

I. EFFECTS OF ALKYL SUBSTITUENTS IN THE
CHROMIC ACID OXIDATION OF TETRALINS
II. HYDROGENOLYSIS AND DEUTERIUMOLYSIS OF
KETONES RELATED TO ACETOPHENONE
III. SYNTHESIS AND PURIFICATION
OF HYDROCARBONS

By

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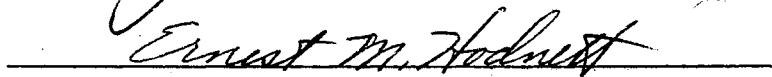
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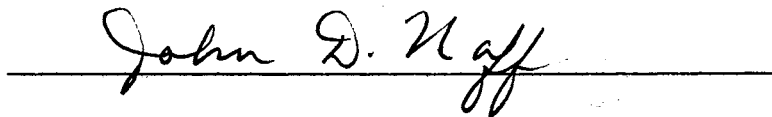
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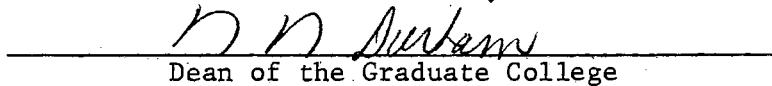
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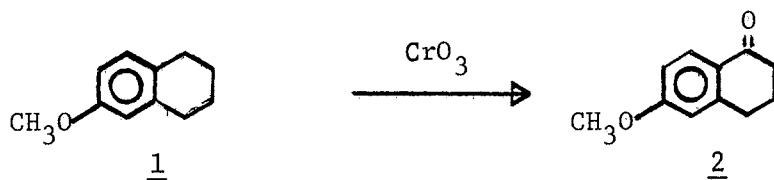
PART I

EFFECTS OF ALKYL SUBSTITUENTS IN THE
CHROMIC ACID OXIDATION OF
TETRALINS

CHAPTER I

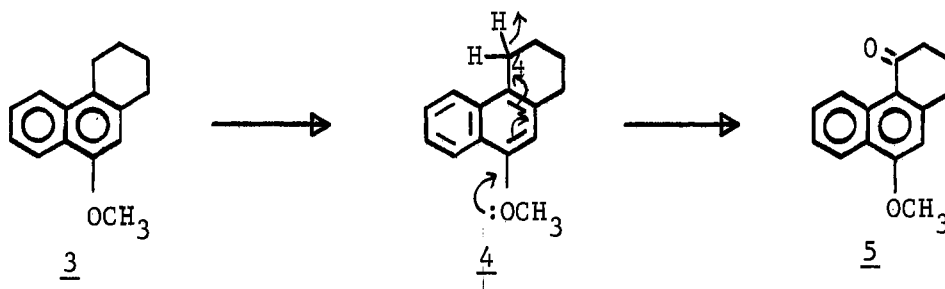
INTRODUCTION AND HISTORICAL

Chromic acid oxidation of hydrocarbons has been intensively studied.^{1a,b} In general, for aliphatic hydrocarbons, the relative rates of oxidation of primary, secondary, and tertiary C-H bonds have been reported to be 1:110:7000.^{1b} Although considerable data exist concerning the oxidation of aromatic-aliphatic systems,^{2a,b} very little information is available on oxidation of hydrocarbons containing non-equivalent benzylic positions in partially hydrogenated polynuclear aromatic compounds. Thus, Linstead^{3a} has demonstrated the presence of a pronounced electronic effect in the exclusive oxidation of 6-methoxy-tetralin (1) to 6-methoxy-1-tetralone (2).



More recently Ghosal^{3b} observed a similar effect for the oxidation of 9-methoxy-1,2,3,4-tetrahydrophenanthrene (3) to 9-methoxy-2,3-dihydro-4(1H)-phenanthrone (5). Ghosal suggested that this selectivity

results from the ease of hydride ejection from position C-4 of 3. The mesomeric contribution of the 9-methoxy group is illustrated in structure 4.



