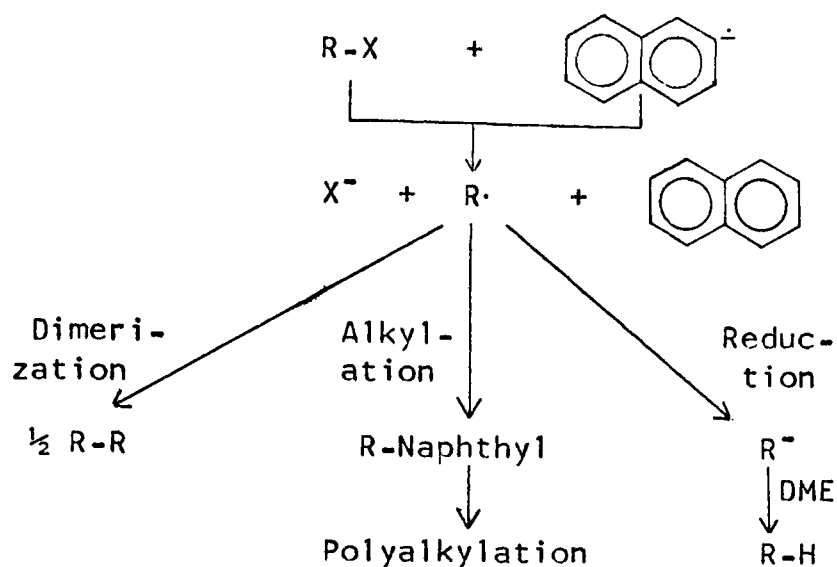


However studies with deuterated methanol as a protonation agent in step 16 have raised doubt as to the validity of the above mechanism. Levin et al have, with the help of spectrophotometric data and the results of deuteration proposed the following mechanism.¹⁷



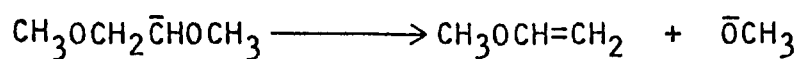
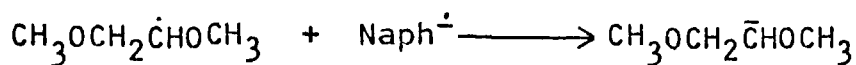
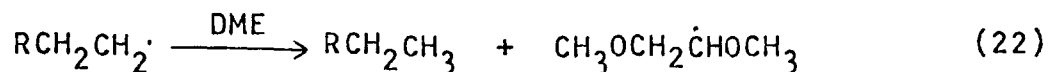
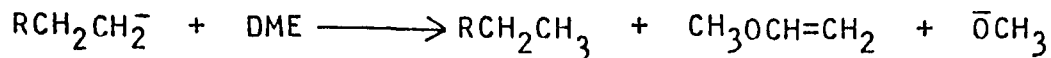
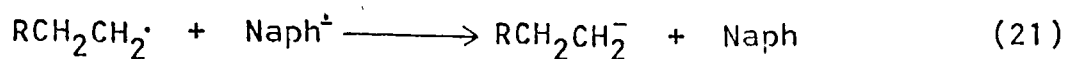
The simple electron transfer mechanism proposed by Dadley and Evans demands the formation of PhCD:CDPh, whereas the mechanism proposed by Levin calls for the formation of PhCH:CDPh which is indeed found in the reaction products.

Treatment of sodium naphthalenide with alkyl halides in 1,2 dimethoxyethane leads to oxidation-reduction, alkylation, and dimerization products.¹⁸

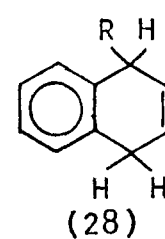
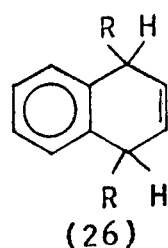
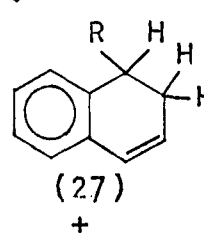
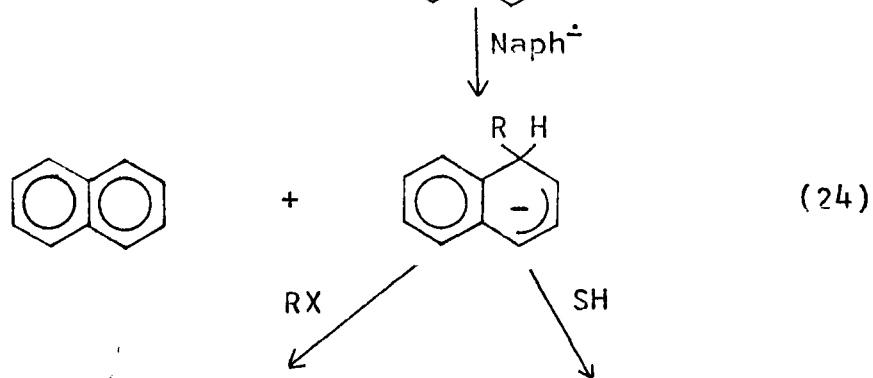
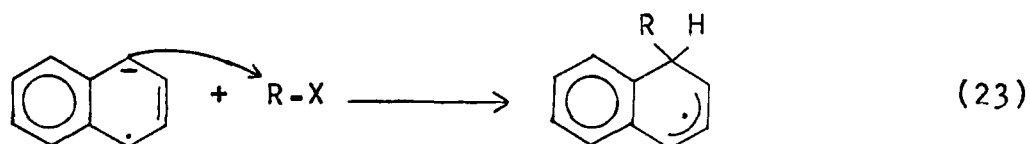


All four alkyl halides (fluorides, chlorides, bromides, and iodides) involve both alkyl radicals and alkyl anions as intermediates. Alkyl halide reduction products R-H arise through disproportionation or successive electron transfer reactions. The reaction of sodium naphthalenide with n-propyl and n-pentyl halides, like other halides, results in a rather large difference in yield between the reduction and oxidation products (Table 4). Obviously only part of the reduction products can be accounted for by a disproportionation of the radical (20). Two mechanisms, via the anion (21) and the radical (22), have been suggested. Studies on 5-hexenyl fluoride indicate that the more likely path is via the anion (21).



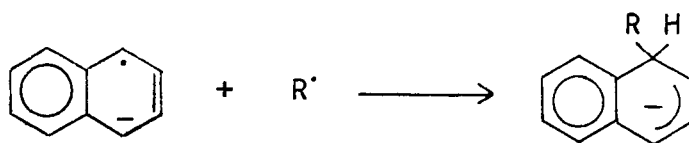


Diverse mechanisms have been suggested to account for the formation of the alkylation products. Lipkin proposes an initial $\text{S}_{\text{N}}2$ attack on the alkyl halide by a nucleophilic radical anion (23).¹⁹

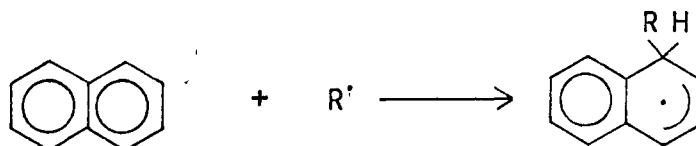
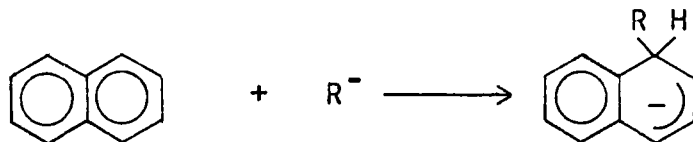


SH = solvent

Subsequent reduction of the resulting free radical leads to a carbanion (24), which can attack another molecule of alkyl halide to form the products 25 and 26 and/or abstract a proton from the solvent to form 27 and 28. Another mechanism proposes free radical type combination of an alkyl free radical with the aromatic radical anion as the initiation step by which alkylation takes place.



