

I. OXIDATIVE DECARBOXYLATION OF γ -OXO ACIDS
USING LEAD DIOXIDE II. ACID CATALYZED
DIMERIZATION OF 1,2-DIHYDRONAPHTHALENE:
NEW STRUCTURE ASSIGNMENTS III. 1,4-
DIHYDRONAPHTHALENE AS AN INTERMEDIATE
IN METAL-AMINE REDUCTIONS OF
NAPHTHALENE IV. METAL-AMINE
REACTIONS OF NAPHTHALENE:
REDUCTIVE DIMERIZATION

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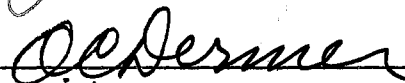
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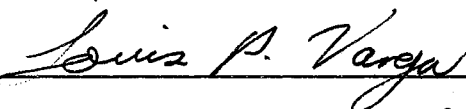
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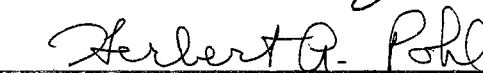
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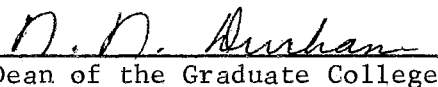


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PREFACE

The first three parts to this thesis either have been published or have been submitted to journals for publication. All parts are in manuscript style and therefore exhibit the same brevity and form required by leading journals in organic chemistry. It is my hope that this form will provide a more readable and informative thesis.

I would like to extend grateful acknowledgement to Dr. E. J. Eisenbraun, my thesis adviser, for his guidance, assistance, and encouragement not only throughout this work but prior to my coming back to graduate school, and to Dr. O. C. Dermer for his sage advice, and able proof-reading.

I thank Dr. P. W. K. Flanagan for providing many of the nmr spectra and Mr. Mynard C. Hamming for the mass spectra described in this thesis. Both chemists provided invaluable assistance in the interpretation of spectra of the compounds in this work.

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Finally, I extend appreciation to my wife, Glenna, for her able guidance of our two daughters, Diane and Donna, both born during the tenure of this work, and for her sacrifice and encouragement without which this dissertation would not have been possible.

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PART I

OXIDATIVE DECARBOXYLATION OF γ -OXO ACIDS

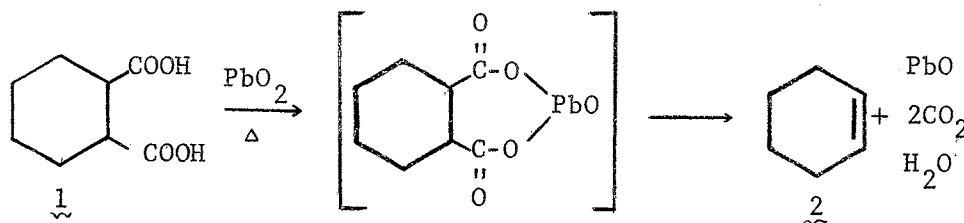
USING LEAD DIOXIDE

CHAPTER I

INTRODUCTION AND HISTORICAL

The general applicability of lead dioxide as a reagent for the oxidative decarboxylation of γ -oxo acids to α,β -unsaturated ketones is reported in this part of the dissertation. The study includes the development of a reaction method which gives high yields of the desired product using commercially available lead dioxide.

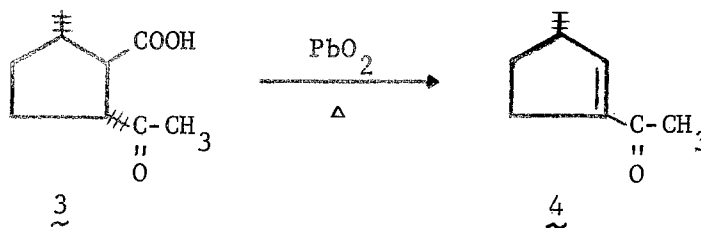
The elimination of vicinal dicarboxylic acid and anhydride functions to yield a double bond at the site [e.g., formation of cyclohexene (2) from cyclohexane-1,2-dicarboxylic acid (1)] may be effected with hot lead dioxide.¹



Grob et al. substituted lead tetraacetate in pyridine for lead dioxide.² This and later modifications have essentially supplanted

oxidative decarboxylation with lead dioxide, probably because higher yields, lower temperature, and better control over the reaction have been reported.^{3, 4} In general, lead tetraacetate decarboxylations give the same olefinic products.

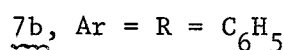
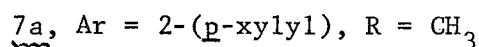
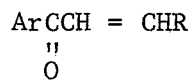
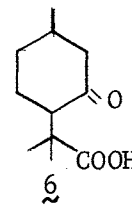
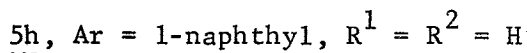
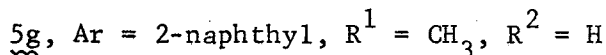
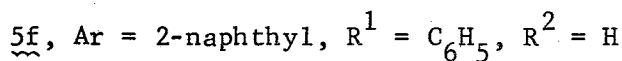
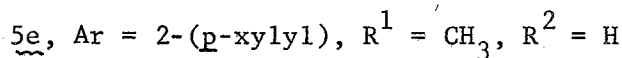
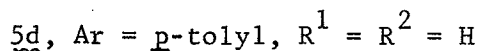
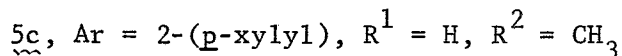
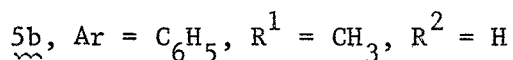
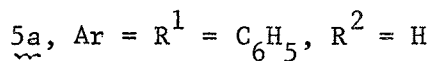
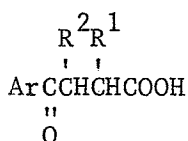
In 1955, it was demonstrated that (-)-3-methylcyclopenten-1-yl methyl ketone (4) is the major product of lead dioxide oxidative decarboxylation of nepetonic acid (3).⁵ These observations have now been confirmed. The decarboxylation of γ -oxo acids with lead dioxide permits survival of the ketone function. This is strikingly different from the reaction of vicinal dicarboxylic acids with hot lead dioxide.



CHAPTER II

DISCUSSION AND RESULTS

The author extended the work referred to in Chapter I to other γ -oxo acids.⁶ The reaction appears to be general, but the yield of α,β -unsaturated ketone usually does not exceed 30-40% for γ -oxo acids having no alkyl or aryl substituents at the α or β position. The best yields were obtained from the α -phenyl- γ -oxo acid 5a and the α,α -dimethyl- γ -oxo acid 6, which gave the corresponding α,β -unsaturated ketones in 84 and 76% yields respectively. A 72% yield was realized from 3-methyl-3-(2,5-dimethylbenzoyl)propionic acid (5c), which is substituted in the β position. However, acid 5d, with no alkyl or aryl substituents in the α or β position, gave a mixture of six products in low yield.



The potential of this reaction for the preparation of α,β -unsaturated ketones in the degradation of natural products can best be appreciated when one includes γ -lactones, which may be converted into γ -oxo acids. The high yields possible with α - and/or β -substituted acids in this one-step decarboxylation, in addition to the ease of product isolation, make lead dioxide a preferred decarboxylating agent.

The oxidative decarboxylations were carried out by one of our techniques. Best yields are realized with method A, in which an intimate mixture of commercially available lead dioxide, the γ -oxo acid and powdered soft glass are added to a sublimation tube. The tube is evacuated and then inserted part way into a preheated sublimation apparatus. The reaction takes place immediately and the product, an α,β -unsaturated ketone in this case, distills out of the reaction mixture and condenses in a cooled portion of the tube. The entire operation requires only about 10 minutes.

Method B also utilizes a hot tube containing lead dioxide. A solution of the γ -oxo acid in xylene is added slowly to the hot lead dioxide to cause decarboxylation. The α,β -unsaturated ketone is washed from the lead dioxide into a receiving flask.

Method C, involving a suspension of lead dioxide in a boiling solution of γ -oxo acid in xylene, was found to be less convenient and produced lower yields.

Decarboxylation can also be effected and the product analyzed in a single operation by injecting a solution of the γ -oxo acid into a hot plug of lead dioxide inside the injection port and at the entrance of a gas chromatography column. The α,β -unsaturated ketone, impurities, and side products are swept by a helium stream through the gas chromatography

column and recorded as peaks on the chromatogram.

Earlier studies⁵ were carried out with granular lead dioxide of the type formerly used by microanalysts in the universal combustion tube filling according to Pregl.⁷ This grade of lead dioxide is no longer commercially available.⁸

Variation in activity of lead dioxide from different sources was encountered with different reaction methods, particularly B and C. Doering and Finkelstein⁹ and others¹⁰ reported that commercial lead dioxide was not effective in the decarboxylation of some 1,2-dicarboxylic acids. A method for preparing activated lead dioxide was developed,⁹ and indeed it was found that lead dioxide so prepared shows increased activity in methods B and C, but the activated material does not approach the effectiveness of the original sample⁵ of lead dioxide. Sufficient lead dioxide remained in the original bottle to permit direct comparisons.

Initially decarboxylation using methods B and C was studied. However, the low yields obtained with commercial lead dioxide necessitated development of method A, which worked satisfactorily with all samples of lead dioxide tried. The oxo acid 5e used with a variety of lead dioxide samples in method A gave a 76-78% yield of 2',5'-dimethylcrotonophenone (7a) in all cases.^{11a} An even higher yield, 84%, of chalcone (7b) was obtained when 3-benzoyl-2-phenylpropionic acid (5a) was used.^{11b}

The effect of temperature on the oxidative decarboxylation of the γ -oxo acid 5e by method A is shown in Fig. 1. For γ -oxo acids yielding products of low volatility, a reaction temperature of 250° is recommended since an immediate reaction takes place in high yield. However, γ -oxo acids yielding more-volatile products and the half esters 8 and 9

as well as the dicarboxylic acid 1 gave higher yields of decarboxylated material at 135°. In these latter cases, the higher temperature caused formation of cyclohexanedicarboxylic anhydride which sublimed out of the reaction tube.

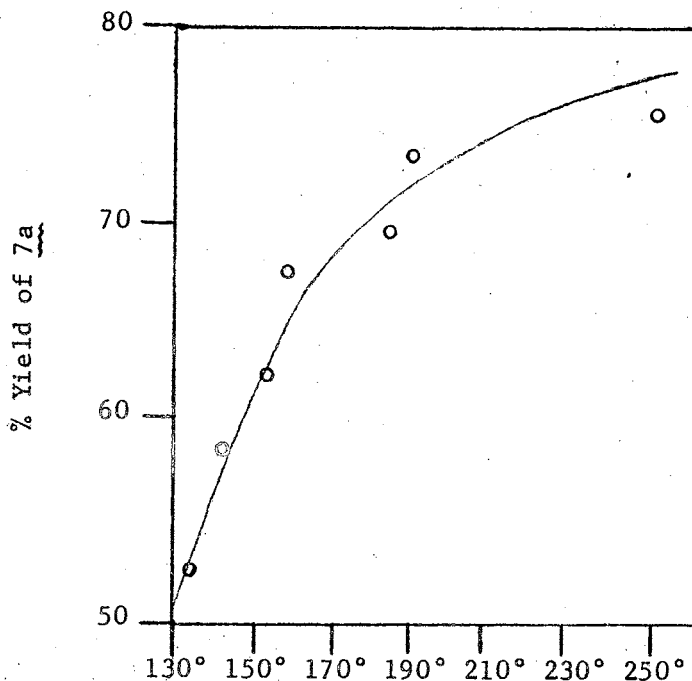


Figure 1. Response of Yield to Reaction Temperature for Decarboxylation of 5e

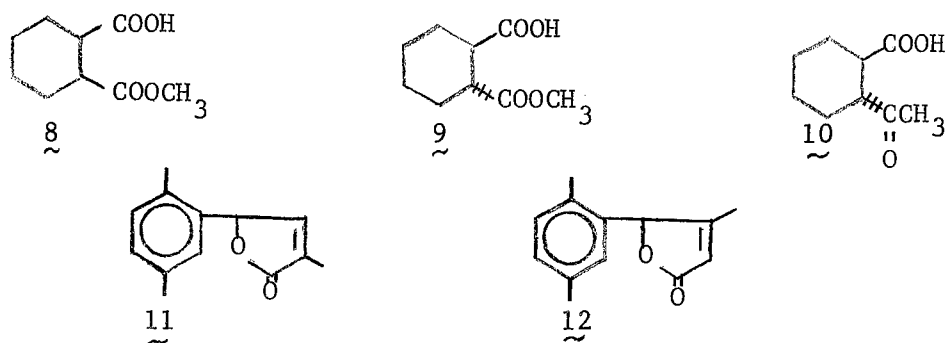
Safety precautions should be observed during oxidative decarboxylation of γ -oxo acids with lead dioxide. The most serious hazard results from admitting air to the hot residue from a lead dioxide decarboxylation. This hazard is most pronounced in method A. Such contact invariably causes some sort of vigorous reaction, due presumably to pyrophoric particles, ranging from formation of sparks to violent