Detailed mechanistic studies have been reported for the chromic acid oxidation of substituted diphenylmethanes.^{2a} Wiberg used the diphenylmethane nucleus to show that electron-releasing groups attached para to the site of methylene oxidation moderately enhance the rate of oxidation to the corresponding benzophenone. The same investigator also demonstrated that a linear free energy relationship existed between kinetic data from the oxidation of substituted diphenylmethanes and the σ^+ values of Brown and Okamoto.⁴ Wiberg^{2a} proposed a hydrogen atom abstraction as the rate-determining step for the oxidation, basing his argument on the observed correlation with σ^+ values and the fact that he obtained a value of -1.17 for ρ^+ . The latter is in good agreement with an earlier observation that values of ρ for hydrogen atom abstractions from toluene fall between -0.75 and -1.5.⁵ In addition, a very large kinetic isotope effect, $k_H/k_D = 6.4$ at 30°, was noted for the oxidation of diphenylmethane- α,α -d₂. In the course of correlating kinetic data

with σ^+ values, Wiberg^{2a} noted that rate data from the oxidation of p-methoxy- and p,p'-dimethoxydiphenylmethane gave a poor fit. This lack of correlation was rationalized on the basis of a mechanism change leading to a cation intermediate for the methoxy-substituted diphenylmethanes. Wiberg⁶ also demonstrated that the chromic acid oxidation of (+)-3-methylheptane (6) produced (+)-3-methyl-3-heptanol (7) with 70-85% retention of configuration.

Růček has shown that the rates of chromic acid oxidation of hydrocarbons parallel the rates for solvolysis of the corresponding tosylates⁷ and has further concluded that steric hindrance is not important in the oxidation of alkylcyclohexanes.⁸ These data and all earlier observations were rationalized^{9,10} by regarding the initially formed