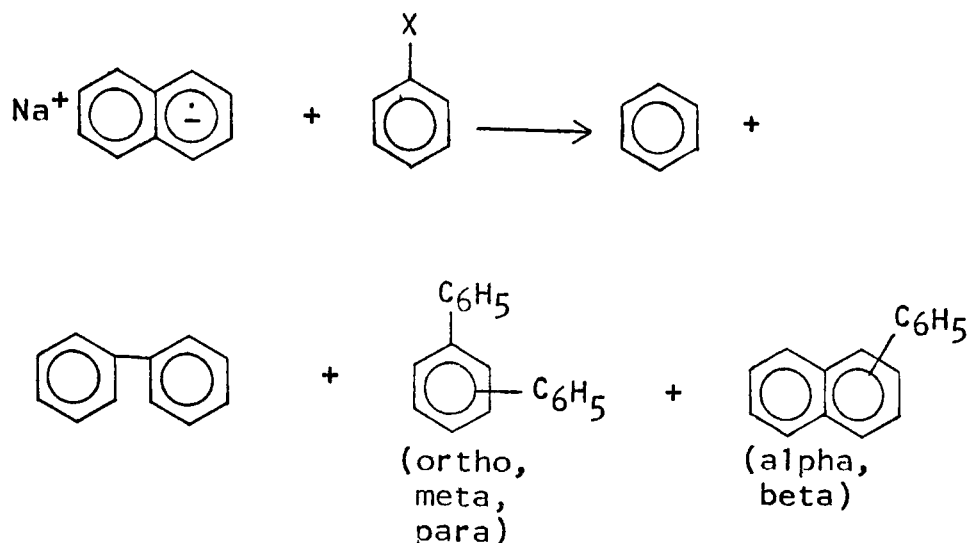
Two additional variations postulate attack by an alkyl radical or alkyl anion on naphthalene. Both reactions lead to intermediates common to the other mechanisms.



Preliminary evidence is more in accord with the combination of two radicals as the mechanism by which the formation of alkylation product is initiated.

The reaction of sodium naphthalenide with halobenzene (F, Cl, Br, and I) in THF has been studied by T. C. Cheng (Table 5).²⁰

The major products of this reaction are as follows:



where X = F, Cl, Br, and I.

The above reaction could proceed by an anionic, radical, or combination anionic-radical mechanism. From analysis of the products by D_2O treatment it appears that the mechanism is predominately radical in nature.

The reaction of sodium naphthalenide in THF with ethyl laurate has been reported by Machtinger.²¹ Following hydrolysis of the above THF solution monolaurylnaphthalene was found in 60% yield.

Closson has reported the cleavage of sulfonamides of secondary amines by sodium naphthalenide.²² Examination of the reaction of several sulfonamides with sodium naphthalenide at room temperature in DME reveals that 2-6 equivalents of anion are required for complete cleavage of one equivalent

of sulfonamide to the corresponding amine. However at -60° complete cleavage of arenesulfonamides of secondary amines requires exactly two equivalents of sodium naphthalenide (Table 6). On analysis of the products of the above reactions at low temperature, the sodium salt of the amine and sodium arenesulfonate are observed. By analysis of competitive reactions, the rate law of the first step has been deduced as

$$\text{rate} = k(\text{radical anion})(\text{sulfonamide})$$

In the reaction of sodium naphthalenide with the toluenesulfonamide of p-toluidine, electron transfer and cleavage are considerably faster than acid-base reaction with the acidic proton.

Treatment of alkyl toluenesulfonates with sodium naphthalenide in THF results in reconversion of toluenesulfonates to alcohols (O-S cleavage), Table 7.²³ The mechanism of this reaction is probably similar to that proposed by Kovacs and Ghatak for the sodium-liquid ammonia cleavage of toluenesulfonamides.

The reductive cleavage of various aliphatic, allylic, and cyclic ethers has been reported by Benjamin Angelo (Table 8).²⁴

TABLE 4

YIELD OF ALIPHATIC HYDROCARBONS IN THE REACTION
OF SODIUM NAPHTHALENIDE WITH RCH_2CH_2X

X	R	% Yield of $R(CH_2)_4R$	% Yield of RCH_2CH_3	% Yield of $RCH=CH_2$
Cl	$CH_3(CH_2)_2$	0	44	0
Br	$CH_3(CH_2)_2$	5.0	29	0
I	$CH_3(CH_2)_2$	56	17	3.7
I	$CH_3(CH_2)_4$	50	22	6

TABLE 5

RELATIVE AMOUNTS OF IDENTICAL PRODUCTS FROM THE REACTION
OF SODIUM NAPHTHALENE WITH HALOBENZENE AFTER HYDROLYSIS^a

Type of X ^b	NaNp ^c X ^b	Temp, °C	% benzene	% bi-phenyl	% o-terphenyl	% m-terphenyl	% p-terphenyl	% alpha phenyl Np	% beta phenyl Np
Bromobenzene	1/1	-60	87.0	8.3	1.0	0.1	0.1	1.2	0.8
Bromobenzene	2/1	-60	86.6	6.3	0.4	0.1	0.1	0.6	0.5
Bromobenzene	1/1	27	89.2	6.3	0.5	0.3	0.4	0.8	0.7
Bromobenzene	2/1	27	85.3	8.0	1.2	0.4	0.5	1.6	9.7
Chlorobenzene	2/1	-60	81.4	8.7	1.5	0.3	0.2	2.1	1.4
Iodobenzene	1/1	27	86.3	9.3	0.6	0.3	0.2	0.9	0.3

^aA % yield is based on halobenzene consumed. ^bX = halobenzene (37.5 mmol/50 ml of THF).
^cNaNp = sodium naphthalene (75 mmol or 37.5 mmol/50 ml of THF; Np = naphthalene).

TABLE 6

CLEAVAGE OF SULFONAMIDES WITH SODIUM NAPHTHALENE^a

Sulfonamide (mp, °C)	Yield of amine, %
N-p-Tolylbenzene-	99
N-p-Tolyl-p-toluene-	87
N-p-Anisyl-p-toluene-	98
N-Octyl-p-toluene-	98
N-(m-Chlorophenyl)-p-toluene-	94
N-p-Toluenesulfonylpiperidine	82

^aReactions were carried out by treating sulfonamide with 3-6 equiv. of sodium naphthalene in dimethoxyethane at 25° under N₂ or Ar and stirring the mixture for about 1 hr. before quenching with water.

TABLE 7

CLEAVAGE OF TOLUENESULFONATES WITH SODIUM NAPHTHALENE

Toluenesulfonate	Sodium naphthalene,	Yield of alcohol, %
Cyclopentyl	2-6	100
cis-4-Cyclooctenyl	6	98
trans-2-Phenylcyclohexyl	6	93
Phenyl	6	99
Stearyl	6	99
Neopentyl	5	85

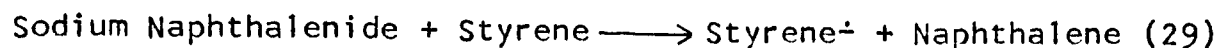
TABLE 8

CLEAVAGE OF ETHERS WITH SODIUM NAPHTHALENIDE

<u>Ether</u>	<u>Product</u>	<u>% yield</u>
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$	$(\text{CH}_2=\text{CH}-\text{CH}_2)_2$	30
$(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{O}$	$(\text{CH}_2=\text{CH}-\text{CH}_2)_2$	50
$\text{C}_6\text{H}_5-\text{CH}_2-\text{O}-(\text{CH}_2)_3-\text{CH}_3$	Toluene	Traces
$\text{C}_6\text{H}_5-\text{O}-\text{CH}_2-\text{C}_6\text{H}_5$	Toluene Phenol	30 44
$\text{C}_6\text{H}_5-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2$	Phenol $(\text{CH}_2=\text{CH}-\text{CH}_2)_2$	60 40

Polymerization Reactions of Sodium Naphthalenide:

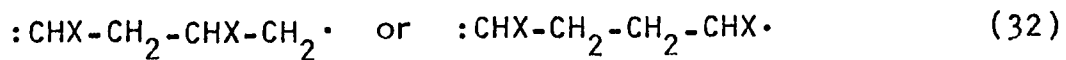
The same type of electron transfer between naphthalenide and anthracene seems to be responsible for the initiation of polymerization by sodium naphthalenide and styrene.²⁵



The negative monomer ions formed by the above reaction (29) may be represented by (30) or (31).



With excess monomer both ends of (30) or (31) propagate polymerization, each by a different mechanism, one end growing as a radical, the other as a carbanion. After addition of the first monomeric unit to either end, a true separation of electrons takes place and species like (32) are formed.



The radical ends are short-lived. At low temperature they dimerize and consequently species (33) are formed.



Inspection of species (33) suggests that they do not terminate, and thus propagation should continue until all the monomer is consumed.

Metallic Sodium Reductions of Aromatic Aldehydes and Ketones:

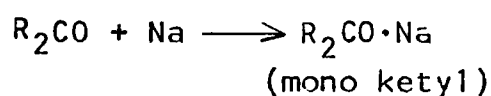
This section is included because of the similarity of the metallic sodium reductions of aromatic aldehydes and ketones with those of sodium naphthalenide. A variety of organic molecules are reduced by reaction with metallic sodium, either in the presence of a proton donor or followed by treatment with a proton donor.

Sodium has been used as a solution in liquid ammonia, low molecular weight amines, and certain ethers (DME). It has also been used as a suspension in inert solvents such as toluene or xylene. For both procedures, a proton source such as water or ethanol is added concurrently with the compound to be reduced. Sodium has also been added directly to solutions of the compound being reduced either in the presence or absence of hydroxylic solvents.