explosions, which in one instance sounded like a shotgun blast and completely demolished a multipiece glass apparatus. The residue from this explosion was a hard lump which resembled lead metal. The experimental methods described are the result of considerable effort to develop safe reaction techniques, and no explosions should be encountered if proper precautions are observed. Insufficient mixing of γ -oxo acid, lead dioxide, and powdered glass may lead to a reaction mixture containing high local concentrations of acid which may also be a cause of the more violent reactions. These reactive centers may be observed as dark spots in an otherwise uniformly yellow-brown reaction residue. Reactions which generate these dark spots usually produce lower yields of α,β -unsaturated ketones. The mixing at ordinary temperatures is without hazard. One should avoid exceeding reported limits without extensive trial.

The presence of the ketone function in the γ -oxo acids being decarboxylated is essential to high yields of α,β -unsaturated ketone. Monomethyl cis-1,2-cyclohexanedicarboxylate (8) and monomethyl trans-1,2-cyclohexanedicarboxylate (9) on reaction with hot lead dioxide give a low yield (ca. 12-15%) of a complex mixture of unsaturated esters while 10, the γ -oxo analog of 9, provides a 45% yield of 1-cyclohexenyl methyl ketone under the same conditions. Decarboxylation of other acids without the ketone function generated extremely complex mixtures of products. Evidently the role of the ketone carbonyl is not limited to resonance stabilization of the double bond formed.

The inability of the enol lactones 11 and 12 to form significant products in the lead dioxide decarboxylation reaction indicates that these easily formed derivatives of γ -oxo acids do not have a role in

the decarboxylation mechanism.



The effect of α substitution on the yield of α,β -unsaturated ketones from γ -oxo acids can be seen in the series of β -aroylpropionic acids 5a, 5b, 5d, 5f, 5g, and 5h. Those acids substituted in the α position gave the α,β -unsaturated ketones in 70-85% yields with only minor impurities. Those acids without substitution in the α or β position, 5d and 5h, gave low yields of complex mixtures of products. The β -substituted acid 5c was oxidatively decarboxylated with lead dioxide to give the α,β -unsaturated ketone in 72% yield. The results of various lead dioxide decarboxylations of γ -oxo acids are summarized in Table I.

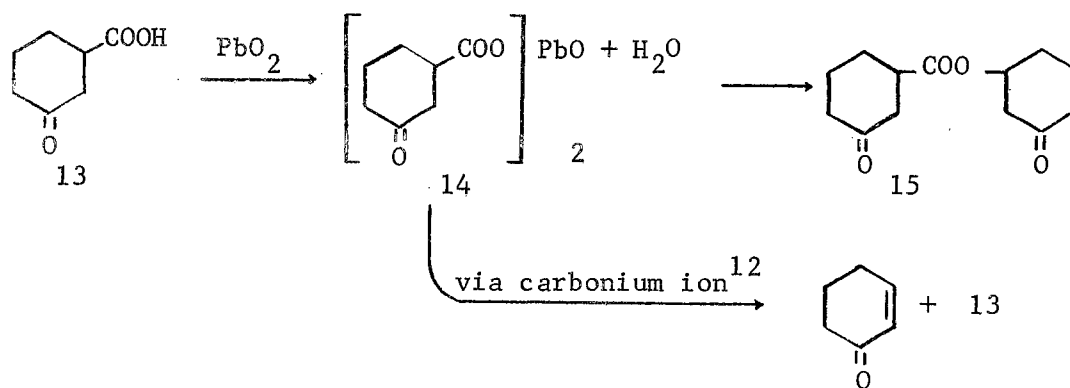
The heterogeneous nature of these reactions presents obvious difficulties in studying the mechanism. The instability of an α,β -unsaturated ketone or occurrence of side reactions could give misleading results. Until better methods of study are available, it will be necessary to rely on product analysis to gain an insight into the reaction

TABLE I
DECARBOXYLATION OF γ -OXO ACIDS TO α,β -UNSATURATED KETONES

Acid	Product	Method ^a	Moles x 10 ⁻³		Powd. Glass g	Xylene ml	Reaction temp °C	Reaction time hr	Yield %	Mp 2,4-DNP °C
			Acid	PbO ₂						
<u>5a</u>	Chalcone (<u>7b</u>)	C	10.0	40.0	-	50	144	10.0	37	241-244 ^b
		B	10.0	40.0	-	120	135	3.0	57	244 ^b
		A	0.5	2.5	3	-	250	0.25	84	245 ^b
<u>5b</u>	Crotonophenone	C	10.0	40.0	-	75	135	4.5	37	194-197 ^c
		A	2.0	10.0	12	-	250	0.5	69	200-201 ^c
<u>5c</u>	2,2',5'-Trimethyl-acrylophenone	A	0.5	2.5	3	-	250	0.5	72	118
<u>5e</u>	2',5'-Dimethyl crotonophenone (<u>7a</u>)	A	0.5	2.5	3	-	250	1.0	76	210-211
<u>5f</u>	3-Phenyl-2'-acrylo-naphthone, mp 105-6 ^{od}	B	3.8	40.0	-	200	125	4.0	40	
		A	0.5	2.5	3	-	250	0.25	83	
<u>5g</u>	2'-Crotononaphthone	C	5.0	20.0	-	50	144	2.0	36	
		A	0.5	2.5	3	-	250	0.25	35	205 ^e
<u>6</u>	Pulegone	B	5.0	40.0	-	50	135	2.0	11	
		A	0.5	2.5	3	-	250	1.0	76	142 ^f
<u>10</u>	1-Cyclohexenyl methyl ketone	B	10.0	40.0	-	10	135	2.0	22	196-201 ^g
		A	0.5	2.5	3	-	250	0.5	45	202-203 ^g
<u>13</u>	2-Cyclohexen-1-one	A	2.0	10.0	12	-	250	0.5	92	163-165 ^h

^aSee Experimental for decarboxylation procedures; ^b245°, C. H. F. Allen and J. H. Richmond, *J. Org. Chem.*, **2**, 224 (1937); ^c204°, V. Franzen, *Ann.*, **602**, 199 (1957); ^d105-106°, A. Maccioni and E. Marongui, *Ann. Chem. (Rome)*, **50**, 1806 (1960); ^e214°, F. Ramirez and M. B. Rubin, *J. Amer. Chem. Soc.*, **77**, 2905 (1955); ^f142°, O. L. Brady, *J. Chem. Soc.*, 758 (1931); ^g202-203°, D. Nightingale, E. C. Milberger, and A. Tomisek, *J. Org. Chem.*, **13**, 357 (1948); ^h163°, P. D. Bartlett and G. F. Woods, *J. Amer. Chem. Soc.*, **77**, 2905 (1955).

mechanism. The evidence suggests a reaction mechanism similar to that proposed by Kochi for the lead tetraacetate decarboxylation of aliphatic acids.^{12, 13} This applied to oxo acid 13 would involve homolytic cleavage of the lead salt 14 and decarboxylation to an alkyl radical which, if stabilized by electron-donating groups, would further react to form alkenes and esters such as 15.¹⁴ An unsubstituted free radical would produce a complex mixture typical of free radical products.



The high yield of α,β -unsaturated ketone from 5c is not consistent with the Kochi mechanism, but more examples will be required to clarify this point.

CHAPTER III

EXPERIMENTAL

Preparation of Starting Materials.— 2-Phenyl-3-benzoylpropionic acid (5a), 2-phenyl-3-(2-naphthoyl)propionic acid (5f), p-menthane-3-one-8-carboxylic acid (6), and 2-acetylcyclohexanecarboxylic acid (10) were obtained by adding cyanide ion¹⁵ to appropriate α,β -unsaturated ketones and subsequently hydrolyzing to the γ -oxo acids.

The α,β -unsaturated ketones were prepared by heating Mannich bases,¹⁶ by Claisen-Schmidt condensation¹⁷ or by Friedel-Crafts acylation of olefins.¹⁸

2-Methyl-3-benzoylpropionic acid (5b) and 2-methyl-3-(2-naphthoyl)propionic acid (5g) were prepared by reaction of benzene or naphthalene with methylsuccinic anhydride in the presence of aluminum chloride.¹⁹

The preparations of 5c and 5e and the enol lactones 11 and 12 are described elsewhere.²⁰

3-(p-Toluoyl)propionic acid (5d) was obtained from the Aldrich Chemical Company and used without further purification.

The monomethyl esters 8 and 9 were prepared from 25 g (0.16 mol) of cyclohexanedicarboxylic anhydride and 9.12 g (0.39 mol) of methanol, which were heated together at the reflux temperature for 4 hrs. The methanol was distilled at reduced pressure and the clear residue was extracted once with 160 ml of 10% sodium bicarbonate. The aqueous alkaline extract was extracted three times (25 ml) with methylene

chloride, and the aqueous layer was acidified. The acidic solution was extracted with three 25 ml portions of methylene chloride and the methylene chloride extracts were combined, dried (MgSO_4), filtered and evaporated. Crystals formed after five days at room temperature. Recrystallization of half the material (Skelly B) gave 4.82 g of 8: mp 66.5-68° [lit.²¹ mp 68-69°]. Distillation of the other half of the reaction product at 100°(0.6 mm) produced only cyclohexanedicarboxylic anhydride and methanol in the distillate, but recrystallization of the undistilled material (Skelly B) yielded 0.98 g of 9: mp 93-95° [lit.²² 95-96°].

Decarboxylation of γ -Oxo acids.— All the γ -oxo acids were decarboxylated by one of the four following methods. Yields of products and methods of preparation are listed in Table I. A specific γ -oxo acid decarboxylation is described for each method.

The reaction products were identified by infrared absorption at 1690 and 1620 cm^{-1} (representing the conjugated carbonyl and double bond respectively), gas chromatography, and preparation of 2,4-dinitrophenylhydrazones. In some cases, gas chromatographic analysis showed the presence of minor impurities (ca. 1-5%).

A. Hot tube with powdered soft glass.— A mixture of 3 g of powdered soft glass, 0.110 g (5.0×10^{-4} mol) of 5e and 0.598 g (2.5×10^{-3} mol) of lead dioxide were ground in a mortar and placed in a 9-mm Pyrex tube closed at one end. After a glass wool plug was placed over the loosely packed mixture, the tube was evacuated to about 0.5 mm and partially inserted horizontally in an aluminum block preheated to 250°. A 5-cm portion of the tubing outside the aluminum block was cooled in powdered dry ice. After 10 min. the reaction appeared to be complete.