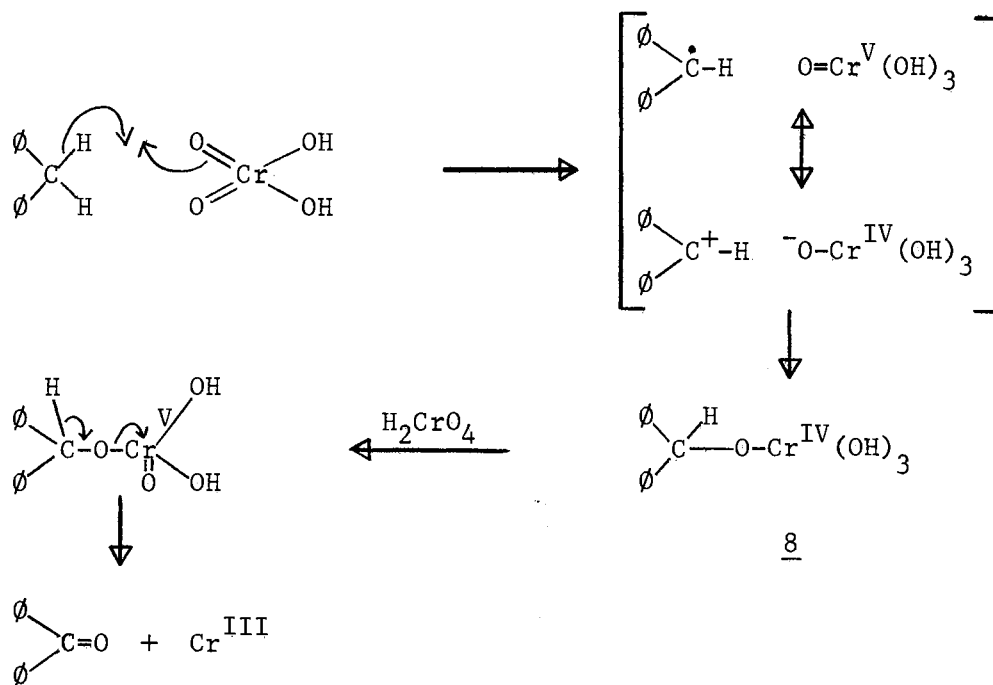


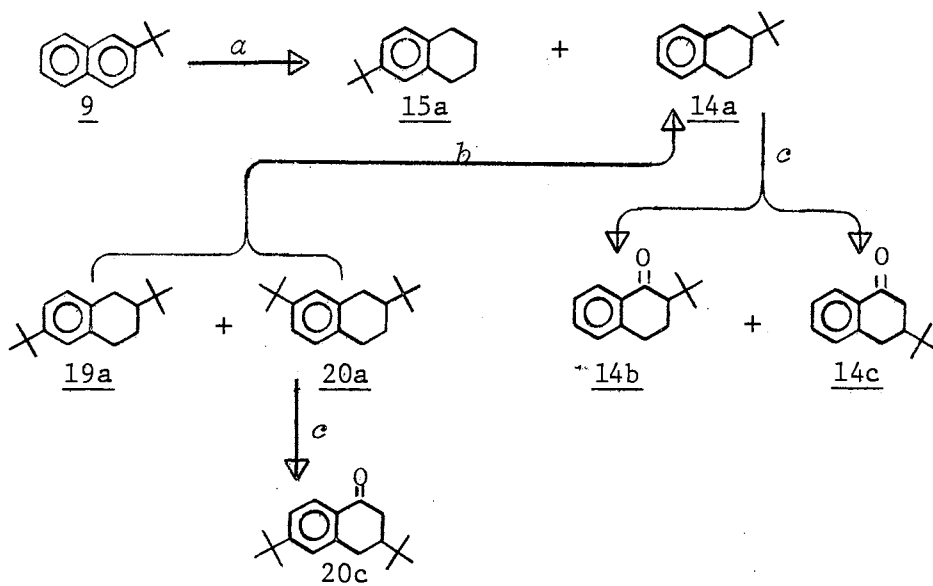
Figure 1. Mechanism for the Chromic Acid Oxidation of Hydrocarbons⁹

species in the oxidation as a resonance hybrid of an alkyl-radical-Cr(V) complex and a carbonium ion-Cr(IV) complex as shown in Figure 1. The hybrid would be expected to possess less energy than either canonical form and would account for the radical-like and carbonium ion-like characteristics observed in earlier investigations.^{2a,6,7,8} The mesomeric hybrid may then collapse to give the Cr(IV) ester 8 followed by further oxidation to benzophenone.

CHAPTER II

DISCUSSION AND RESULTS

The study of the chromic acid oxidation of tetralins was prompted by an earlier observation that some alkyltetralins ^{11a} may be converted to 1-tetralones in high yield with considerable selectivity; the reaction provides otherwise less accessible ketones, as shown in Figure 2, in which 3,6-di-tert-butyl-1-tetralone (20c) is the exclusive product from the oxidation of 2,7-di-tert-butyltetralin (20a). The oxidation



^aH₂, Pd/C, HOAc. ^bAlCl₃, Toluene. ^cCrO₃, HOAc, H₂O.