The reduction of ketones and aldehydes by sodium is best considered as an internal electrolytic reduction in which an electron or electrons are transferred from the metal surface (or from the metal in solution) to the aldehyde or ketone being reduced.

In 1891 E. Beckmann and T. Paul found that certain aromatic ketones reacted with sodium in the proportion of one atom of metal to one molecule of ketone, forming highly colored addition products.²⁶ Schlenk confirmed this result

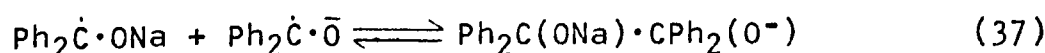
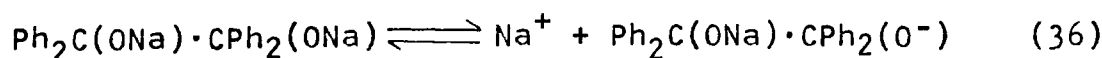
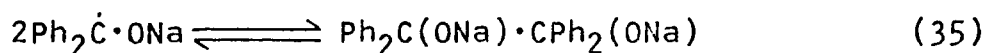
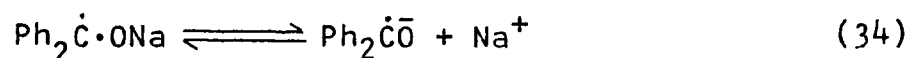
and also found that disodium derivatives could be prepared by further action of the metal.²⁷ These reactions were carried out in benzene or etherial solutions, under nitrogen, and took place rather slowly. Kraus found that the reaction of sodium and benzophenone in liquid ammonia solution occurred readily and resulted in the formation of either a mono or disodium ketyl; the latter formed by addition of two equivalents of sodium.²⁸



On hydrolysis of the disodium ketyl, benzhydrol was obtained. Schlenk and co-workers concluded that because of the intense color of the compound and the reactions with iodine and oxygen that the sodium compound was a free radical of the type R_2CONa , formed by the addition of an atom of sodium to a molecule of ketone. According to Schlenk, these ketyls were monomolecular and did not associate to the dimolecular form, sodium pinacolate, $\text{R}_2\text{C}(\text{ONa})\cdot(\text{ONa})\text{CR}_2$. Support for the monomolecular structure was provided by the observation that hydrolysis did not give pinacols but a mixture of ketone and hydrol.

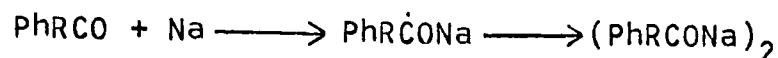
Bachmann in 1933, noting that aromatic ketones react with a mixture of magnesium and magnesium iodide and are reduced to iodomagnesium pinacolates, $\text{R}_2\text{C}(\text{OMgI})\cdot(\text{OMgI})\text{CR}_2$,

reinvestigated the sodium benzophenone system.²⁹ It was found that the pinacol formed on hydrolysis is subsequently broken down into the ketone and hydroxyl by the action of alkali liberated simultaneously on hydrolysis. Therefore, the products obtained by the action of sodium on aromatic ketones in anhydrous ether medium are chiefly sodium pinacolates, and hydrolysis of these pinacolates with dilute acid gives pinacols in good yields. Electrical conductivity measurements show that quite a complex series of equilibria exist in the solutions of sodium and benzophenone.³⁰ The equilibria



all exist in solutions of the benzophenone ketyl. Bachmann confirmed that (35) exists in ether and Wooster showed that in liquid ammonia the equilibrium in equation (35) lies about 85% in favor of the monomeric products. A considerable body of evidence is available showing that the addition of both the first and the second electron can be reversed. For example, mercury acts upon $\text{Ph}_2\text{C}(\text{Na})\text{ONa}$ to form Ph_2CONa and sodium amalgam, and the reaction can be reversed if sufficiently concentrated (high sodium content) amalgam is used.

Acetophenone and substituted acetophenones on reaction with sodium form the expected highly colored ketyl or free radical first, and then slowly combine to form the corresponding pinacolate.³¹



R = Me, Et, Pr, iso-Pr

In the case of dimethyl and diethylacetophenone, the addition of excess sodium resulted in PhRCONaNa. Hydrolysis of the ketyls gave a variety of products: original ketones, pinacols, alcohols and unidentified products.

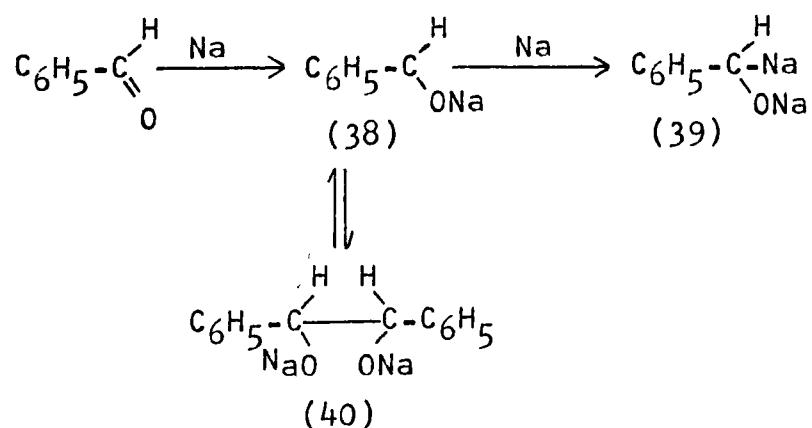
The reaction of sodium with aliphatic ketones in inert media has been investigated by Drweski and Wiemann, and S. Dev. The products of these reactions are pinacols, alcohols, condensation products, and resins.³²

Because most aldehydes react readily with liquid ammonia, this medium is ordinarily suitable only for reactions between aldehyde derivatives and solutions of metals. Benzaldehyde reacts with liquid ammonia to form a precipitate which is acted upon by sodium. This reaction, however, has not been thoroughly investigated.³³

The reaction between metallic sodium and benzaldehyde in inert media was first studied by Church, who reported a green benzaldehyde-sodium addition product that was decomposed by water with the formation of equivalent amounts of

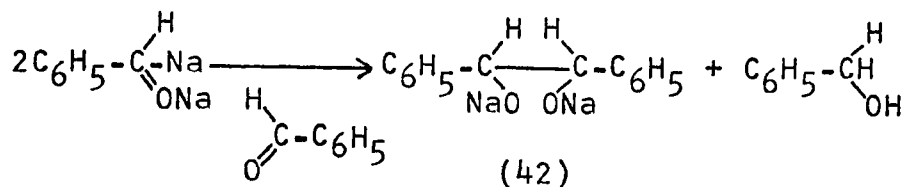
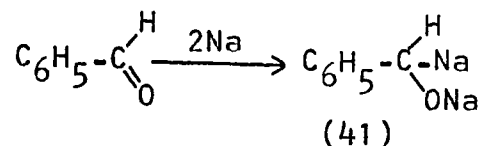
benzyl alcohol and benzaldehyde.³⁴ Beckmann and Paul next investigated the reaction and found that the benzaldehyde-sodium compound was extremely sensitive toward water, oxygen, and carbon dioxide.³⁵ In the interaction with water, hydrobenzoin and sodium hydroxide were the reaction products. The aldehyde sodium compound was formed, according to Beckmann, by the addition of one atomic equivalent of sodium to one molecular equivalent of aldehyde.³⁶

In 1924 F. F. Blicke further investigated the sodium benzaldehyde reaction in absolute ether.³⁷ He assumed that benzaldehyde and sodium react with the formation of a mono (38) or a disodium (39) addition product, depending on the amount of sodium present.



Intermediate (38) will tend to dimerize to (40) which exists in equilibrium with the monomolecular compound. When compound (38) is hydrolyzed, benzyl alcohol and benzaldehyde are isolated. Compound (39), upon addition of water is hydrolyzed to benzyl alcohol. In a similar manner compound

(40) should undergo hydrolysis with the formation of hydrobenzoin. However Blicke found no hydrobenzoin when one equivalent of sodium was used. The reactions which take place when benzaldehyde reacts with two equivalents of sodium are indicated below.



From the hydrolysis of compound (41), Blicke obtained benzyl alcohol and from (42), hydrobenzoin.

According to Kraus and White, aliphatic aldehydes or the products of the reaction between aldehydes and ammonia react readily with sodium in liquid ammonia.³⁸ However, aliphatic aldehydes seem to be rather unreactive with sodium in inert solvents.