The product collected before the dry-ice-cooled portion of the tube just outside the sublimmer. The portion of the tube which contained the product was broken away from the rest to give 0.066 g (76%) of yellow 7a: bp 90° (0.3 mm); ir (liq film) 1656 (C=O), 1625 (C=C) cm^{-1} , and no absorption at 1615 cm^{-1} (absence of CO_2H); nmr (CCl_4) δ 7.11 (s, 1, HAr), 7.01 (s, 2, HAr), 6.47 (s, 1, CH=C), 6.63 (q, 1, CH=C decoupled at 6.63), 2.27 (s, 6, CH₃) and 1.813-1.900 (d, 3, CH₃); mass spectrum (60 eV) m/e (rel intensity) 174 (21.4), 159 (100), 133 (36.6), 105 (33.3), 77 (25.4), 41 (24.4), 39 (31.2). Analysis by gas chromatography²³ showed the product to be free of impurities.

Anal. Calcd. for $\text{C}_{12}\text{H}_{14}\text{O}$: C, 82.72; H, 8.10. Found: C, 82.73; H, 8.21.

Application of method A to 5c gave a 72% yield of 2,2',5'-trimethylacrylophenone: bp 64° (0.33 mm); nmr δ 6.97 (m, 3, ArH), 5.81 (m, 1, CH=C), 5.47 (m, 1, CH=C), 2.23 (s, 3, CH₃), 2.16 (s, 3, CH₃), and 1.95 (m, 3, CH₃); mass spectrum (70 eV) m/e (rel intensity) 174 (78.2), 159 (100), 133, (88.2), 105 (56.5), 77 (36.7), 39 (38.6).

Anal. Calcd. for $\text{C}_{12}\text{H}_{14}\text{O}$: C, 82.72; H, 8.10. Found: C, 82.85; H, 7.73.

Comparison of the use of Pyrex glass and soft glass in method A.— A mixture of 0.220 g (0.001 mol) of 5e, 0.957 g (0.004 mol) of lead dioxide, and 2 g of powdered Pyrex glass was heated according to method A at 135° to give 0.070 g (40%) of the α,β -unsaturated ketone. Substitution of powdered soft glass for the Pyrex glass gave the same product in 42% yield. Doubling the quantity of soft glass raised the yield, 0.080 g (46%).

B. Hot tube with solvent.— Lead dioxide (9.60 g, 0.040 mol) was placed between glass wool plugs in a vertical 9-mm Pyrex tube which passed through an aluminum heating block. The top of the tube was fitted with a dropping funnel and the bottom with a receiver side arm flask immersed in an ice bath. Nitrogen was passed through the system as the lead dioxide was heated to 135°. A solution of 2.540 g (0.010 mol) of 5a in 120 ml of o-xylene was dripped through the lead dioxide (one drop/4-6 sec). After all the acid had been added, the lead dioxide was washed with 50 ml of o-xylene and the combined xylene solutions were extracted twice (20 ml) with 10% sodium bicarbonate and once (20 ml) with distilled water. The bright yellow nonaqueous solution was dried (MgSO_4), filtered and concentrated at reduced pressure. The remainder of the xylene was separated from the product by chromatography through a column of Merck acid-washed alumina. The column was washed with 50 ml of hexane and the product eluted with 150 ml of benzene. The benzene solvent was distilled at reduced pressure, leaving a yellow oily residue which crystallized on standing overnight. Recrystallization from ethanol gave 1.180 g (57%) of yellow needles of 7b; mp 53-55° [lit.²⁴ 58°].

The aqueous bicarbonate solution was acidified and extracted three times with ether. The ether layer was dried (MgSO_4), filtered, and evaporated to give 0.398 g (67% based on recovered acid) of unreacted acid melting at 148-150°.

C. Refluxing-solvent method.— In a 200-ml flask were placed 1.920 g (0.010 mol) of 5b, 9.600 g (0.040 mol) of lead dioxide and 75 ml of xylene. Nitrogen was passed through the apparatus at room temperature for 1 hr. The mixture was agitated with magnetic stirring and

heated at reflux for 4.5 hrs. After cooling and filtering, the xylene was distilled at reduced pressure, the liquid residue was dissolved in ether, and the ether solution was washed with a saturated sodium bicarbonate solution and a saturated salt solution and dried (MgSO_4). Distillation of the ether through a spiral column left a residue which was treated with 2,4-dinitrophenylhydrazine reagent.²⁵ The red precipitate was purified by elution through alumina with benzene and distillation of the benzene at reduced pressure to give 1.213 g (37%) of crystals of the 2,4-dinitrophenylhydrazone of crotonophenone: mp 194-197° [cf, Table I].

D. On-column reaction.— A 0.2 g sample of lead dioxide between glass wool plugs was placed in the injection port of an F&M Model 700 gas chromatograph. A 100 μ l sample of 10^{-3} M γ -oxo acid in ether was injected directly into the lead dioxide plug. The yield of α,β -unsaturated ketone produced was determined by comparing the peak area with those found for known amounts of the product.

With the injection port at 200° a 30% yield of 7b was realized from acid 5a while the α,β -unsaturated ketones derived from acids 5c and 5e were detected in 20% yields. In each case none of the enol lactone which would be formed by unreacted acid was found. Examination of the lead dioxide plugs after reaction showed very little charring.

Decarboxylation of Other Compounds -- (1) cis-1,2-Cyclohexanedicarboxylic Acid.— A mixture of 0.100 g (5.8×10^{-5} mol) of 1, 0.557 g (2.33×10^{-4} mol) of lead dioxide, and 5 g of powdered Pyrex glass was heated at 135° by method A above. After 1 hr, the product which collected along with water in the cooled portion of the tube was taken up in ether, and the ether layer dried (MgSO_4) and evaporated to give

0.021 g (44% yield) of cyclohexene. The infrared spectrum of the product was identical to that of reagent grade cyclohexene.

(2) The Enol Lactone of 2-Methyl-3-(2,5-dimethylbenzoyl)propionic Acid (11).— A mixture of 0.202 g (0.001 mol) of 11, 0.957 g (0.004 mol) of lead dioxide, and 2 g of powdered Pyrex glass was heated, using method A, at 135° for 1 hr. The only material other than water which collected in the tube was 0.015 g of unreacted starting material. However, the lead dioxide had turned yellow, indicating that a reaction occurred.

(3) The Enol Lactone of 3-Methyl-3-(2,5-dimethylbenzoyl)propionic Acid (12).— A mixture of 0.404 g (0.002 mole) of 12, 2.392 g (0.010 mole) of lead dioxide and 12 g of powdered soft glass was allowed to react according to method A at 250° for 15 min. Material condensed in two zones, ahead of the sublimator and in the portion of the tube cooled with dry ice. Analysis by gas chromatography and infrared spectroscopy showed the former to be unreacted enol lactone while the latter was a 7-mg mixture of six compounds, one of which was the α,β -unsaturated ketone in about 0.1% yield.

(4) Monomethyl cis-1,2-Cyclohexanedicarboxylate (8).— The following procedure for 9 was applied to 8 to give 0.017 g of decarboxylated product with an infrared spectrum very similar to the product from the trans half ester. Gas chromatography showed this material to be primarily three compounds but there were 17 peaks in all.

(5) Monomethyl trans-1,2-Cyclohexanedicarboxylate (9).— A mixture of 0.20 g (1.8×10^{-4} mole) of 9, 1.03 g (4.3×10^{-3} mole) of lead dioxide and 2 g of powdered Pyrex glass was treated at 135° by method A. The products condensed in three zones outside the sublimator and were

separated by severing the tubing between each pair of zones. Unreacted starting material (0.221 g) and 0.005 g of the anhydride of 1,2-cyclohexanedicarboxylic acid were isolated from the first two zones and were identified by comparisons of the infrared spectra with those of standard samples. In the third zone, 0.0203 g of material appeared; it showed no carboxyl group absorption in its infrared spectrum between 2500-2700 cm^{-1} but did have absorption bands at 1725 cm^{-1} ($\begin{array}{c} \text{O} \\ \parallel \\ \text{COR} \end{array}$) and 1648 cm^{-1} (C=C). Gas chromatographic analysis showed the condensate to be a mixture of mainly three compounds which were not identified.

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PART II

ACID-CATALYZED DIMERIZATION OF

1,2-DIHYDRONAPHTHALENE :

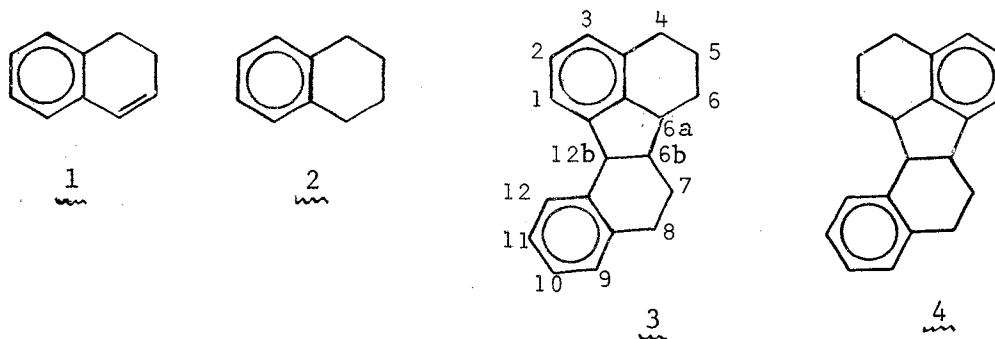
NEW STRUCTURE

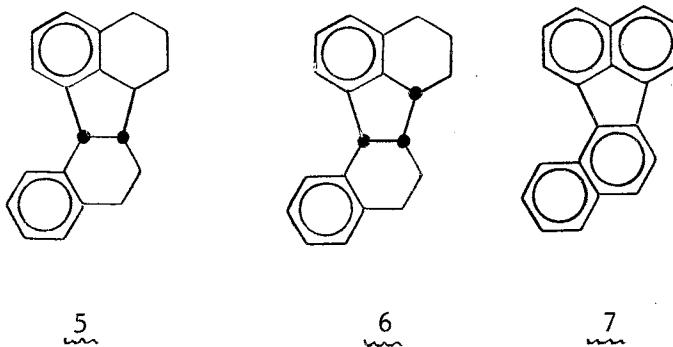
ASSIGNMENTS¹

CHAPTER I

INTRODUCTION, HISTORICAL, AND EXPERIMENTAL

Confusion exists about the structures of the products resulting from the acid-catalyzed dimerization of 1,2-dihydronaphthalene (1).^{2,3,4} We show that the C₂₀H₂₀ hydrocarbon dimer (mp 93°) derived from the sulfuric acid-catalyzed dimerization of 1 and the C₂₀H₂₀ hydrocarbon dimer (mp 153°) resulting from the action of phosphorous pentoxide on 1 and 1,2,3,4-tetrahydronaphthalene (2) are stereoisomers of 4,5,6,6a,6b,7,8,12b-octahydrobenzo[*j*]fluoranthene (3) and that 4 is not the correct structure for the lower melting dimer as previously reported.^{2,3} In addition, we offer instrumental evidence for the assignment of the configuration of these hydrocarbons, specifically cis, anti-4,5,6,6a,6b,7,8,12b-octahydrobenzo[*j*]fluoranthene (5), mp 93°, and cis, syn-4,5,6,6a,6b,7,8,12b-octahydrobenzo[*j*]fluoranthene (6), mp 153°.





The formation of these dimers from a variety of starting materials^{3,5,6,7,8} as well as their structural relationship to the well-known carcinogen benzo[*j*]fluoranthene (7)⁹ make the correct structural assignment important and of concern since it has been shown that partially hydrogenated polynuclear aromatic hydrocarbons may retain carcinogenic properties.¹⁰

Interestingly, gas chromatographic analysis shows that no detectable quantity of dimer melting at 93° is formed in the phosphorous pentoxide-catalyzed reaction which produces the dimer melting at 153°. Similarly, the sulfuric acid-catalyzed reaction produced the lower melting dimer but none of the other dimers.

The C₂₀H₂₀ dimer, mp 153°, has been synthesized by several routes^{2,12} designed to produce structure 3. Apparently without knowledge of the synthesis of 3, Campbell, et al., rationalized structure 3 for the lower melting isomer.⁴ As recently as 1968 however, structure 4 continues to be incorrectly used to describe the lower melting isomer.³ Stereochemical assignment to 3 or 4 has not previously been made.