Figure 2. Preparation and Selective Oxidation of tert-Butyltetralins ^{11a}

TABLE I
CHROMIC ACID OXIDATION PRODUCTS

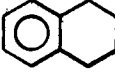
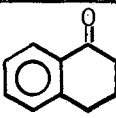
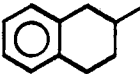
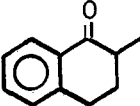
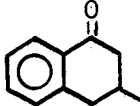
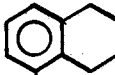
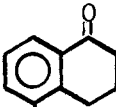
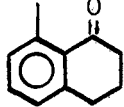
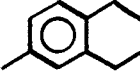
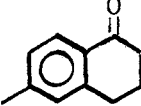
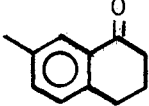
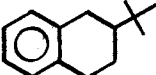
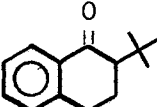
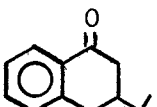
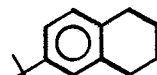
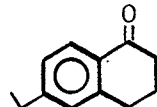
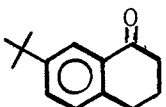
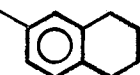
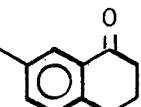
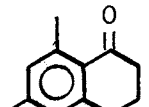
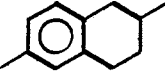
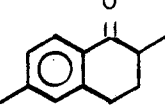
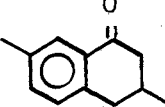
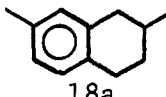
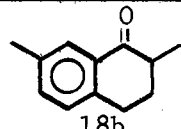
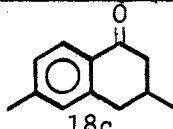
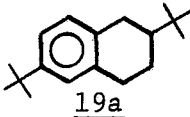
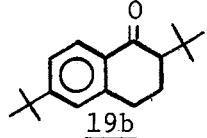
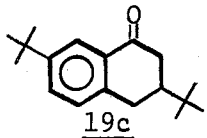
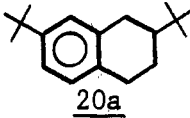
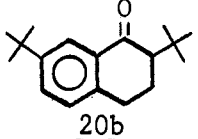
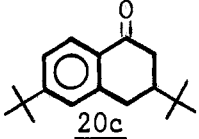
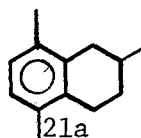
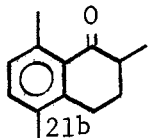
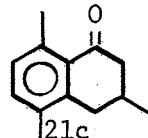
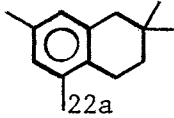
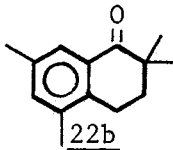
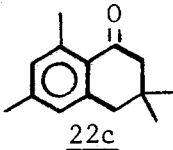
Tetralins ^a	1-Tetralones	Ratio <u>b</u> : <u>c</u>	% Yld. Combined 1-Tetralones
 <u>10a</u>	 <u>10b</u>		55
 <u>11a</u>	 <u>11b</u>	 <u>11c</u>	1.0:2.1 ^{b,c} 72
 <u>12a</u>	 <u>12a</u>	 <u>12c</u>	1.0:1.3 ^b 60
 <u>13a</u>	 <u>13b</u>	 <u>13c</u>	2.7:1.0 ^{b,c} 72
 <u>14a</u>	 <u>14b</u>	 <u>14c</u>	1.0:5.8 ^{b,e} 70
 <u>15a</u>	 <u>15b</u>	 <u>15c</u>	2.4:1.0 ^b 58
 <u>16a</u>	 <u>16b</u>	 <u>16c</u>	1.0:4.4 ^e 62
 <u>17a</u>	 <u>17b</u>	 <u>17c</u>	2.0:1.0 ^{d,e} 65

TABLE I (Continued)

Tetralins ^a	1-Tetralones	Ratio <u>b</u> : <u>c</u>	% Yld. Combined 1-Tetralones	
 <u>18a</u>	 <u>18b</u>	 <u>18c</u>	1.0:8.0 ^{d,e}	66
 <u>19a</u>	 <u>19b</u>	 <u>19c</u>	1.0:3.0 ^{d,e}	75
 <u>20a</u>	 <u>20b</u>	 <u>20c</u>	0.0:1.0 ^{d,e}	71
 <u>21a</u>	 <u>21b</u>	 <u>21c</u>	1.0:24 ^e	74
 <u>22a</u>	 <u>22b</u>	 <u>22c</u>	1.0:6.1 ^{e,d,e}	57

^aConsult experimental for preparation of tetralins.

^bRatio determined and separation achieved by glc.^{12a,b,c}

^cAuthentic samples of 11b, 12c, 13c, 14b, 16b, 16c, 21b, 21c, and 22c were available.

^dRatio determined by pmr analysis based upon the differences in chemical shifts of protons contained in the alkyl substituents at C-2 and C-3. It is assumed that the C-2 alkyl is deshielded relative to the C-3 alkyl group.

^eRatio verified by triangulation of glc curve.^{12a,b,c}

of 14a afforded 14b and 14c as a mixture (Table I). Recrystallization of this mixture provided 14c in 50% overall yield.^{11a} Pure 14a required for this oxidation is more readily obtained as shown in Figure 2 from a mixture of 19a and 20a than by hydrogenating 2-tert-butyl-naphthalene. (9). Chromic acid has been previously used in the conversion of indans to indanones in high yields.^{11b}

The data presented in Table I provide ample evidence that an electronic effect is operative in the oxidation of alkyl-substituted tetralins. This is apparent from the ratio of tetralones 12b:12c (1.0:1.3) and 13b:13c (2.7:1.0). Comparison of the latter ratio to that of 15b:15c (2.4:1.0) shows that the methyl and tert-butyl group possess approximately the same electronic effect. The electronic effect responsible for the formation of the ratio of products obtained from 12a and 13a is manifest throughout the entire series. Steric effects may result from alkyl groups at the peri position of the aromatic ring or from an alkyl group situated adjacent to a potential carbonyl site (C-2) in the saturated ring. The latter is illustrated by the products from 11a and 14a. The most obvious combined effect, steric and electronic, is exhibited in the oxidation of 19a, 20a, and 21a. Less pronounced steric influences appear in the oxidation of tetralins 11a, 17a, 18a and 22a which have methyl groups rather than tert-butyl groups.