V. O. Lukashevich and E. N. Dokunikh have investigated the reaction of the quinones with sodium in absolute ether.³⁹ It was found that no reaction occurred between finely divided sodium and p-benzoquinone. However when the sodium is used in the form of a liquid amalgam, a number of quinones (phenanthrenequinone, beta-naphthoquinone) form

brightly-colored green compounds when agitated in absolute ether under an atmosphere of nitrogen. Such quinones as 1,4-naphthoquinone and p-benzoquinone do not react directly with sodium amalgam. An electron transfer agent such as nitrobenzene seems to be necessary to facilitate the reaction of the above mentioned quinones with sodium. Thus when an equivalent amount of benzoquinone in absolute ether is introduced into a mixture of nitrobenzene and sodium amalgam, reduction occurs with the formation of a deep blue precipitate. In the interaction of sodium with a quinone, two sodium atoms are added to form the disodium salt of the hydroquinone. However, the possibility cannot be excluded that this reaction occurs in a stepwise manner with the formation first of products of the addition of one sodium atom to the quinone, as in the case of aromatic ketones.

CHAPTER III

EXPERIMENTAL MATERIALS AND METHODS

Sodium Naphthalenide:

Unless otherwise specified, the sodium naphthalenide solution used in these experiments is made in the following manner:

Tetrahydrofuran is dried over sodium sulfate, distilled onto molecular sieves and allowed to stand overnight before using. The dry THF is then added to a three neck flask fitted with a gas inlet and exit stopcock, and a rubber stopple. Next, the desired amount of naphthalene is added and the solution is stirred under nitrogen for one hour prior to the addition of sodium. Metallic sodium is cut and weighed under pentane and added to the above solution under a stream of nitrogen. The deep green color of the sodium naphthalenide radical anion is visible immediately upon addition of the sodium, and within 15 minutes the solution turns from colorless to dark green. In order to insure complete reaction the solution is allowed to stir, under nitrogen, for 8 hours before use.

The Reaction of Benzaldehyde with Sodium Naphthalenide:

A solution of 300 ml of dry THF, 51.2 grams (.4 mole) of naphthalene, and 9.2 grams (.4 mole) of sodium is allowed to react 8 hours in a nitrogen filled 500 ml flask as described above. A solution of 20 grams of distilled benzaldehyde and 100 ml of dry THF is then added dropwise from an addition funnel to the above solution with continuous stirring. A brownish-orange color is detected when the aldehyde mixes with the sodium naphthalenide solution; however at the completion of the reaction the solution remains dark green. Slow addition of ice turns the solution from dark green to orange-brown, and further addition of ice water causes the solution to turn yellow. When no further color change is evident, the solution is poured into a separatory funnel and neutralized with .1M acetic acid. Extraction with ethyl ether and repeated washings with water and ether results in a clear water layer and a yellowish-white organic layer. After separation, the water layer shows a pH of 6. The organic layer is dried with sodium sulfate, filtered and then evaporated down to 100 ml on a flash evaporator. Distillation of the remaining solution yields three fractions. The first fraction distills over at 70° under atmospheric pressure. GLC analysis shows this

fraction to be nearly pure THF. The second fraction is collected at 95° under 20mm pressure. Analysis by GLC shows this fraction to be predominately naphthalene with a small amount of THF and unreacted aldehyde. The third fraction, 13.2 grams of a viscous yellow-green oil, is collected at 170° under 1mm pressure. Repeated recrystallization of this viscous oil in ethanol-water solution results in the formation of 4.7 grams (24% yield) of white needles, melting pt. 118° .

The infrared spectra of this compound contains a strong absorption band at 2.9 microns, OH stretch, and broad bands between 12 and 15 microns indicating aromatic character. NMR spectra, using TMS as a standard, reveals the following: a broad singlet at 3.1δ with an integration area of 5 units; a singlet at 4.65δ with an integration area of 5.8 units; and an aromatic band at 7.1 to 7.3δ with an integration area of 30 units.

The NMR and IR spectra of the suspected product, d1-hydrobenzoin, are found to be almost identical with those mentioned above. The melting point of pure d1-hydrobenzoin is given in the literature as $117-118^{\circ}$.

The difficulties in recrystallizing an isomeric mixture of hydrobenzoin prompts a search for an alternative

method of determining yield in the above reaction. Since the reaction products have already been identified by comparison of spectral properties and melting points with authentic samples, determination of yield by GLC seems feasible. Therefore 200 ml of a 1M sodium naphthalenide solution is prepared in the usual manner for use in small volume reactions for GLC analysis. Ten ml of this solution is withdrawn by syringe and added to a nitrogen filled 25 ml three neck flask equipped with a gas inlet and exit valve, a rubber stopple, and a teflon magnetic stirrer. Next 10.6296 grams (.1M) of benzaldehyde and 10.6293 grams of biphenyl ether (internal standard) are poured into a 100ml volumetric flask and diluted to the mark with dry THF. Five ml of this solution is added by syringe through the rubber stopple of the small flask to the 10 ml of sodium naphthalenide solution with vigorous stirring. The reaction mixture turns orange-brown as in the larger reaction and subsequent protonation with a small amount of water turns the solution yellow. While still under a nitrogen atmosphere, a sample is taken from the organic layer for GLC analysis.

Product yield is determined by the internal standard method. A known standard solution consisting of the following

is made: .5003 grams of hydrobenzoin, .5045 grams of benzaldehyde, .5005 grams of benzyl alcohol, .5004 grams of biphenyl ether (internal standard), and sufficient THF to dilute a 50 ml volumetric flask to the mark. Samples of this standard are analyzed by GLC and compared with those from the reaction mixture. For example, the percent yield of hydrobenzoin is determined in the following manner. From the known standard the signal responses (peak areas) of an equal amount of hydrobenzoin and biphenyl ether is determined. From these the ratio of the peak area of hydrobenzoin to the peak area of biphenyl ether is obtained. Next the ratio of hydrobenzoin to biphenyl ether in the reaction mixture is determined in the same manner. And finally the ratio of hydrobenzoin to biphenyl ether in the reaction mixture is divided by the ratio of hydrobenzoin to biphenyl ether in the standard and multiplied by 100 to give the percent hydrobenzoin formed from the reaction.

It is necessary to use two GLC columns in this analysis because of the rather extreme column conditions required to elute the highly polar hydrobenzoin molecule. A 10% Carbowax 20M column is used to obtain the percent reaction of benzaldehyde and the percent formation of benzyl

alcohol, while a 3% SE-30, methyl silicone, column is used to obtain the percent yield of hydrobenzoin. Table 9 shows the results of the GLC analysis of the above samples.

The Reaction of Toluialdehyde with Sodium Naphthalenide:

A solution of sodium naphthalenide composed of 9.2 grams (.4 mole) of sodium, 51.2 grams (.4 mole) of naphthalene, and 400 ml of dry THF is prepared in the usual manner. A solution composed of 21 grams (.19 mole) of tolu-aldehyde and 100 ml of dry THF is added slowly to the sodium naphthalenide solution from an addition funnel with continuous stirring. On addition of the aldehyde a red-brown color is visible, however the deep green color of the naphthalenide radical anion is still prevalent at the completion of the reaction. Small pieces of ice are subsequently added to the solution until the color is a stable yellow-brown. The solution is then poured into a separatory funnel and acidified with 1M HCl. Extraction with ethyl ether results in the formation of a cloudy white organic layer which is washed several times with water, and then poured over sodium sulfate and allowed to stand for 1 hour. After drying, the solution is filtered and flash evaporated

TABLE 9

CARBOWAX 20M COLUMN^a

Compound	Retention time (min.)	Peak area	% yield
Known Standard			
Benzaldehyde	2.2	226	-----
Benzyl alcohol	7.3	170	-----
Biphenyl ether	13.1	202	-----
Reaction Mixture			
Benzaldehyde	2.2	40	-----
Naphthalene	6.0		
Benzyl alcohol	7.4	70	6
Biphenyl ether	13.2	555	-----

SE-30 COLUMN^b

Compound	Retention time (min.)	Peak area	% yield
Known Standard			
Biphenyl ether	2.5	536	-----
Hydrobenzoin	10.0	376	-----
Reaction Mixture			
Biphenyl ether	2.3	840	-----
Hydrobenzoin	9.2	484	90

^aColumn temperature 160°; He flow rate 10cm/3sec.
^bColumn temperature programed from 120° to 190°; He flow rate variable.

down to 100 ml. The pH of the separated water layer is found to be in the range of 3-4. The remaining 100 ml of organic solution is distilled into three fractions. The first two fractions are THF and naphthalene, respectively. The third fraction, 12.36 grams of a viscous light green oil, is distilled over at 190° under a pressure of 1mm. Recrystallization of this oil in a benzene-petroleum ether solvent gives 6.7 grams of a white powder with a melting point of $161-162^{\circ}$.