The similarity^{7,8} of the ultraviolet spectra of both dimers to 2 and their facile dehydrogenation^{4,11} to 7 narrows the selection of their carbon skeletons to 3 or 4. The application of nmr spectroscopy now permits differentiation between structure 3 and 4.

Dimerization of 1 with sulfuric acid¹³ afforded white crystals of 5: mp 93° [lit.¹³ mp 93°]; uv max (95% C₂H₅OH) 268 (log ε 3.04) and 276 mμ (log ε 3.02), min 273 (log ε 2.86) and 2.43 mμ (log ε 2.32) [lit.⁸ uv max (n-hexane) 268 (log ε 3.08) and 277 mμ (log ε 3.13), min 273 (log ε 2.98) and 245 mμ (log ε 2.58)]; nmr (CCl₄) δ 6.67-7.41 (m, 7, ArH), 3.96 [d, 1, CH(Ar)₂], 2.2-2.95 (overlapping m, 6), 0.9-2.10 (overlapping m, 6).

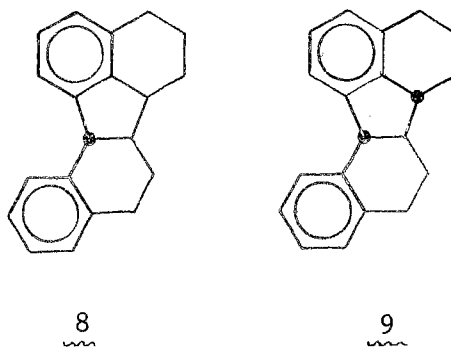
Reaction of a mixture of 1 and 2 with phosphorous pentoxide² gave the crystalline dimer 6: mp 152.5-153° (from C₂H₅OH) [lit.² mp 150.5°]; uv max (95% C₂H₅OH) 267 (log ε 3.07) and 274 mμ (log ε 3.03) [lit.⁸ uv max (n-hexane) 265 (log ε 3.12) and 273 mμ (log ε 3.05)]; nmr(CCl₄) δ 6.67-7.40 (m, 7, ArH), 4.17 [d, 1, CH(Ar)₂], 2.85-3.28 (m, 1, ArCH in plane of aromatic ring), 2.4-2.85 (overlapping m, 5), 0.8-2.35 (overlapping m, 6).

The presence of a benzhydryl-type proton doublet absorption in the nmr spectra of both dimers shows that they are stereoisomers of 3 and this is supported by the absorption due to seven aromatic protons in each spectrum.

Dreiding models of the cis fused ring stereoisomers 5 and 6 show that the benzhydryl-type proton of 6 lies nearer to the plane of the benzo ring than that in 5. This accounts for the downfield shift of this proton in the nmr of the dimer melting at 153°. Further evidence confirming structure 6 for the higher melting isomer is the general

broadening of the saturated proton multiplets indicating increased rigidity of the saturated rings in 6 caused by severe steric interference between the aromatic protons at positions 1 and 12. Also, the proton at position 8 is constrained in the plane of the adjacent phenyl ring and is probably responsible for the appearance of a multiplet at the unusual position between δ 2.85 to 3.28.

The lower melting isomer must then be assigned to structure 5 or to one of the two trans ring fused isomers 8 or 9. Drieding models of the highly strained trans isomers 8 and 9 cannot be made. Flexible bond models show the benzhydryl-type proton of each of these trans structures is approximately perpendicular to both aromatic rings and would be expected to absorb at a higher field than was found for the dimers m.p. 93 and 153°. Thus, configuration 5 is assigned to the lower melting dimer.



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PART III

1,4-DIHYDRONAPHTHALENE AS AN INTERMEDIATE IN
METAL-AMINE REDUCTIONS OF NAPHTHALENE

CHAPTER I

INTRODUCTION AND HISTORICAL

The Birch reduction¹ and related metal-amine reactions^{2a-d} involving alkali or alkaline earth metals dissolved in ammonia, a monoamine or a diamine have been widely applied to the reduction of aromatic systems.^{2e} Naphthalene (1) was one of the first aromatic hydrocarbons to be reduced.³ Hückel and Bretschneider⁴ observed that 1 is reduced at -70° , giving a red complex which is decomposed by methanol to 1,4-dihydronaphthalene (2). It has also been reported that the red complex reacts with ammonia at higher temperatures, giving 2 and 1,2-dihydronaphthalene (3). The latter is reduced to 1,2,3,4-tetrahydronaphthalene by sodium in ammonia at -50° .^{2f}

The reduction of 1 with sodium dissolved in a variety of amines has been studied.⁵ These reactions, unlike most of the work previously reported, have been carried out at room temperature. It was felt that the mechanism for the reduction of naphthalene proposed by Hückel and Bretschneider⁴ should apply equally well to a room temperature reaction, despite the occurrence of reductive amination⁵ and reductive dimerization.^{6a,b} Although the formation of 2 was not observed in the early phase of this work,^{6b} a knowledge of its presence or absence among the reaction products became important in order to provide assurance whether the mechanism in Fig. 2, derived from Hückel and Bretschneider⁴ and others,^{7a-d} could be used as a working model.

CHAPTER II

DISCUSSION AND RESULTS

In the present investigation, 1 was reduced by stirring with finely dispersed sodium and an amine (hexamethylenediamine, diisopropylamine, or cyclohexylamine) at room temperature. When the reaction mixture was quenched with water before all of 1 had reacted, 2 was found among the volatile reaction products.

As shown in Fig. 2, it is possible to rationalize the formation of 3 directly from 1 without first forming 2. However, since in this work 2 is shown to be present as a reaction product, it must be considered for mechanisms involving these reactions.

The argument that 2 may have arisen from 3 may be eliminated because 2 may be completely isomerized to 3 in the presence of such bases as alkali metal hydroxides^{8a} or anions derived from ammonia^{4,8b} or presumably amines.^{8c} Compound 3 does not appear to isomerize to 2 since the latter could not be detected during the sodium-diisopropylamine reduction of 3. Naphthalene (1) did not appear during this reduction and, although there is no evidence to show that the individual steps in these reductions of naphthalene are not reversible, it seems likely from reports of similar reactions that a series of equilibria^{7c,7d,8a-f} exist and the reduction of 3 or some closely related intermediate is sufficiently rapid^{8d} that 2 or 1 are not formed.

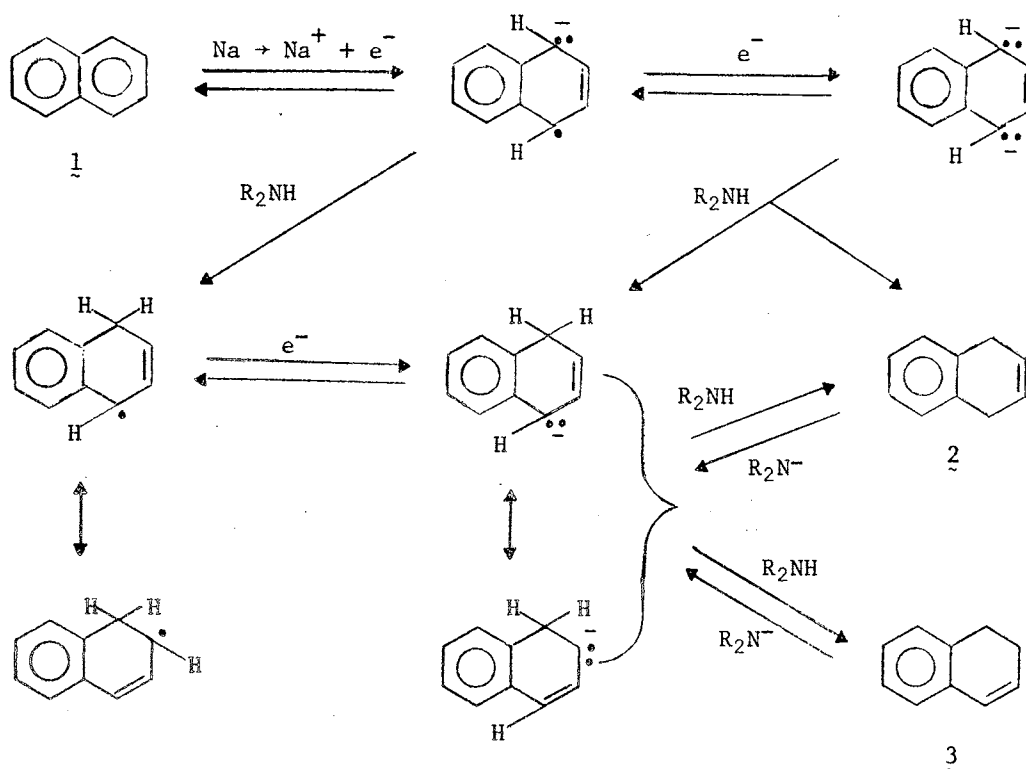


Figure 2. Mechanism for the Reduction of Naphthalene With Sodium

1,2- and 1,4-Dihydronaphthalene were shown to be present among the reduction products of 1 by combination gas chromatography-mass spectrometry in which a chromatographic fraction is trapped and then introduced into the mass spectrometer while the remaining fractions are held stationary on the column by stoppage of the carrier gas flow.^{9a-c} This technique is useful and efficient where carrier gas separators and fast-scanning mass spectrometers are not available.

A line drawing of the apparatus is shown in Fig. 3. A conventional

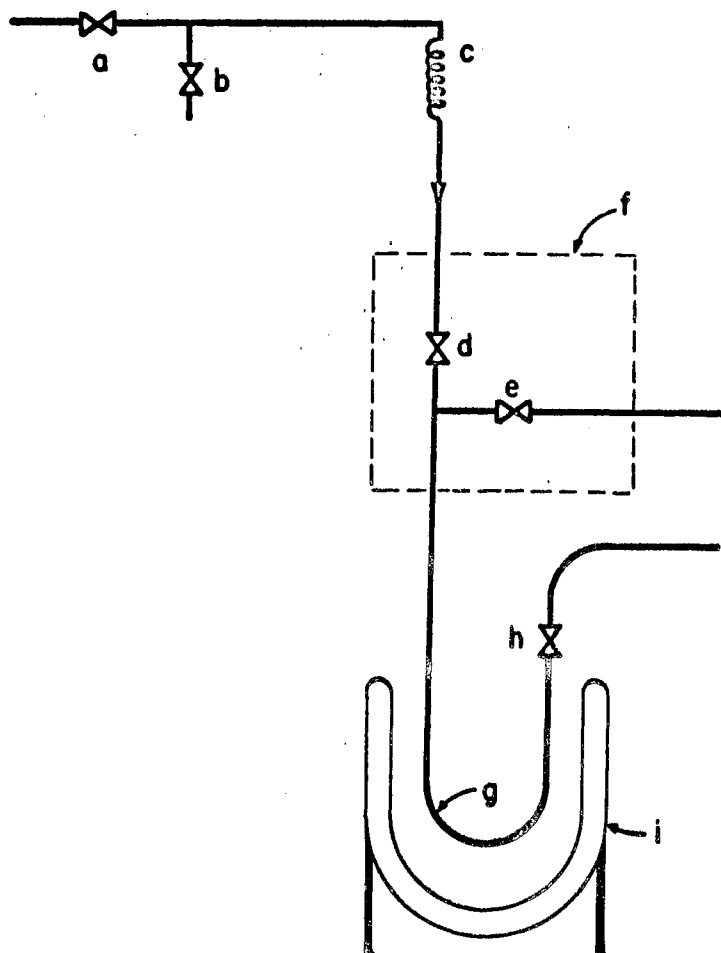


Figure 3. The Trapping System for Combination Gas Chromatography-Mass Spectrometry. ^acarrier gas inlet and injection port; ^bpressure release valve; ^cgas chromatographic column; ^dvalve to trap; ^evalve to mass spectrometer; ^fheated jacket; ^gtrap wrapped with heating wire; ^hvalve to vacuum; and ⁱDewar flask

chromatograph equipped with a thermal-conductivity detector was used in combination with a Bendix Model 12 time-of-flight mass spectrometer. As the material corresponding to a peak emerged from the chromatographic column, it was directed into the trap cooled by liquid nitrogen. After the carrier gas was pumped away, the trap was warmed to a temperature sufficient to vaporize the component. The mass spectrum could then be obtained. As soon as the spectrum was recorded, the remaining component was pumped out of the trap, whereupon the apparatus was ready for the next fraction.