A subtle diminution in the ratio owing to steric influence of methyl at C-2 appears in the ratio of products obtained from oxidation of 13a and 18a, in which there is a change from 2.7:1.0 to 2.0:1.0. Comparison of the ratios of the 1-tetralones obtained from 15a, 19a, and 20a indicates a very pronounced alkyl (tert-butyl) steric effect at the C-2 position. As expected, this effect decreases in changing to methyl for 13a, 17a, and 18a.

The electronic effect from alkyl groups in the aromatic ring may have a pronounced influence on the ratio of 1-tetralones, as evidenced by comparison of the products from 12a and 16a, in which 12c and 16c predominate over 12b and 16b respectively despite possible steric interference of the methyl group at the peri position.

The ratio of 1-tetralones formed from tetralins by chromic acid oxidation may become established at the time of initial hydrogen abstraction or at the next stage, during conversion of alcohol or related species to ketone. We believe the former is more important since we can point to the oxidation of 20a to 20c with none of 20b being formed. We argue that differences in rate of oxidation of alcohols can have no influence if one of the alcohols is not formed.

CHAPTER III

EXPERIMENTAL¹²

Preparation of Tetralins.— The tetralins used in this study were obtained in part from our API hydrocarbon synthesis project^{13a} and as a gift.^{13b} These tetralins were synthesized as outlined below and their purity established by glc and spectral data.¹²

Tetralins 11a, 13a, 16a, and 21a.— These were prepared via a previously described general Friedel-Crafts synthesis¹⁴ applied to benzene and methylsuccinic anhydride for 11b, toluene and succinic anhydride for 13c, m-xylene and succinic anhydride for 16b, and p-xylene and methylsuccinic anhydride for 21b and 21c. Hydrogenolysis was used to convert 11b, 13c, 16b, and 21b or 21c to 11a,¹⁵ 13a,¹⁵ 16a,¹⁶ and 21a¹⁴ respectively.

Tetralin 14a.— A 210-g (1.14-mol) sample of 2-tert-butylnaphthalene (9)¹⁷ in acetic acid (750 ml) in the presence of Pd/C (3 g, 10%) was hydrogenated for 60 hr at 45 psi and 45° to a mixture of 15a:14a (1.1:1.0).^{12c} This mixture was distilled and then treated with AlCl₃ (44 g, 0.33 mol) in dry toluene (6.1 l., 55 mol) at 25°. ¹⁸ After 15 min, the reaction mixture was poured onto ice water (4.4 l.) and extracted with toluene (2.2 l.) and the extracts were combined, washed with water, dried (MgSO₄), and concentrated. The resulting oil was diluted with petroleum ether (250 ml)^{12d} and decolorized by elution through a column of acidic alumina (12 cm x 2.5 cm diam.). Distillation

gave 79 g (81%) of pure 14a, bp 72-80° (0.1mm); mass spectrum (70 eV) m/e (rel intensity) 188 (48), 132 (78), 131 (100), 130 (29), 104 (35), 57 (64); pmr spectrum (CCl₄) δ 6.91 (s, 4, ArH), 2.87-2.34 (m, 4, ArCH₂), 2.04-1.75 (m, 1, ArCH₂CH), 1.59-1.11 (m, 2, ArCH₂CH₂), 0.92 (s, 9, tert-butyl).

Anal. Calcd for C₁₄H₂₀: C, 89.29; H, 10.71. Found: C, 89.20; H, 10.76.

A similar procedure applied to a mixture of 19a:20a (1.0:1.6) resulted in an 84% yield of 14a.