Identification of this product is accomplished by mass spectra, IR, NMR, and melting point. The melting point of pure dl-hydroto1uoin is given in the literature as 162° . Prominent peaks on the mass spectra are observed at 65, 77, 121, 91, 93, 107, 165, 178, 195, 208, and 224 atomic mass units. The parent peak is observed at 242 atomic mass units. A comparison of the most abundant mass fragments of this spectra with those of the hydroto1uoin molecule reveals close agreement. The parent peak of the hydroto1uoin molecule is at 242 atomic mass units and the remaining mass fragments such as the phenyl radical cation (77 atomic mass units) are verification of the identity of the two spectra.

The IR spectra reveals a strong OH band in the region of 2.9 microns and broad aromatic bands beyond 12 microns.

No band is observed in the region of 6 microns, indicating the absence of a carbonyl group.

NMR spectra, using TMS as a reference, reveals the following: a singlet at 2.3 δ with an integration area of 22 units; a broad singlet at 2.7 δ with an integration area of 7 units; a singlet at 4.7 δ with an integration area of 6 units; and an aromatic band at 7.15 δ with an integration area of 32 units. The NMR spectra of hydrotoluoin should contain an upfield singlet due to the primary protons, a broad singlet slightly down field from the former, due to the alcoholic protons, a singlet still further down field due to the tertiary protons, and an aromatic band in the region of 7-8 δ . The integration area should be approximately 6:2:2:8, respectively. It is evident that the spectra obtained from the reaction mixture product is very similar to this.

Due to recrystallization difficulties, product yield is determined by GLC as in the previous reaction of benzaldehyde with sodium naphthalenide. Ten ml of 1M sodium naphthalenide is added by syringe to a nitrogen filled 25 ml flask described earlier. A solution containing 12.0228 grams of p-tolualdehyde and 12.0267 grams of biphenyl ether (internal standard) is next added to a 100 ml volumetric flask and diluted to the mark with dry THF. Five ml of this solution

is added by syringe to the above sodium naphthalenide solution with vigorous stirring. The reaction mixture turns red-orange until protonation with 1M HCl which changes the color to yellow. A sample is then taken for GLC analysis from the organic layer.

A known standard composed of 1.0003 grams of hydro-toluoin, 1.0036 grams of p-methylbenzyl alcohol, 1.0005 grams of tolualdehyde, 1.0085 grams of biphenyl ether, and sufficient THF to fill a 100 ml volumetric flask to the mark is prepared. Product yield is determined, as in the previous reaction, by the internal standard method using samples from the above standard and the reaction mixture. Two different GLC columns are also necessary in this analysis. The 3% SE-30 column is used to determine the % formation of hydro-toluoin, and the 6% Carbowax 20M column is used to determine the % reaction of tolualdehyde and the % formation of p-methylbenzyl alcohol. Table 10 contains the results of the GLC analysis.

The Reaction of p-Anisaldehyde with Sodium Naphthalenide:

A solution of 300 ml of THF, 51.2 grams (.4 mole) of naphthalene, and 9.2 grams (.4 mole) of sodium is prepared as before. A solution consisting of 21.5 grams (.19 mole) of p-anisaldehyde and 100 ml of THF is added slowly with

TABLE 10

CARBOWAX 20M COLUMN^a

Compound	Retention time (min.)	Peak area	% yield
Known Standard			
Tolualdehyde	3.2	384	-----
p-Methylbenzyl alcohol	7.9	324	-----
Biphenyl ether	10.0	332	-----
Reaction Mixture			
Tolualdehyde	3.0	60	-----
Naphthalene	3.9		
p-Methylbenzyl alcohol	7.3	30	-----
Biphenyl ether	9.0	472	-----

SE-30 COLUMN^b

Compound	Retention time (min.)	Peak area	% yield
Known Standard			
Biphenyl ether	2.3	528	-----
Hydrotoluoin	11.7	290	-----
Reaction Mixture			
Biphenyl ether	2.2	800	-----
Hydrotoluoin	11.1	240	87

^aColumn temperature 170^o; He flow rate 10cm/3sec.

^bColumn temperature programed from 120^o to 200^o; He flow rate variable.

stirring to the sodium naphthalenide solution from an addition funnel. The characteristic reddish-brown color is observed when the aldehyde mixes with the sodium naphthalenide solution. Addition of ice water turns the solution yellow-white. When no further color change is apparent, the solution is poured into a separatory funnel and acidified with 10% acetic acid. The solution is extracted with ethyl ether, washed several times with water, and separated into the organic and water fractions. The pH of the water fraction is in the range of 6-8 units. The organic layer is dried, flash evaporated down to 100 ml, and then distilled. As in the previous reactions, three fractions are obtained. The first fraction is THF. The second fraction is mostly naphthalene with some unreacted aldehyde also present. The third fraction is collected at a temperature of 180-220° under a pressure of 1mm. This fraction, 10.2 grams of a viscous light yellow oil, is recrystallized in benzene-petroleum ether. After repeated recrystallizations, 3.1 grams of a fine white powder is obtained with a melting point of 111°.

Product identification is made by mass spectra, NMR, and melting point. The melting point of the suspected product, d1-hydroanisoin, is found to be 110° in the literature. The mass spectra reveals prominent peaks at 66, 77,

94, 109, 137, 227, 240, and 257 atomic mass units. The parent peak is observed at 274 atomic mass units. The mass fragment at 137 atomic mass units is the most abundant peak, followed by the peaks at 109 and 77 atomic mass units. The mass spectra of dl-hydroanisoin should have a parent peak of 274 atomic mass units. Alpha cleavage of the parent molecular cation to form the oxonium ion, mass 137 in this case, is a favored mode of fragmentation for alpha glycols. This further verifies the assumption that the compound is dl-hydroanisoin because the peak at 137 atomic mass units is the most abundant peak on the mass spectra. A comparison of other fragments of the spectra, with those expected from the dl-hydroanisoin molecule, reveals close agreement. The NMR spectra is inconclusive, revealing what appears to be a doublet at 3.7-3.8 δ , a singlet at 4.1 δ , a broad band at 6.7-7.3 δ , and a doublet at 7.9-8.1 δ .

Determination of product yield is attempted by GLC. A small volume reaction of anisaldehyde with sodium naphthalenide is run and a sample is taken for GLC analysis. Standard known solutions of the various reactants, products, and internal standards are prepared as in the previous reactions. However, hydroanisoin fails to give a sharp reproducible peak on GLC analysis, and therefore only the % reaction of the aldehyde and the % formation of the alcohol

can be determined by GLC. A Carbowax 20M column is used to determine the above, while the 3% SE-30 column is used in an attempt to analyze the hydroanisoin. Extreme conditions are required to obtain even a broad unanalyzable peak from hydroanisoin. Various other columns are tried with less success than the SE-30 column. Due to the high temperatures required to elute the molecule and the relatively large migratory tendency of the anisyl group, rearrangement in the injector or on the column is a possibility. Table 11 shows the results of the analysis using the Carbowax 20M column.

In a further effort to determine the yield of hydroanisoin, another reaction between sodium naphthalenide and anisaldehyde is carried out in exactly the same manner as in the previous large scale reaction. However, separation of products is effected by column chromatography instead of by distillation. A glass column 2 inches in diameter and 30 inches long is packed with a silicia gel-petroleum ether adsorbent. The organic layer from the reaction, after extraction and separation, is flash evaporated down to a brown viscous oil, mixed with benzene, and then poured on the column. Petroleum ether, benzene, ethyl ether, and ethyl alcohol are used as eluents. Naphthalene is eluted in the benzene-petroleum ether fractions along with some unreacted anisaldehyde. The ethyl ether fractions contain hydroanisoin

TABLE 11

CARBOWAX 20M COLUMN^a

Compound	Retention time (min.)	Peak area	% yield
Known Standard			
Anisaldehyde	7.5	225	-----
Anisyl alcohol	15.0	160	-----
Biphenyl ether	6.8	210	-----
Reaction Mixture			
Anisaldehyde	7.7	40	-----
Naphthalene	3.5		
Anisyl alcohol	15.8	90	7
Biphenyl ether	7.0	560	-----

^aColumn temperature 200°; He flow rate 10cm/2.8sec.

and a small amount of anisyl alcohol. The first alcohol fraction contains some hydroanisoin, but subsequent fractions reveal only alcohol. Addition of the ethyl ether and alcohol fractions and immediate evaporation on the flash evaporator results in the collection of 13.3 grams of a viscous brown oil. Recrystallization is attempted as before in a benzene-petroleum ether solvent, but no crystals are obtained. Repeated attempts at recrystallization in various solvents other than benzene-petroleum ether also meet failure.