The gas chromatogram of the volatile products from the sodium-hexamethylenediamine reduction of 1 is shown in Fig. 4. The chromatograms of the other two systems are similar but not shown. The relevant peaks are numbered 4, 5, and 6 (1,2,3,4-tetrahydronaphthalene, 3, and 2 respectively). Fig. 4 is a continuous chromatogram and not from the stopped-flow technique. When the stopped-flow technique is used, some peak spreading is observed. This is not detrimental except where two or more peaks are closely spaced. In such cases, some overlap will result. Because peaks for 2 and 3 were located on the trailing edge of peak No. 4, they were analyzed during a separate run. Good spectra of the materials corresponding to the other 5 peaks were obtained during a single run.

The mass spectra of the hydrocarbons represented by peaks 4, 5, and 6 were obtained and are presented in Table II. As expected from the close proximity to peak No. 4, the fractions containing the two dihydronaphthalenes are contaminated with tetrahydronaphthalene. By subtracting out the spectrum of the latter, two mass spectra essentially the same as from pure 3 and 2 were obtained for peaks 5 and 6

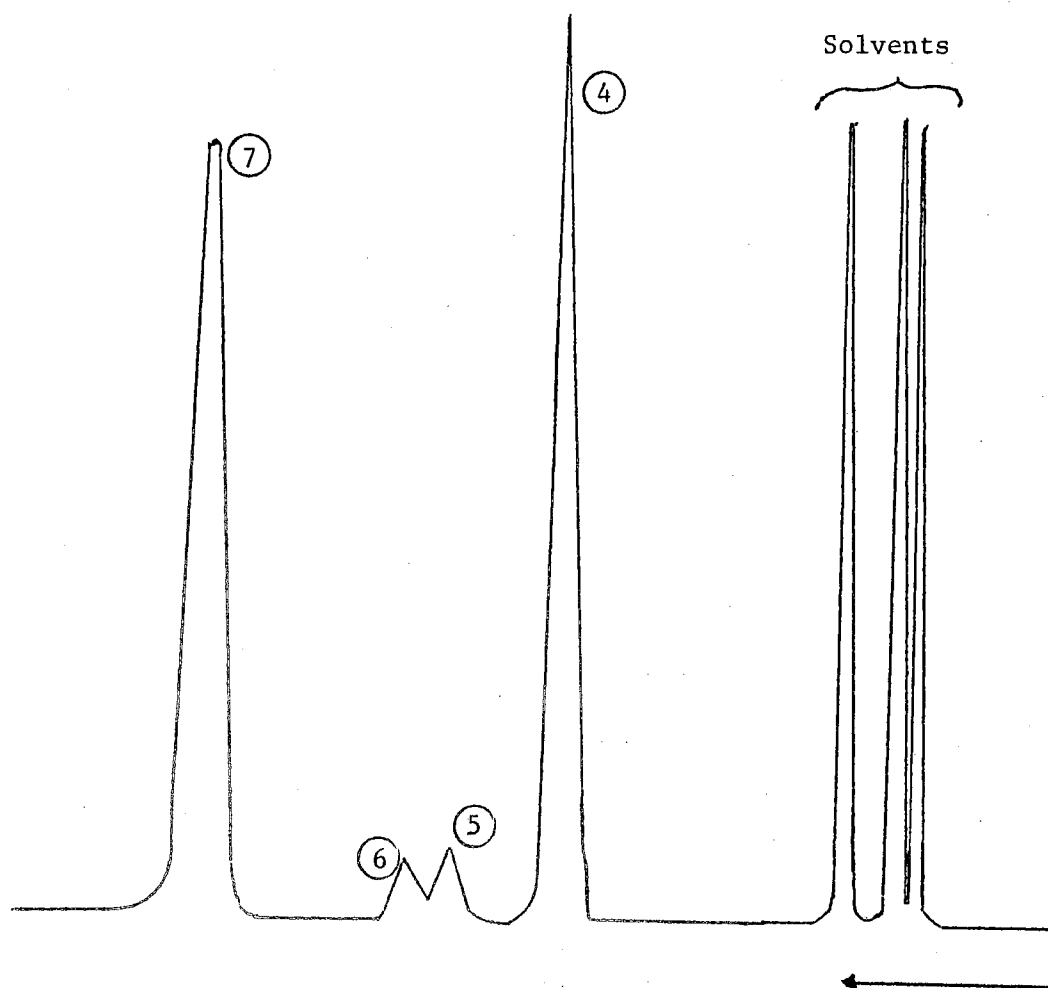


Figure 4. Gas Chromatogram of Volatile Hydrocarbons From the Reduction of 1 With Hexamethylenediamine and Sodium

respectively. Partial spectra compared with those of standard samples are also shown in Table II.

Since the mass spectra of 2 and 3 are very similar, it is not possible, on the basis of the spectra alone, to distinguish 2 and 3. However, the difference in chromatographic retention times for the two standards permits correlation of 3 with peak No. 5 and 2 with peak No. 6.

The presence of 2 and 3 was also confirmed in the Na-diisopropylamine system by the combination gas chromatograph-mass spectrometer. Although the mass spectra were not obtained for the third system (Na-cyclohexylamine), the two isomers were identified by the two characteristic peaks present in the gas chromatogram.

TABLE II
 MASS SPECTRA OF NAPHTHALENE REDUCTION PRODUCTS^a

Mass	Relative Intensity						
	<u>1,2-Dihydronaphthalene</u>			<u>1,4-Dihydronaphthalene</u>			<u>1,2,3,4-Tetrahydro-</u> <u>naphthalene</u>
	Uncorrected ^b (Corrected) ^c	Standard	Standard	Uncorrected ^d (Corrected) ^e	Standard	Standard	Standard
91	48	(5)	5	47	(5)	5	51
104	100	(8)	7	100	(8)	8	100
115	25	(38)	37	37	(37)	37	15
127	12	(19)	19	20	(20)	20	6
128	29	(38)	39	48	(42)	42	8
129	31	(70)	71	47	(75)	76	7
130	38	(100)	100	52	(100)	100	5
131	26	(16)	17	33	(18)	18	17
132	58	(8)	7	81	(7)	7	53

^aFrom the reduction of 1 with sodium and hexamethylenediamine; ^bpeak No. 5, Fig. 4; ^cmass spectrum of peak No. 5 minus contribution from 1,2,3,4-tetrahydronaphthalene; ^dpeak No. 6, Fig. 4; ^emass spectrum of peak No. 6 minus contribution from 1,2,3,4-tetrahydronaphthalene.

CHAPTER III

EXPERIMENTAL

Reduction of 1 with Sodium and Hexamethylenediamine.— A mixture of 1, 6.4 g (0.05 moles), dispersed sodium, 4.6 g (0.2 g atom), and 100 ml of hexamethylenediamine was stirred under nitrogen with a magnetic bar. The 250-ml reaction vessel was equipped with an air condenser and a drying tube. Within 5 min, the reaction turned dark red and in 30 minutes the sodium agglomerated to form a shiny ball. After 12 hrs, the lump of sodium was removed and the remaining slurry was cautiously poured over 400 ml of crushed ice. The reaction mixture was extracted three times with ether and the ether layer was washed with 20% hydrochloric acid until free of amine and then washed with water to neutrality. The acid extract was then combined with the aqueous washings.

The ether extract was steam distilled and both the residue and the distillate were extracted with ether. The separate ether extracts were then dried (Na_2SO_4) and freed of ether to give 2.8 g of volatile hydrocarbons and 1.7 g of nonvolatile hydrocarbons. The latter was a complex mixture of dimers and trimers.^{6b} The volatile products were analyzed by the gas chromatography-mass spectrometry technique on a 10-ft x 0.25-in. column containing Carbowax 20M on 80-100 mesh, acid-washed Chromosorb W at 190° and found to contain small quantities of ethanol introduced as an impurity from the ether used in the extraction, xylenes (from the dispersed sodium), 1,2,3,4-tetrahydronaphthalene, 3, 2, and 1

(see Fig. 4). The approximate ratio of $\underline{2}$ to $\underline{3}$ was 0.43:1.

The acidic aqueous extract was made basic with 30% sodium hydroxide and steam distilled. The residue was extracted with ether and the ether extract was dried (Na_2SO_4) and distilled to give 3.2 g of crude non-volatile amine.⁵

Reduction of 1 with Sodium and Cyclohexylamine.— Cyclohexylamine was substituted for diisopropylamine in the above procedure. The yields of products were: nonvolatile hydrocarbons, 2.1 g; volatile hydrocarbons, 1.6 g; and nonvolatile amines, 4.3 g. The approximate ratio of $\underline{2}$ to $\underline{3}$ was 0.25 to 1.

Reduction of 1 with Sodium and Diisopropylamine.— Diisopropylamine was substituted for hexamethylenediamine in the earlier procedure. The yields of products were: nonvolatile hydrocarbons, 2.7 g; volatile hydrocarbons, 2.4 g; and nonvolatile amines, 0.1 g. The approximate ratio of $\underline{2}$ to $\underline{3}$ was 2.4:1.

Reduction of 3 with Sodium and Diisopropylamine.— 1,2-Dihydronaphthalene ($\underline{3}$) (5.00 g), 3.54 g sodium dispersion and 154 ml diisopropylamine were combined as previously described. Samples were removed after 1 and 2 hours. These samples were quenched with water and extracted into ether and the ether extracts were dried (Na_2SO_4) and filtered. The gas chromatograms of these samples on the Carbowax column at 190° showed complete absence of $\underline{2}$ and $\underline{1}$.

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PART IV

METAL-AMINE REACTIONS OF NAPHTHALENE:

REDUCTIVE DIMERIZATION

CHAPTER I

INTRODUCTION AND HISTORICAL

The formation of C_{20} hydrocarbons as side reaction products of metal-ammonia reduction of 1,2-dihydronaphthalene was reported by Hückel and Bretschneider^{1a} in 1939, who referred to Lebeau and Picon's^{1b} "dimere des tetralin," mp 99°. More recently Hückel and Wartini² have shown that slow addition of sodium to 1,2-dihydronaphthalene in liquid ammonia gives a 2,2'-octahydrobinaphthyl, mp 114°. Benkeser,³ et al. probably isolated C_{20} dimeric hydrocarbons from the reduction of naphthalene with sodium and ethylamine but did not report the composition of their "polymeric material." Reggel, et al.⁴ reported that hexahydro- and octahydrobinaphthyl were present among the reaction products. In contrast to previous reports,^{1,2} the octahydrobinaphthyl isolated by Reggel melted at 85°. We have confirmed^{5,6} one of the products from this reaction to be 1,1',2,2',3,3',4,4'-octahydro-2,2'-binaphthyl (1), mp, 84-85°. A recent study by Markov, et al.⁷ using magnesium and ammonia in the reduction of naphthalene provided presumably the same product, mp 119° ($C_{20}H_{22}$), as previously obtained by Hückel and Wartini² from sodium and 1,2-dihydronaphthalene.