2,6- and 2,7-Di-tert-butyl-1,2,3,4,-tetrahydronaphthalene (19a) and (20a).— A sample (240 g, 1.00 mol) of a mixture¹⁷ of 2,6- and 2,7-di-tert-butylnaphthalene (1.0:1.6)^{12c} was hydrogenated for 60 hr using Pd/C catalyst (6 g, 10%) and acetic acid (1.25 l.) as described above. A work-up analogous to that previously described gave 236 g (97%), bp 138° (0.5 mm), of a mixture of 19a and 20a.

Isolation of 19a and 20a Using Thiourea.— Application of a procedure¹⁹ described previously for the separation of 2,6- and 2,7-di-tert-butylnaphthalene to a mixture of 19a and 20a gave 19a as the thiourea adduct whereas 20a was excluded. Hydrocarbon 19a was leached from the thiourea adduct by Soxhlet extraction with petroleum ether.^{12d} Concentration and crystallization gave 19a, mp 90-92°; mass spectrum (70 eV) m/e (rel intensity) 244 (19), 230 (19), 229 (100), 57 (64), 41 (36), 29 (26); pmr spectrum (CCl₄) δ 7.05-6.76 (m, 3, ArH), 2.92-2.26 (m, 4, ArCH₂), 2.07-1.78 (m, 1, ArCH₂CH), 1.61-1.16 (m, 2, ArCH₂CH₂), 1.27 (s, 9, tert-butyl attached at C-6), 0.95 (s, 9, tert-butyl attached at C-2).

Anal. Calcd for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.53; H, 11.48.

Hydrocarbon 20a, excluded from the thiourea adduct, was obtained as colorless crystals, mp 40-42°; mass spectrum (70 eV) m/e (rel intensity) 244 (17), 230 (20), 229 (100), 57 (73), 41 (36), and 29 (23); pmr spectrum (CCl_4) δ 7.04-6.76 (m, 3, ArH), 2.93-2.28 (m, 4, $ArCH_2$), 2.10-1.78 (m, 1, $ArCH_2CH$), 1.61-1.17 (m, 2, $ArCH_2CH_2$), 1.26 (s, 9, tert-butyl attached at C-7), 0.94 (s, 9, tert-butyl attached at C-2).

Anal. Calcd for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.58; H, 11.53.

Tetralin 15a.— Prepared by tert-butylation of tetralin.¹⁷

Tetralins 17a and 18a.— Prepared by Pd/C-catalyzed hydrogenation of the corresponding naphthalenes in acetic acid. The purification of the gift^{20a} dimethylnaphthalenes was accomplished via their picrates.^{20b}

General Procedure for Chromic Acid Oxidations.— To a magnetically stirred solution of 0.04 mol of hydrocarbon in 1 l. of acetic acid was added dropwise 170 ml of 10% aqueous CrO_3 acetic acid solution²¹ over a period of 30 min. The reaction temperature was maintained between 17-21° using an ice bath. Each reaction was allowed to proceed to completion (ca. 2 hr) as evidenced by glc.^{12a,c} The reaction mixture was then diluted with 6 l. of distilled water and extracted with ether (2 x 1.5 l.). The combined ether extract was washed with water and saturated $NaHCO_3$, dried (Na_2SO_4), decanted, and concentrated. The resulting crude products were distilled and ratios determined by pmr and triangulation of the glc curve.

Yield Optimization of 1-Tetralone (10b) from Tetralin (10a).— A series of five experiments in which the mol ratio of CrO_3 :10a ranged

from 7.4:1 to 3.1:1 were carried out to determine optimum conditions. The maximum yield of 10b was obtained with the ratio 5:1 as described above. In addition, three experiments varying the volume of acetic acid indicated that dilution over the recommended amount in the procedure lowers the yield and allows survival of tetralin.

11b: bp 76-78° (0.3 mm) [lit.^{22a} 135-37° (16 mm)]; ir (neat) 1680 cm^{-1} (C=O); mass spectrum (70 eV) m/e (rel intensity) 160 (47), 131 (17), 118 (100), 90 (61), 89 (21), 28 (26); pmr (CDCl_3) δ 8.03-7.79 (m, 1, ArH peri to carbonyl), 7.49-6.94 (m, 3, ArH), 3.05-2.72 (m, 2, ArCH_2), 2.67-1.29 (m, 3, $\text{ArCH}_2\text{CH}_2\text{CH}$), 1.16 (d, 3, ArCOCH_3).