The Reaction of p-Dimethylaminobenzaldehyde with Sodium Naphthalenide:

A solution of sodium naphthalenide composed of 9.2 grams (.4 mole) of sodium, 51.2 grams (.4 mole) of naphthalene, and 300 ml of dry THF is prepared under nitrogen as usual. Fifty ml of a solution containing THF and 15 grams of p-dimethylaminobenzaldehyde is added dropwise with stirring to the above sodium naphthalenide solution. Addition of the aldehyde solution results in the usual red-orange color appearing momentarily, and then vanishing at the completion of the reaction. Protonation with dilute acetic acid turns the reaction mixture bright yellow. The yellow solution is poured into a separatory funnel, extracted with ethyl ether, and washed several times with water. The

organic fraction is dried over sodium sulfate, filtered and flash evaporated down to a yellow crystalline solid. Column chromatography is used to separate the reaction mixture components. A glass column 2 inches in diameter and 30 inches long is packed with a petroleum ether-silicia gel adsorbent. The crystalline reaction mixture is dissolved in a small amount of benzene and poured onto the column. The eluents are petroleum ether, benzene, ethyl ether, and ethyl alcohol, respectively. Naphthalene is eluted in the petroleum ether and benzene fractions. The first ether fraction elutes a small amount of unreacted p-dimethylaminobenzaldehyde. The second ether fraction reveals two peaks at high temperature from GLC analysis using the SE-30 column. The following ether and alcohol fractions contain the same two peaks in diminishing amounts. These peaks appear to be the main reaction products. Addition of the fractions containing the two unidentified peaks into a large flask and subsequent flash evaporation of the solvent results in the formation of 11 grams of a brown oil. Recrystallization of this oil is attempted in various solvents without success.

The Reaction of o-Anisaldehyde with Sodium Naphthalenide:

A sodium naphthalenide solution composed of 51.2 grams (.4 mole) of naphthalene, 300 ml of dry THF, and

9.2 grams (.4 mole) of sodium is prepared as usual. Fifty ml of THF containing 12 grams of o-anisaldehyde is added slowly to the above sodium naphthalenide solution with stirring. When the aldehyde mixes with the sodium naphthalenide solution, the usual red-brown color is detected. Protonation with dilute HCl solution turns the reaction mixture light pink. The pink solution is poured into a separatory funnel, extracted with ethyl ether, and washed with water. The organic fraction is dried over sodium sulfate, filtered, and flash evaporated down to a pink-white solid. This solid is mixed with a small amount of benzene and poured onto a column packed with a petroleum ether-silicia gel adsorbent. The eluents are petroleum ether, benzene, ethyl ether, and ethyl alcohol. As usual naphthalene is eluted in the petroleum ether and benzene fractions. Some unreacted aldehyde is found in the first ether fraction. Subsequent fractions reveal a compound which gives a sharp reproducible peak on GLC analysis. This compound is definitely the major product of the reaction. When all the fractions containing this product are added together and stripped of solvent on the flash evaporator, 10.7 grams of a brown oil results. Recrystallization is attempted in various solvents without success.

The Reaction of Benzophenone with Sodium Naphthalenide:

Ten ml of a 1M benzophenone solution containing an equal amount of biphenyl ether as an internal standard is added by syringe to 20 ml of 1M sodium naphthalenide under helium. The reaction vessel is a three neck 50 ml flask equipped with a gas inlet and exit stopcock, a rubber stopple, and a magnetic stirrer. The helium is allowed to flow continuously through the duration of the reaction. Addition of the benzophenone solution causes the color of the reaction mixture to turn from dark green to dark blue. Five ml of dilute acetic acid is added to protonate the reaction mixture. Addition of the acid causes the solution to turn cloudy white. The contents of the flask are then poured into a small separatory funnel and washed with 20 ml of water. Extraction with 50 ml of ethyl ether yields a clear organic layer which is poured over sodium sulfate to remove any remaining water. A sample is then taken for GLC analysis.

The internal standard method is used to determine the product yield. A known THF solution containing equal amounts of benzophenone, benzhydrol, and biphenyl ether (internal standard) is prepared to determine the relative GLC response of the above components. The GLC results of this known standard and the reaction mixture sample are shown in Table 12.

TABLE 12

FFAP COLUMN^a

Compound	Retention time (min.)	Peak area	% yield
Known Standard			
Benzophenone	9.8	448	-----
Benzhydro1	18.7	252	-----
Biphenyl ether	2.9	504	-----
Reaction Mixture			
Naphthalene	2.0		
Benzophenone	9.7	104	-----
Benzhydro1	18.5	308	92
Biphenyl ether	2.9	672	-----

^aColumn temperature 210^o; He flow rate 10cm/2.5sec.

The Reaction of p-Benzoquinone with Sodium Naphthalenide:

Twenty ml of a 1M sodium naphthalenide is injected by syringe into a nitrogen filled 50 ml three neck flask equipped with a gas inlet and exit stopcock, and a rubber stopple. A solution containing 10.8940 grams of p-benzoquinone, 10.8996 grams of biphenyl ether (internal standard), and sufficient THF to dilute a 100 ml volumetric flask to the mark is then prepared. Ten ml of this 1M solution is added by syringe to the above sodium naphthalenide solution with vigorous stirring. Upon addition of the 1M quinone solution a deep blue complex forms. This complex seems to coagulate, stopping the magnetic stirrer from rotating momentarily. Subsequent protonation with dilute HCl changes the color of the solution to dark brown. The protonated solution is then poured into a separatory funnel containing 25 ml of 6M HCl, extracted with ethyl ether, and washed several times with water. The extraction results in the formation of a brown organic layer and a water layer with a pH of 2-3. The organic layer is distilled down to 25 ml at a temperature of 65° under atmospheric pressure. The distillate is found by GLC analysis to be pure THF. The residue thus contains all of the reactants and products. A sample of this residue is taken for GLC analysis.

The internal standard method is used to determine product yield. A known standard containing equal amounts of p-benzoquinone, hydroquinone, and biphenyl ether is prepared and a sample of this solution is analyzed by GLC. As in previous experiments, the relative GLC response of hydroquinone is compared to that of the internal standard in the known solution and used to calculate the percent yield of hydroquinone from the reaction mixture. Table 13 shows the results of the GLC analysis.

TABLE 13

3% SE-52 COLUMN^a

Compound	Retention time (min.)	Peak area	% yield
Known Standard			
p-Benzoquinone	1.8	570	-----
Hydroquinone	8.0	420	-----
Biphenyl ether	11.8	800	-----
Reaction Mixture			
Naphthalene	4.1	---	-----
p-Benzoquinone	1.6	---	-----
Hydroquinone	7.8	560	92
Biphenyl ether	11.3	1160	-----

^aColumn temperature 75°; He flow rate 10cm/4.5sec.

CHAPTER IV

RESULTS AND DISCUSSION

The Action of Sodium Naphthalenide on Carbonyl Compounds:

A search of the literature on the reactions of sodium naphthalenide reveals that reactions with the carbonyl group are limited to acid-base interactions. In particular, the aromatic carbonyl compounds previously studied all contained one or more acidic hydrogens, thus enhancing the probability of acid-base interaction as compared to other possible reaction modes such as electron transfer. The strong basicity of sodium naphthalenide has been amply demonstrated by B. Angelo et al⁴⁰ in the previously mentioned papers concerning the condensation of carboxylic acids with aldehydes and ketones in sodium naphthalenide and by the action of sodium naphthalenide on camphor and acetophenone. Angelo noted also that sodium naphthalenide was sufficiently basic to abstract a proton from diphenyl methane while a strong base such as sodium amide requires extreme conditions to react with biphenyl methane, and metallic sodium does not react at all. There are no ex-

amples of reactions of sodium naphthalenide with aromatic carbonyl compounds lacking an acidic hydrogen. Additionally the reaction of sodium naphthalenide on aliphatic aldehydes and ketones is unclear.

General Reaction Procedure:

In the course of this investigation, various carbonyl compounds were introduced into a solution of sodium naphthalenide and subsequently hydrolyzed with water or acid. The reaction products were then separated by distillation or column chromatography and analyzed by GLC, NMR, IR, melting point, or mass spectra. Preliminary investigation revealed that two or more equivalents of sodium naphthalenide were necessary to insure complete reaction of the various carbonyl compounds.

Results:

The reactants, major reaction products, per cent consumption of reactants, and the per cent formation of the major products are given in Table 14.