Our study has included a number of metal-amine reactions of naphthalene and the dihydronaphthalenes to learn the nature of these C_{20} dimeric products which are considered to arise from a reaction competing with the Birch-type reduction^{8a,b} and reductive amination.^{5a}

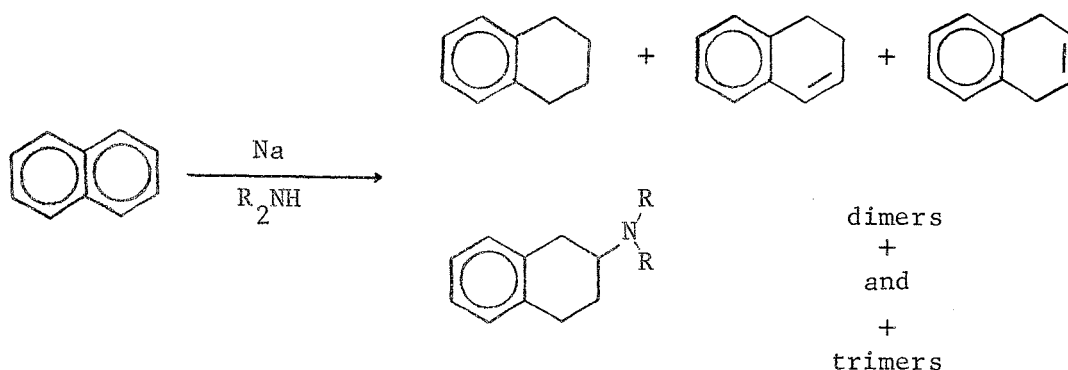
Although Lebeau and Picon^{1b} first studied the reduction of naphthalene with sodium in liquid ammonia as early as 1914, it remained for Wooster and Smith⁹ to carry out a more detailed study of this reaction. It became of interest to determine whether our products were the same as those previously reported.^{1,2,3,4} Repetition of Wooster and Smith's reduction showed that dimers are indeed formed. Higher yields of these dimers may be realized by the slow addition of sodium to the naphthalene-liquid ammonia solution.

Dimers have also been formed from reactions of dihydronaphthalenes utilizing solvents other than amines. The polymerization of 1,2- and 1,4-dihydronaphthalene in nonprotic solvents gives a thermally stable, brittle polymer.¹⁰ After initiation by sodium-naphthalene, the reaction solution becomes bright red. At low temperatures (-20° to -30°) in dimethyl ether, "dimers of dihydronaphthalene" have been obtained.¹¹ The same workers isolated a crystalline dihydronaphthalene dimer (mp 51-2°) when 80% sulfuric acid was used as a catalyst.^{10,12}

CHAPTER II

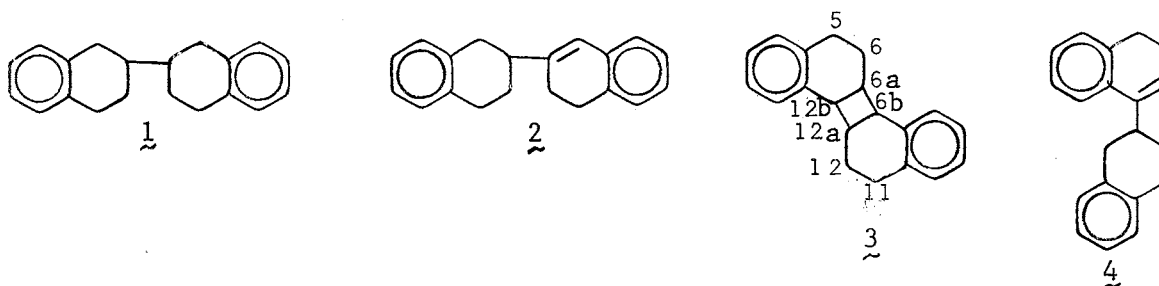
DISCUSSION AND RESULTS

In addition to the expected Birch-type reduction, sodium and primary or secondary amines cause reductive amination^{5a,b,c} and reductive dimerization and trimerization of naphthalene, but interestingly, very little higher polymerization products are observed.^{5d}



The versatility of this reaction can best be illustrated by citing the change in product composition with change in amine solvent which is a reflection of the relative rates of the various competing reactions.^{5b} Reductive dimerization of naphthalene in different amines may provide

any of the structures shown below as a major product or part of a more complex mixture (cf. Table III).



Mass spectrometric analysis of the dimeric products from the reaction of sodium and naphthalene in ethylamine showed a 19% yield of a $C_{20}H_{20}$ dimer which was assigned structure 2.⁴ We now show that this dimer is 3 (Table III). Structure 1 is reported to comprise 72% of the dimer fraction. Since the melting point range ($114-119^\circ$)^{1,2,7} of 1 formed in homogeneous reactions in ammonia is higher than the melting point (85°)^{4,5} obtained for the product from the heterogeneous reactions of sodium in various amines, one may conclude that the heterogeneous reaction produces another diastereoisomer or a mixture of diastereoisomers of 1. This problem remains under study. Catalytic reduction of 1,2,3,3',4,4'-hexahydro-2,2'-binaphthyl (2) with palladium on carbon forms 1, mp 102° , while reduction of 2 with sodium and ethylamine provides 1, mp 84° .

Some control of specific dimer formation in reductive dimerization is possible through selection of the appropriate amine solvent. In

TABLE III
REDUCTIVE DIMERIZATION OF NAPHTHALENE^a

Amine Solvent	Nonvolatile Hydrocarbons Yield, %	Reaction Time, hr	Relative Ratios of Dimers				Other Dimers Peak No. (Yield)
			1	2	3	4	
Ammonia ^b	87	26	2	29	-	30	1(40)
Ammonia ^c	8	12	-	39	-	11	1(17), 4&5(32), 6(1)
Ethylenediamine	91	12	14	-	76	-	1(2), 3(8)
N,N-Dimethylethylenediamine	58	12	88	-	5	3	2(4)
1,3-Diaminopropane	90	12	38	-	53	-	1(0.5), 5(2.3), 3(6)
1,4-Diaminobutane	70	12	91	-	9	-	
1,5-Diaminopentane	47	12	96	-	3	1	
1,6-Diaminohexane	44	12	52	-	34	-	1(trace), 3(4), 5(10)
<u>n</u> -Hexylamine	47	24	19	-	54	7	4(11), 5(9)
Cyclohexylamine	43	12	42	-	21	7	2(11), 5(4), 6(14)
Ethylamine	80	12	65	-	23	-	2(12)

TABLE III (Continued)

Amine Solvent	Nonvolatile Hydrocarbons Yield, %	Reaction Time, hr	Relative Ratios of Dimers				Other Dimers Peak No. (Yield)
			1	2	3	4	
Di- <u>n</u> -propylamine	66	12	-	-	-	71	1&2(19), 4(10)
Di- <u>iso</u> -propylamine	58	12	33	-	-	65	2(2)
Di- <u>n</u> -butylamine	50	12	-	-	-	63	1(19), 3(18)
Pyrrolidine	36	12	98	-	2	-	
Piperidine	11	12	94	-	2	-	2(1), 3(3)
Hexamethyleneimine	56.5	12	72	-	6	trace	1(5), 2(14), 3(3), 4(2)
N-Methylpiperazine	5	12	71	-	1	17	3(8), 4(4)
Morpholine	12	8	94	-	-	-	2(1), 3(5)
3,5-Dimethylmorpholine	12	12	20	-	-	71	3(9)

^aFor reaction conditions see the reduction of naphthalene with sodium and ethylenediamine described in the experimental section. ^bSodium added slowly to a solution of naphthalene in ammonia. ^cNaphthalene added rapidly to a solution of sodium in ammonia.

general, lower-molecular-weight diamines favor the formation of 5,6,6a, 6b,11,12,12a,12b-octahydrodibenzo[a,g]biphenylene (3). However, as the number of methylene units separating the amine groups is increased, the diamine takes on the qualities of a monoamine, and little cyclobutane dimer 3 is produced (cf. Fig. 5), whereas the sterically hindered secondary amine, dipropylamine, causes the preferential formation of the α,β -coupled dimer, 1',2',3,3',4,4'-hexahydro-1,2'-binaphthyl (4).

Figure 5 shows that in the homologous series of diamines, as the number of methylene units is increased, the total yield of dimers decreases. This decrease in dimeric products is accompanied by an increase in the yield of reductive-amination product. It is generally true in sodium-amine reactions with naphthalene that most of the reacted naphthalene may be accounted for through the formation of reductive-dimerization and reductive-amination products. The volatile hydrocarbons (1,2-dihydronaphthalene, 1,2,3,4-tetrahydronaphthalene, and occasionally 1,4-dihydronaphthalene) are formed in low yield.

The reduction of naphthalene with sodium in liquid ammonia was found to give not only tetralin as reported by Wooster and Smith,⁹ but also a low yield (8%) of dimers and trimers. This yield of polymeric material is increased to 87% when sodium is added slowly to a solution of naphthalene in ammonia as opposed to Wooster and Smith's⁹ original method of adding naphthalene to a solution of sodium in ammonia. Gas chromatographic analysis of the dimer fraction showed that the composition of the mixtures did change somewhat with change in procedure. The major dimeric products were 2, 4, and an unknown compound in about equal proportions from the inverse addition of sodium, while a mixture of five dimers was produced by the Wooster reaction⁹ of which 4 and 2

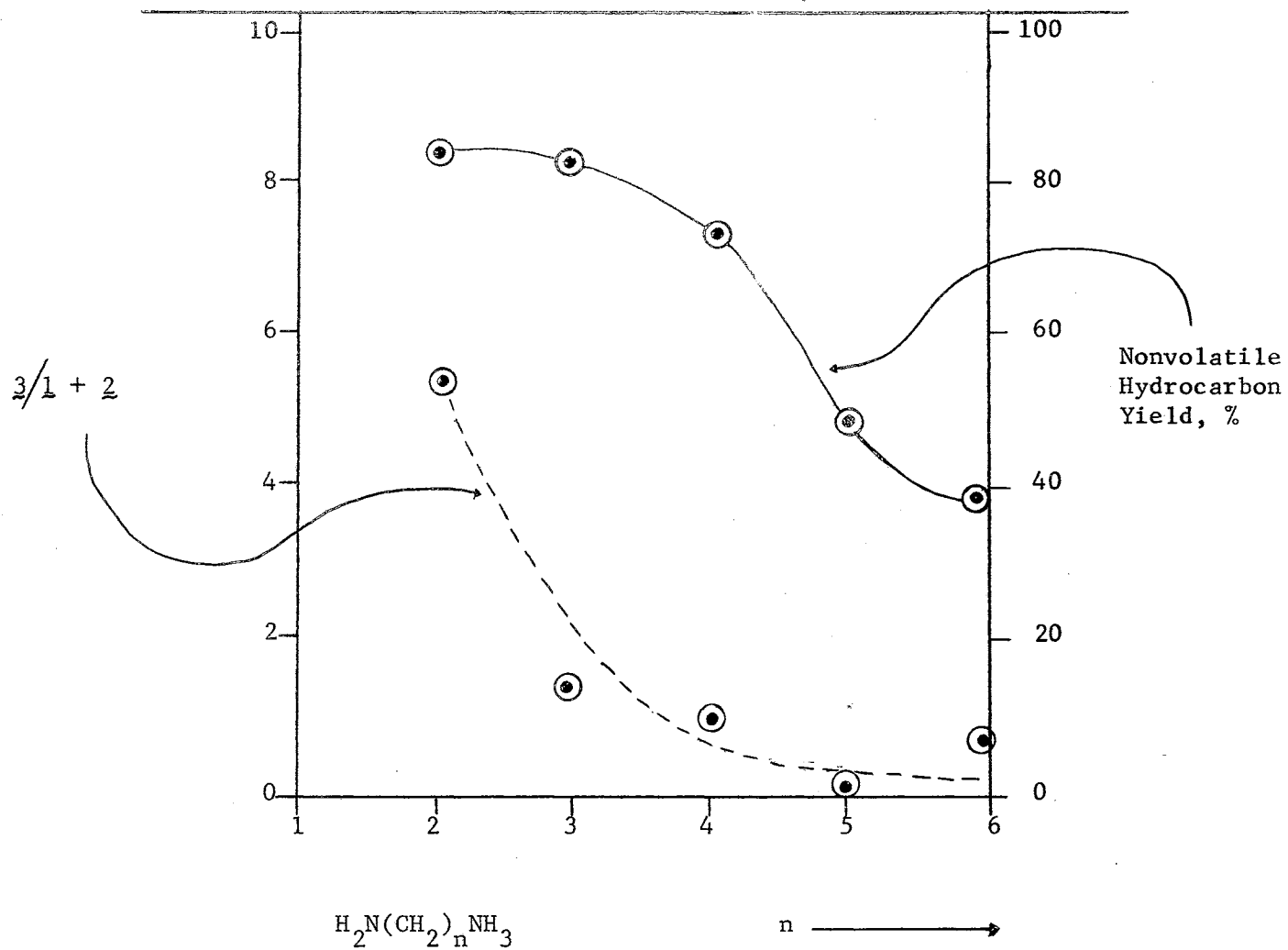


Figure 5. Effect of Change in Homologous Series of Diamines on the Ratios of Dimeric Products and the Total Yield of Polymeric Material

were the only identified components.

The dimers 2, 3, and 4 are also formed by base-catalyzed reactions of 1,2-dihydronaphthalene or 1,4-dihydronaphthalene in certain solvents under nonreducing conditions. The critical role of both solvent and cation in polymerization reactions has already been documented.^{13,14} These two factors have a profound effect on the yields of dimers and trimers from dihydronaphthalenes. Potassium hydroxide is sufficiently basic to cause dimerization of dihydronaphthalenes in dimethyl sulfoxide. The effect of other solvents and bases on this reaction is shown in Table IV. Although the low solubility of sodium hydroxide in ethylenediamine does not permit realization of high yields of dimeric products, the ratio of specific dimers formed is similar to that from the reaction of sodium and naphthalene in ethylenediamine.

The reaction of sodium with naphthalene in ethylenediamine displays a variety of colors. After 10-15 minutes of stirring, the colorless mixture develops the green color typical of the naphthalene radical ion.¹⁵ In less than 60 seconds, the green mixture changes to the brown color of the relatively stable anion of dihydronaphthalene.^{15,16} The brown color progressively darkens until after two hours it becomes opaque. A deep red or purple color which has been attributed to both the dianion of naphthalene¹⁷ and to living polymers of dihydronaphthalenes¹⁰ develops in about five hours. Soon after the appearance of this red color a blue color is sometimes observed. Admittance of air causes the upper part of the red reaction mixture to turn blue. This blue color gradually reverts to red in the absence of air. The color of the mixture is red to red-brown during reductive dimerization in most other amine solvents.

TABLE IV
BASE-CATALYZED DIMERIZATION OF DIHYDRONAPHTHALENES

Dihydronaphthalene	Solvent	Base	Hours	Temp.	Dimer Hydrocarbons ^a Yield, %	Relative Yields ^b			
						2 ~	3 ~	4 ~	Unknown ^c
1,4-	DMSO	KOH	5	100°	73	54	12	34	-
1,2-	DMSO	$\text{Na}^+\text{CH}_2^-\text{SCH}_3$	2	100°	100	79	11	10	-
1,2-	EDA	BuLi	5	28°	91	83	4	13	-
1,2	EDA	NaOH	24	28°	0.5	26	59	trace	15
1,2	Dioxane	KOH	22	101°	trace				
1,2-	HMPA	KOH	48	75°	trace				
1,2-	Hexane	BuLi	1.5	28°	trace				

^aNot steam volatile. ^bDetermined through gas chromatography studies. ^cPeak three in Fig. 7.

Reductive dimerization of naphthalene under nonprotic conditions in tetramethylethylenediamine results in five new compounds which are not found in the dimeric fractions when primary and secondary amines are used as solvents.¹⁸ Other workers¹⁹ have shown that the naphthyl radicals will react with naphthalene to produce 1,1'-, 1,2'-, and 2,2'-binaphthyl. Since dimerization would be expected to occur only by free-radical coupling under nonprotonating conditions, it may be concluded that the products from the dimerization in tetramethylethylenediamine were the result of a free-radical mechanism and that the different dimers formed in primary and secondary amines may arise by a different pathway, i.e., an ionic mechanism. The probability of an ionic mechanism being operative in the reductive dimerization of naphthalene using protic amine solvents is further supported by the fact that the base-catalyzed dimerization of dihydronaphthalenes gives the same dimers.

A mechanistic rationalization for the ionic dimerization is shown in Fig. 6. As shown in these reaction schemes, several dimers which should appear in the initial part of the reaction, would be consumed as the reaction proceeds and the end products should be some combination of 1, 3, and 5. The gas chromatograms in Fig. 7 verify this for the ethylenediamine reaction. Peaks 2, 4, and 5 correspond to compounds 1, 3, and 2 respectively. Structural assignments to the compounds responsible for peaks 1, 3, and 5 have not been made. After six hours reaction time only dimers 1 and 3 remain in significant yields. The unknown compounds represented by peaks 1 and 3 are present only in trace quantities. The absence of 4 and 5 in the reactions in ethylenediamine but their presence in the products from most other reductive-dimerization reactions using different amine solvents is probably a reflection

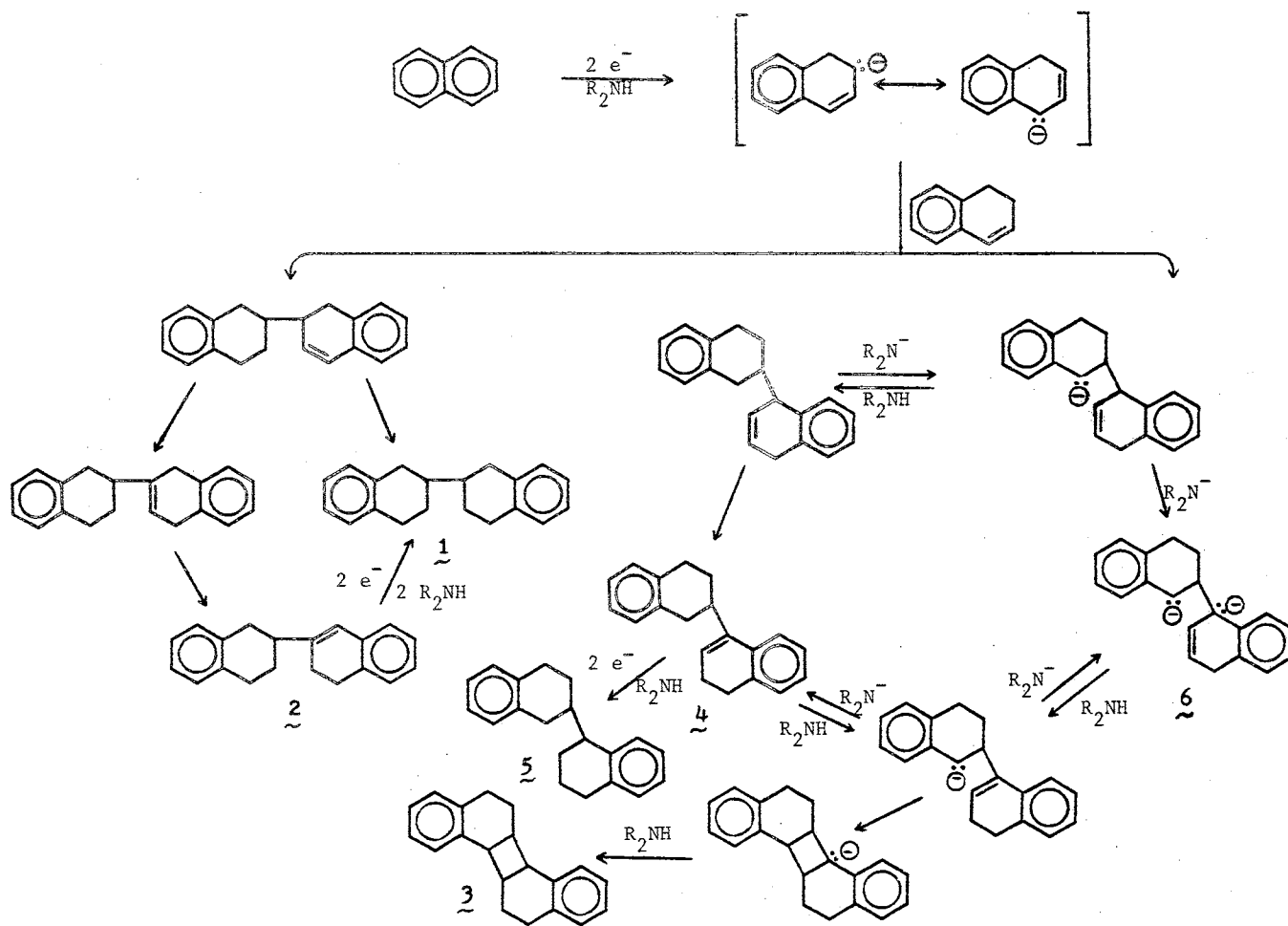


Figure 6. An Ionic Mechanism for Reductive Dimerization

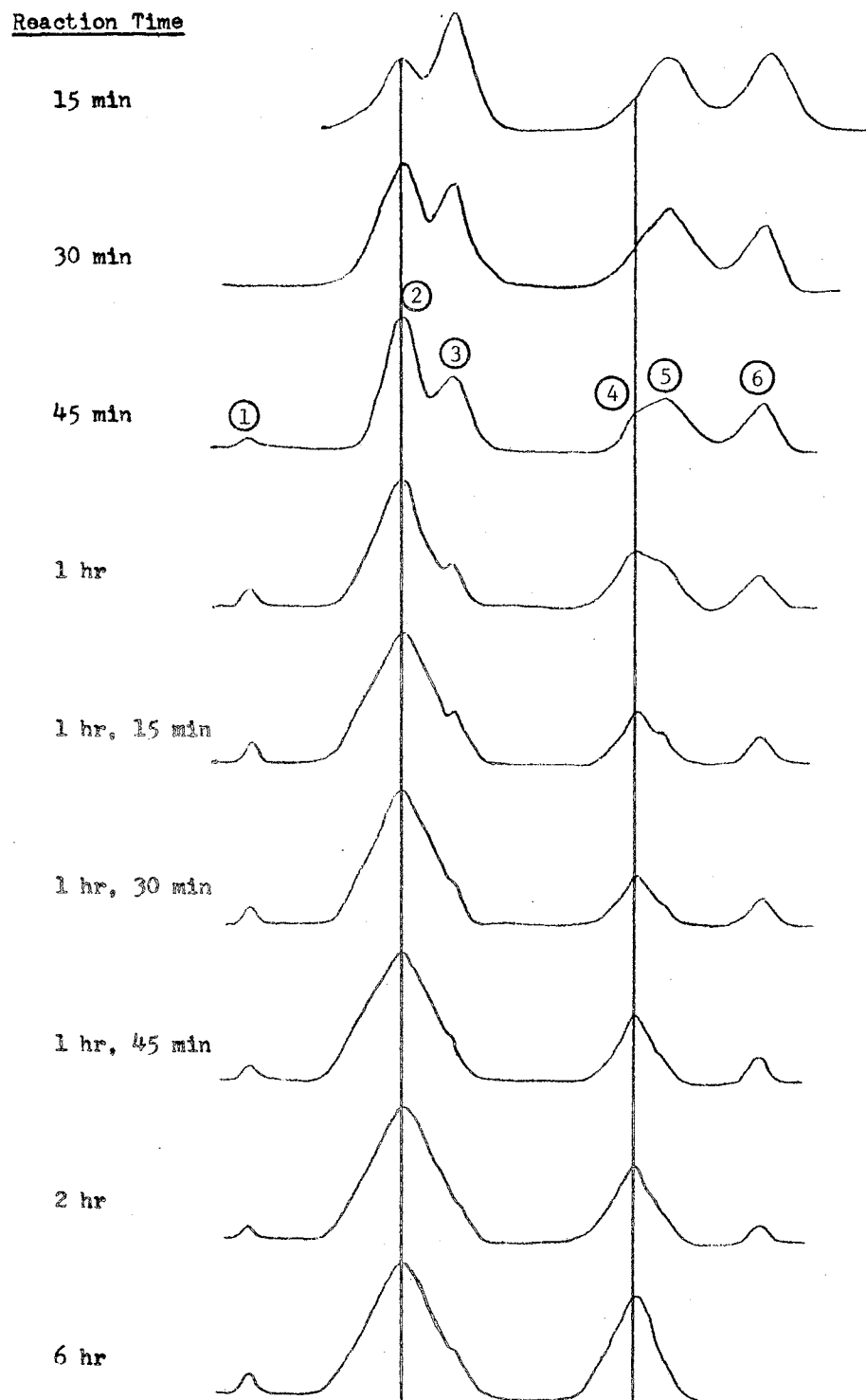


Figure 7. Gas Chromatograms of the Reaction Products of Naphthalene and Sodium in Ethylenediamine

of differences in the solubility of intermediate dimer ions in these amines.