TABLE 14

RESULTS OF ALL REACTIONS IN TABULAR FORM

<u>Compound</u>	<u>% Reaction</u>	<u>Major Products</u>	<u>% Formation Major Products</u>
Benzophenone	60-90	Benzhydrol	60-92
Quinone	80-90	Hydroquinone	85-92
Benzaldehyde	92-96	Hydrobenzoin	90
Tolualdehyde	90-95	Hydrotoluoin	85-87
p-Anisaldehyde	88-90	Hydroanisoin	-----
o-Anisaldehyde	88-91	a	-----
p-Dimethylaminobenzaldehyde	88-90	a	-----
p-Chlorobenzaldehyde	80-90	a	-----
Cyclohexanone	40	a	-----
3-Pentanone	50	b	-----
Pentanal	50	b	-----
Benzonitrile	88-92	a	-----
Cinnamaldehyde	85	Telomer	-----

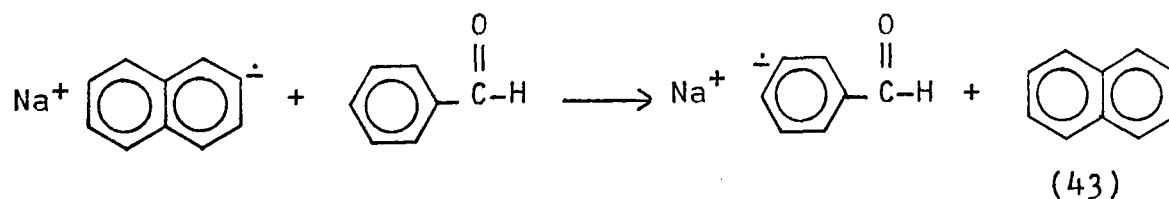
^aRefer to Chapter IV for discussion of reaction products.

^bMajor products, determined by, M. Vora, result from nucleophilic attack (page 66).

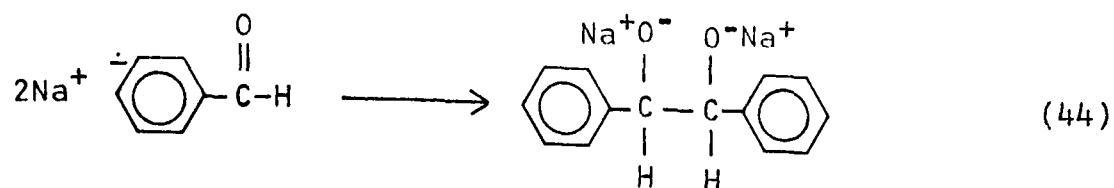
Discussion of Results:

As mentioned previously, the reactions of sodium naphthalenide are usually the result of proton abstraction, electron transfer, or radical-radical coupling. In the presence of an acidic proton the naphthalenide radical anions become protonated very rapidly (10^{-8} - 10^{-10} sec $^{-1}$). In the absence of an acidic proton electron transfer is a distinct possibility.

Inspection of Table 14 reveals that aromatic carbonyls containing no acidic hydrogens undergo almost quantitative reaction when treated with two equivalents of sodium naphthalenide per one equivalent of aromatic carbonyl compound. The products of these reactions are mainly glycols and alcohols. Glycol formation from the reaction of aromatic aldehydes and ketones lacking acidic hydrogens with sodium naphthalenide can best be visualized by an electron transfer from the naphthalenide radical anion to the π system of an aromatic aldehyde

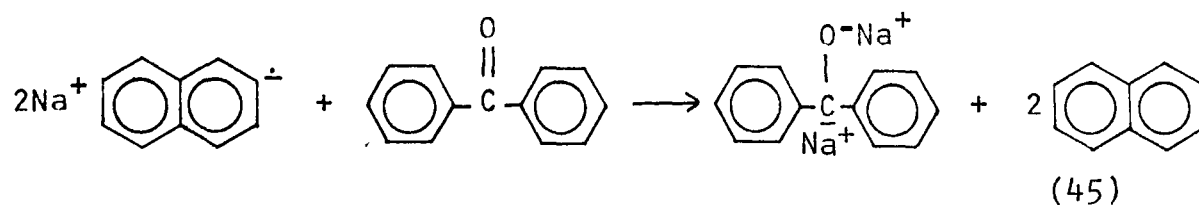


followed by coupling of two aldehyde radical anions to give (44).



Hydrolysis of (44) gives the resulting glycol. A similar mechanism has been proposed in the electrolytic reduction of aromatic aldehydes. Both steric and electronic effects should be of importance in deciding the preferred orientation of the intermediate radicals just prior to dimerization. A mixture of isomeric glycols (meso and d,l) is possible.

Alcohol formation can be rationalized by a two electron transfer mechanism. Two molecules of naphthalenide radical anion could each transfer one electron to an aromatic ketone or aldehyde



giving the disodio salt of the aromatic ketone or aldehyde, which on hydrolysis gives the alcohol. This mechanism is known to occur in the basic electrochemical reduction of benzophenone. It is also consistent with the metallic sodium reduction of benzophenone when two equivalents of sodium are used.

If the first step in the reduction of aromatic carbonyl compounds lacking acidic hydrogens is electron transfer in nature, the reduction potentials of the compounds would be a critical factor in determining whether or not the reaction will take place. The polarographic reduction potentials of various carbonyl compounds are shown in Table 15. The aliphatic aldehydes show reduction potentials in the vicinity of 1.9V. The phenyl alkyl ketones show a lower reduction potential on the order of 1.5 to 1.6V. Benzophenone and the aromatic aldehydes are still lower at approximately 1.3V. Acetone, cyclopentanone, and presumably other saturated aliphatic ketones have higher reduction potentials than 2.1V, which is the voltage at which the cations of the electrolyte begin to be reduced. Certain substituents such as methoxy and hydroxy groups raise the potential of the parent aromatic aldehyde. The highly unsaturated ketones such as the quinones have the lowest reduction potentials of the compounds listed, p-benzoquinone being reduced at .1V or less.

A number of aliphatic aldehydes and ketones were tested for reaction with two equivalents of sodium naphthalenide per one equivalent of carbonyl compound. From Table 14 it is evident that most aliphatic or aromatic-aliphatic carbonyls show limited reactivity with sodium naphthalenide. Recent investigations and preliminary results indicate the

TABLE 15

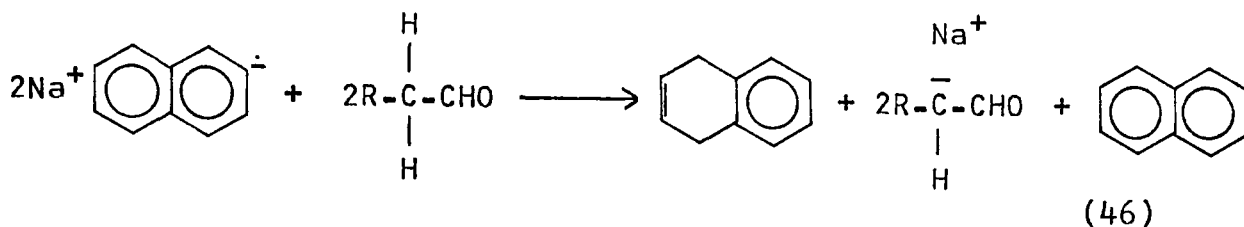
REDUCTION POTENTIALS OF CARBONYL COMPOUNDS^a

Compound	Reduction Potential
ethanal	1.92
pentanal	1.90
benzaldehyde	1.34
p-anisaldehyde	1.46
cinnamaldehyde	1.37
benzophenone	1.35
acetophenone	1.52
p-benzoquinone	0.10

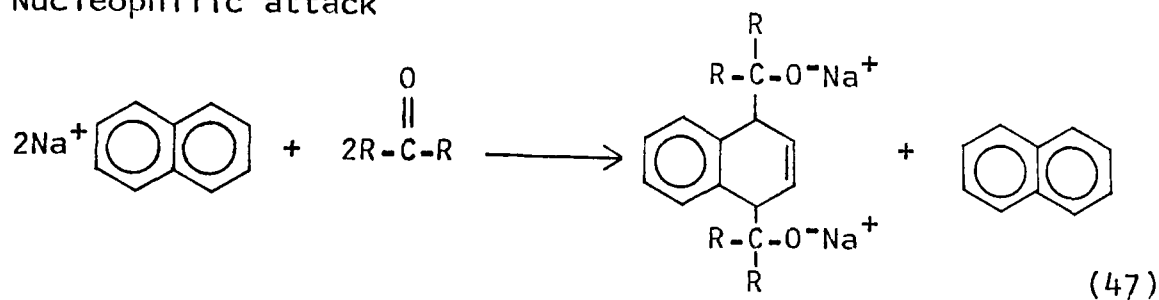
^aDetermined in tetramethylammoniumhydroxide solution.

products of these reactions to be the result of proton abstraction (46), nucleophilic attack (47), and coupling.

Proton abstraction



Nucleophilic attack



The availability of acidic hydrogens in these compounds together with their high reduction potentials seems to dramatically lessen electron transfer as the major initial step in these reactions.