The much greater cation solvation by tetrasubstituted ethylenediamines when compared with monotertiary amines has been well documented.²⁰ It follows a priori that ethylenediamine will be a better solvent for the dimer salts than other diamines or monoamines. The general decrease in total yield of dimers as the solvent is varied from ethylenediamine through the homologous series of diamines (cf. Fig. 5) is probably a direct consequence of this decreased solvation of the organometallic intermediate. The greater solvating ability of the ethylenediamine also may account for the greater yields of the cyclobutane dimer 3 since the dianion 6 would be expected to be more soluble in this solvent.

The clean conversion of 2 to 1 in sodium and ethylenediamine verifies that particular portion of the mechanism (Fig. 6). Van Tamelen, et al.,²¹ have shown that the radical ion of cyclopentadiene couples to give a dianion which, upon hydrolysis, produces equal amounts of the dl and meso forms of 3-(3'-cyclopentenyl)cyclopentene. The reader should be reminded that only one 2,2'-octahydrobinaphthyl, mp 85°, was obtained in the metal-amine reactions. Repeated recrystallizations from ether and acetone do not change its melting point.

Interestingly the presence of oxygen or iron salts in these reaction systems results in significant yields of 2,2'-binaphthyl. However, no detectable amount of this dimer is produced in normal reactions run under an inert atmosphere.

CHAPTER III

EXPERIMENTAL

Nuclear magnetic resonance (nmr) spectra were obtained with a Varian HR-60 spectrometer. Peak positions are reported in terms of δ = parts per million (ppm) downfield from internal tetramethylsilane standard in carbon tetrachloride solvent. Mass spectra were obtained with a Consolidated Electrodynamics Corporation Model 21-103 C mass spectrometer. Gas chromatographic analyses for the hydrocarbons were obtained with an F&M Model 5750 gas chromatography apparatus fitted with dual thermal conductivity and hydrogen flame detectors using helium as a carrier gas.

The amines used in this work were distilled from potassium hydroxide. The dispersed sodium was prepared by stirring molten sodium at high speed in xylene and then allowing the suspension to cool without agitation.

Structural Assignments.— The structures of the reductive dimerization products 1, 2, 3, and 4 were assigned from nmr and mass spectral data summarized in Tables V and VI.

General Reaction Conditions.— With the exception of ammonia and ethylamine, all reductions were carried out at room temperature under a nitrogen atmosphere in a 250-ml, three-necked flask equipped with an air condenser and magnetic stirring bar. When ethylamine was used as a solvent, a water condenser kept at 5° was used. A dry ice condenser

TABLE V
 NUCLEAR MAGNETIC RESONANCE SPECTRA OF REDUCTIVE
 DIMERIZATION PRODUCTS (60 Hz)

Compound	Proton Absorptions (CCl ₄)
1	δ6.99 (s, 8, ArH), 2.73 (m, 8, ArCH), and 1.2-2.3 (overlapping m, 6, ArCCH).
2	δ6.96 (s, 8, ArH), 6.21 (s, 1, C=CH), 2.77 (m, 6, ArCH), and 1.5-2.5 (m, 5, C=CCH & ArCCH).
3	δ6.99 (s, 8, ArH), 2.6-3.5 (m, 6, ArCH), and 1.1-2.2 (m, 6, ArCCH).
4	δ6.97 (m, 8, ArH), 5.83 (s, 1, ArC=CH), 2.45-3.2 (m, 6, ArCH), and 1.4-2.4 (overlapping m, 5, ArCCH & C=CCH).

TABLE VI
 MASS SPECTRAL DATA OF REDUCTIVE DIMERIZATION PRODUCTS (70 eV)

Compound	m/e (rel intensity)
1	262 (47), 131 (100), 130 (36), 129 (32), 115 (21), 104 (40), 21 (33).
2	260 (19), 131 (31), 130 (58), 129 (100), 128 (63), 115 (21), 104 (18), 91 (16).
3	260 (45), 131 (37), 130 (33), 129 (100), 128 (68), 127 (14), 115 (23).
4	260 (51), 131 (63), 130 (62), 129 (100), 128 (74), 115 (43), 104 (69).

was used to retain refluxing ammonia.

Reduction of Naphthalene With Sodium and Ethylenediamine.— A mixture of naphthalene, 6.4 g (0.05 mol), dispersed sodium, 4.6 g (0.2 g atom) and 100 ml of ethylenediamine was stirred under nitrogen with a magnetic bar. The 250-ml reaction vessel was equipped with an air condenser and a soda-lime drying tube. Within 5 min, the reaction mixture turned dark blue and in 30 minutes the sodium agglomerated to form a shiny ball. After 12 hrs, the lump of unreacted sodium was removed and the remaining slurry was cautiously poured onto 400 ml of crushed ice. The reaction mixture was extracted three times with ether and the ether layer was washed with excess 20% hydrochloric acid and then washed with water to neutrality. The acid extract was then combined with the aqueous washings.

The ether extract was steam distilled and both the residue and the distillate were extracted with ether. The separate ether extracts were then dried (Na_2SO_4) and freed of ether to give 1.1 g of volatile hydrocarbons and 5.8 g of nonvolatile hydrocarbons. The latter material was shown by mass spectral analysis to contain a 4:1 ratio of dimers to trimers (m/e 390) with a trace of tetramers (m/e 520).

Gas chromatographic analysis of the dimer fraction on a 10-ft x 1/8-in. column containing 5% silicone UCW-98 on 80-100 mesh, DMCS-treated, acid-washed Chromosorb W at 230° showed the total yield of the two major components to be 8.7% of 1 and 52% of 3. Equal relative molar responses of these compounds was assumed. The total yield of trimers was 19%. The nonvolatile hydrocarbon oil was dissolved in a minimum amount of ether. On standing overnight 0.32 g (5%) of 3, mp 176-178°, crystallized from the solution. Recrystallization in acetone

and purification by zone refining gave white crystals melting at 179-180°.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.25; H, 7.85.

The volatile hydrocarbons were analyzed by the gas chromatography on a 10-ft x 0.25-in. column containing Carbowax 20M on 80-100 mesh, acid-washed Chromosorb W at 190° and found to be primarily tetralin with traces of 1,2-dihydronaphthalene and naphthalene.

The acidic aqueous extract was made basic with 30% sodium hydroxide and steam distilled. The residue was extracted with ether and the ether extract dried (Na_2SO_4), and the ether distilled to give 0.1 g of crude nonvolatile amine.

The reaction procedure and product analysis techniques given above are identical to those used with the other amine solvents shown in Table III.

Reaction of Naphthalene With Sodium and Dipropylamine.— Dipropylamine was substituted for ethylenediamine in the above procedure. The yields of products were: 0.92 g of volatile hydrocarbons including 0.06 g recovered naphthalene, 0.08 g nonvolatile amines, and 4.2 g nonvolatile hydrocarbons. Gas chromatographic analysis of the latter showed the yield of individual dimers based on reacted naphthalene to be 13% of an unknown dimer, 2.2% of 1 and 51% of 4. Dimer 4 was isolated by preparative gas chromatography.

Reaction of Naphthalene With Sodium and Ethylamine.— Ethylamine was substituted for ethylenediamine in the above procedure. The yields of products were: 0.08 g (1.2%) of tetralin, 1.5 g (17%) of crude N-ethyl-1,2,3,4-tetrahydro-2-naphthylamine, and 5.2 g (80%) of nonvolatile

hydrocarbon dimers. Gas chromatographic analysis of this latter product showed it to contain 1 (65%), 3 (23%), and an unknown dimer (12%). A saturated ether solution of the viscous oil crystallized to give 2.5 g of white crystals of 1, mp 84-85°.

Anal. Calcd for $C_{20}H_{20}$: C, 91.55; H, 8.45. Found: C, 91.64; H, 8.51.

Reaction of Sodium With Naphthalene in Ammonia.— To a mixture of naphthalene, 25 g (0.2 mol), and 200 ml of freshly distilled liquid ammonia, 8 g of sodium spheres (1/8 to 1/4 in.) were added piecemeal over a 26-hr period. Each portion of sodium was allowed to react before the next addition was made. Total reaction time for each piece of sodium varied from 10 min at the start of the reaction to 45 min after three hours reaction time. Addition of sodium caused the solution to turn light green, then dark green and finally become colorless. The reaction was stopped by allowing the ammonia to evaporate at room temperature. Work up of the reaction products is given in the preceding experiment with ethylenediamine. The product yields based on reacted naphthalene were: 7% 1,2-dihydronaphthalene, 5% tetralin, and 87% nonvolatile hydrocarbons. Gas chromatographic analysis of this latter material showed that the dimer fraction contained 1 (2%), 2 (29%), 4 (30%), and an unknown dimer (40%).

Reaction of 1,2,3,3',4,4'-Hexahydro-2,2'-binaphthyl (2) With Sodium and Ethylenediamine.— A mixture of 0.1 g (0.0039 mol) of 2, 0.359 g (0.0156 g atom) of sodium, and 5 ml of ethylenediamine were stirred for 24 hr under a nitrogen atmosphere. After about 10 min, a blue color developed which gradually changed to red-orange.

The product was poured into ice water and then extracted with ether. The ether extract was washed once with 20% hydrochloric acid, washed twice with water, dried (MgSO_4), filtered and freed of ether. Gas chromatographic analysis of the residue showed only dimer 1 and none of dimer 3.

Reaction of 1,2,3,3',4,4'-Hexahydro-2,2'-binaphthyl (2) With Hydrogen and Palladium Over Carbon.— A mixture of 1.0 g of 2 was dissolved in 15 ml of ethyl acetate and 500 mg of 10% palladium on carbon were added. The mixture was hydrogenated at room temperature and atmospheric pressure for 48 hr, then filtered and distilled to give a viscous oil which crystallized from an ether-petroleum ether solvent mixture to give 300 mg of colorless crystals, mp 102° . Further purification gave material mp $107-109^\circ$. The nmr and mass spectra of this solid were identical to those of 1.²²

Dehydrogenation of 1,2,3,3',4,4'-Hexahydro-2,2'-binaphthyl (2).— A mixture of 1.5 g of 2 and 500 mg of 10% palladium on carbon was heated at 280° under nitrogen for 6 hr. The solid residue was sublimed to give 700 mg of colorless crystals, mp $184-185^\circ$. The melting point of a mixture of these crystals and 2,2'-binaphthyl was not depressed and their nmr spectra were identical.

Reaction of 1,4-Dihydronaphthalene With Potassium Hydroxide and Dimethyl sulfoxide.— A mixture of 7.8 g (0.06 moles) of 1,4-dihydronaphthalene, 2.8 g (0.07 moles) of potassium hydroxide, and 50 ml of dimethyl sulfoxide were heated at 100 to 110° for 5 hr under a nitrogen atmosphere. The solution first turned yellow, then green, and finally brown. The cooled mixture was poured into 400 ml of water and extracted three times with ether. The ether extract was washed once with excess

20% hydrochloric acid and twice with water, then steam distilled. The steam distillation residue was taken up in ether and the ether was dried (Na_2SO_4) and evaporated to give 5.68 g (73%) of nonvolatile hydrocarbon material. Gas Chromatographic analysis showed that the ratio of dimers 2, 3, and 4 was 54:12:34.

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- II. ACID CATALYZED DIMERIZATION OF 1,2-DIHYDRONAPHTHALENE: NEW STRUCTURE ASSIGNMENTS
- III. 1,4-DIHYDRONAPHTHALENE AS AN INTERMEDIATE IN METAL-AMINE REDUCTIONS OF NAPHTHALENE
- IV. METAL-AMINE REACTIONS OF NAPHTHALENE: REDUCTIVE DIMERIZATION

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