The reaction of benzophenone with sodium naphthalenide illustrates the reducing action of sodium naphthalenide with aromatic ketones. When two equivalents of naphthalenide radical anion are added to one equivalent of benzophenone, reduction takes place within a minute, with approximately 90% of the reactant being consumed. On analysis of the reaction products by GLC, benzhydrol is found in yields ranging from 60 to 85%. The formation of benzhydrol can be rationalized in two ways. A one electron transfer from the naphthalenide

radical anion to the benzophenone molecule is to give the benzophenone radical anion as in mechanism (43). Subsequent dimerization with another benzophenone radical anion forms the pinacolate. Then, upon hydrolysis the pinacol could be simultaneously broken down into the ketone and hydroxyl. Alternately, the benzophenone molecule could accept two electrons from two naphthalenide radical anions to form the benzophenone dianion as in mechanism 45, which would give benzhydrol on hydrolysis.

The ease with which benzophenone was reduced by sodium naphthalenide prompted an investigation into the possible reduction of other aromatic ketones in a similar manner. The low reduction potentials of the quinones made them an obvious choice for further study. The reaction of p-benzoquinone with sodium naphthalenide on quinones. When one equivalent of p-benzoquinone is added to two equivalents of sodium naphthalenide in THF solution a deep blue complex is formed. Hydrolysis of this deep blue complex with water or HCl results in the formation of hydroquinone in 90% yield. The fact that metallic sodium does not react with p-benzoquinone makes this an especially useful reaction. As mentioned earlier, Lukashevich found that the disodio derivatives of nitrobenzene react with quinone to form the diacetyl derivatives of hydroquinones in 60 to 70% yield upon acylation. In this reaction two sodium atoms are added to the oxygen

atoms of the quinone with the formation of the disodium salt of the hydroquinone. The reaction likely occurs in a step-wise manner, proceeding through a semiquinone intermediate. The reaction of sodium naphthalenide with p-benzoquinone probably proceeds by a similar mechanism.

As with quinones, the low reduction potentials of the aromatic aldehydes suggest that these compounds might be easily reduced by sodium naphthalenide. Therefore benzaldehyde and five substituted benzaldehydes were introduced into solutions of sodium naphthalenide and subsequently hydrolyzed. Table 14 shows that all of the aromatic aldehydes undergo almost quantitative reaction, however, product isolation is difficult in some cases. The main reaction products are seen to be pinacols, with a small amount of alcohol formed also. The analogous reactions of aromatic aldehydes with metallic sodium in etheral solutions also result in the formation of pinacols and alcohols although no yields are reported. The mechanism of the reduction of aromatic aldehydes with sodium naphthalenide is probably similar to the mechanism of the electrolytic reductions of the aromatic aldehydes. The first step is the transfer of one electron from the naphthalenide radical anion to an aldehyde molecule to form the aldehyde radical anion as shown in mechanism (43). Dimerization of two of these aldehyde radical anions then leads to the

sodium pinacolate, which upon hydrolysis gives the pinacol. The difficulty in isolating the products from these reactions lies in the possibility that a mixture of isomeric pinacols (meso and d,l) can be produced, which make recrystallization difficult. Thus reaction of sodium naphthalenide and o-anisaldehyde after hydrolysis, extraction with ether, and separation by column chromatography gives a brown oil which could not be recrystallized. However the reductions of benzaldehyde, tolualdehyde, and p-anisaldehyde give oils which can be recrystallized to give the respective pinacols in good yield. Chlorobenzaldehyde fully reacted with sodium naphthalenide, however, no isolable product could be obtained from the reaction mixture. From the recent work on aromatic halides, this could be interpreted as a reaction at both the carbonyl and halogen centers, with a high molecular weight product resulting.

Two other functional groups were shown to react almost quantitatively with sodium naphthalenide but no product was visible on GLC. Benzonitrile and cinnamaldehyde undergo almost complete reaction when one equivalent of each of the above is reacted with two equivalents of sodium naphthalenide and hydrolyzed. When product isolation was attempted a viscous oil was obtained from the cinnamaldehyde reaction which appeared to be a polymer. This would seem to be in agreement with

the fact that unsaturated aldehydes tend to polymerize in the presence of an electric strain. Isolation of products from the benzonitrile was not attempted because of the likelihood of polymer formation.

BIBLIOGRAPHY

1. N. D. Scott, J. F. Walker,
and V. L. Hansley, J. Am. Chem. Soc., 58,
2442 (1936).
2. G. J. Hoijtink, E. de Boer,
P. H. van der Meig, and
W. P. Weijland, Rec. Trav. Chim., 75,
487 (1956).
3. G. J. Hoijtink, E. de Boer,
P. H. van der Meig, and
W. P. Weijland, Rec. Trav. Chim., 75,
487 (1956).
4. J. Jagur-Grodzinski, M.
Feld, S. L. Yang, and M.
Szwarc, J. Phys. Chem., 69, 628
(1965).
5. R. L. Ward and S. I.
Weissman, J. Am. Chem. Soc., 79,
2086 (1957).
6. Ting Li Chu and Shan
Chi Yu, J. Am. Chem. Soc., 76,
3367 (1954).
7. D. E. Paul, P. Lipkin,
and S. I. Weissman, J. Am. Chem. Soc., 78,
116 (1956).
8. S. Bank and B. Bockrath,
J. Am. Chem. Soc., 93:2,
430 (1971).
9. D. E. Paul, P. Lipkin,
and S. I. Weissman, J. Am. Chem. Soc., 78,
116 (1956).
10. S. Arai and L. M. Dorfman,
J. Chem. Phys., 41, 2190
(1964).
11. H. Normant and B. Angelo,
Bull. Soc. Chim., (France),
354 (1960).
12. B. Angelo,
Bull. Soc. Chim., (France),
1848 (1970).

14. S. Bank, T. A. Lois, and M. C. Prislowski, J. Am. Chem. Soc., 91:19, 5407 (1969)
15. A. G. Evans and J. C. Evans, J. Chem. Soc., 6036 (1963).
16. A. D. Dadley and A. G. Evans J. Chem. Soc., B, 107 (1968).
17. G. Levin and J. Jagur-Grodzinski, J. Am. Chem. Soc., 92:8, 2273 (1970).
18. N. L. Holy and J. D. Marcum, Angew. Chem. Internat. Edit., 10, 115 (1971).
19. D. Lipkin, F. R. Galiano, and R. W. Jordan, Chem. Ind. (London), 1963 (1957).
20. T. C. Cheng, L. Headley, and A. F. Halasa, J. Am. Chem. Soc., 93:6, 1502 (1971).
21. D. Machtinger, J. R. Centre Natl. Rech. Sci., Lab. Bellevue (Paris), 60, 231 (1962).
22. W. D. Closson, S. J. and S. Schulenberg, J. Am. Chem. Soc., 92:3, 650 (1970).
23. W. D. Closson, P. Wriede, and S. Bank, J. Am. Chem. Soc., 88, 1581 (1966).
24. B. Angelo, Bull. Soc. Chim., (France), 1091 (1966).
25. M. Szwarc, M. Levy, and R. Milkovich, J. Am. Chem. Soc., 78, 2656 (1956).
26. E. Beckmann and T. Paul, Ann., 266, 1 (1891).
27. Schlenk and Weickel, Ber., 44, 1182 (1911).
28. C. A. Kraus and G. F. White, J. Am. Chem. Soc., 45, 771 (1923).
29. W. E. Bachmann, J. Am. Chem. Soc., 55, 1179 (1933).

30. C. B. Wooster, J. Am. Chem. Soc., 59, 377 (1937).
31. I. Nazarov, Compt. rend. acad. sci. (U.R.S.S.) (N.S.), 1, 325 (1934).
32. S. Dev, J. Indian Chem. Soc., 33, 777 (1956).
33. C. A. Kraus and F. White, J. Am. Chem. Soc., 45, 768 (1923).
34. Church, Ann., 128, 295 (1863).
35. E. Beckmann and T. Paul, Ann., 266, 25 (1891).
36. E. Beckmann and T. Paul, Ann., 266, 25 (1891).
37. F. F. Blicke, J. Am. Chem. Soc., 46, 2560 (1924).
38. C. A. Kraus and F. White, J. Am. Chem. Soc., 45, 768 (1923).
39. V. Lukashevich and E. Dokunikhi, Akadem 2A, Nauk (S.S.S.R.), 166 (1966).
40. B. Angelo, Bull. Soc. Chim., (France), 1848 (1970).

BIOGRAPHICAL SKETCH

James William Stinnett, Jr. was born in Oak Ridge, Tennessee on March 5, 1945. He graduated from Owensboro High School in June, 1963.

He attended Kentucky Wesleyan College, receiving the degree of Bachelor of Science in June, 1967. He enrolled in the Graduate School of Western Kentucky University in September, 1967, and was granted the degree of Master of Science from that institution in August, 1972.