11c: bp 78° (0.5 mm) [lit.^{22b} 142-43° (16 mm)]; mass spectrum (70 eV) m/e (rel intensity) 160 (53), 145 (39), 118 (100), 115 (15), 91 (15), 90 (42); pmr (CDCl_3) δ 8.00-7.75 (m, 1, ArH peri to carbonyl), 7.52-6.92 (m, 3, ArH), 2.91-1.79 (envelope, 5, $\text{ArCH}_2\text{CHCH}_2$), 1.07 (d, 3, $\text{ArCH}_2\text{CHCH}_3$).

12b: mp 48-50°; mass spectrum (70 eV) m/e (rel intensity) 160 (63), 132 (100), 104 (56), 103 (22), 78 (23), and 51 (22); pmr (CCl_4) δ 7.73 (d, 1, ArH peri to carbonyl), 7.33-6.90 (m, 2, ArH), 2.78 (t, 2, ArCH_2), 2.27 (s, 3, ArCH_3), 2.60-1.84 (m, 7, $\text{ArCOCH}_2\text{CH}_2$ and ArCH_3).

Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{O}$: C, 82.46; H, 7.55. Found: C, 82.58; H, 7.59.

12c: bp 75-78° (0.2 mm); mass spectrum (70 eV) m/e (rel intensity) 160 (48), 132 (100), 104 (35), 103 (17), 78 (19), and 51 (16); pmr (CCl_4) δ 7.30-6.76 (m, 3, ArH), 2.86 (t, 2, ArCH_2), 2.56 (s, 3, ArCH_3), 2.72-2.42 (m, 5, ArCOCH_2 and ArCH_3), 1.98 (m, 2, $\text{ArCOCH}_2\text{CH}_2$).

Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{O}$: C, 82.46; H, 7.55. Found: C, 82.39; H, 7.55.

13b: bp 75-77° (0.2 mm); mass spectrum (70 eV) m/e (rel intensity) 160 (51), 145 (18), 132 (100), 104 (40), 78 (19), and 51 (18); pmr (CCl₄) δ 7.76 (d, 1, ArH peri to carbonyl), 7.06-6.84 (m, 2, ArH), 2.81 (t, 2, ArCH₂), 2.19 (s, 3, ArCH₃), 2.56-1.86 (m, 4, ArCOCH₂CH₂).

Anal. Calcd for C₁₁H₁₂O: C, 82.46; H, 7.55. Found: C, 82.60; H, 7.53.

13c: mp 32-34° [lit.^{22a} 35-36°]; ir (neat) 1680 cm⁻¹ (C=O); mass spectrum (70 eV) m/e (rel intensity) 160 (73), 132 (100), 104 (75), 103 (23), 28 (21); pmr (CCl₄) δ 7.76 (s, 1, ArH peri to carbonyl) 7.08 (m, 2, ArH), 2.83 (t, 2, ArCH₂), 2.55-1.91 (m, 4, ArCH₂CH₂CH₂), 2.30 (s, 3, ArCH₃).

14b:^{11a} bp 109° (0.1 mm); ir spectrum (film) 1680 cm⁻¹ (C=O); mass spectrum (70 eV) m/e (rel intensity) 202 (2), 147 (37), 146 (100), 145 (27), 131 (19), 118 (19); pmr spectrum (CCl₄) δ 7.94-7.80 (m, 1, ArH peri to carbonyl), 7.40-7.01 (m, 3, ArH), 3.02-2.84 (m, 2, ArCH₂), 2.38-1.69 (m, 3, ArCOCHCH₂), 1.08 (s, 9, tert-butyl).

Anal. Calcd for C₁₄H₁₈O: C, 83.12; H, 8.97. Found: C, 82.87; H, 8.82.

The red-orange 2,4-dinitrophenylhydrazone of 14b melted at 228-230°.

Anal. Calcd for C₂₀H₂₂N₄O₄: C, 62.81; H, 5.80. Found: C, 62.83; H, 5.80.

14c:^{11a} mp 68-70°; ir spectrum (CCl₄) 1675 cm⁻¹ (C=O); mass spectrum (70 eV) m/e (rel intensity) 202 (24), 146 (100), 145 (37), 117 (21), 115 (22), 57 (47); pmr spectrum (CCl₄) δ 7.98-7.83 (m, 1, ArH peri to carbonyl), 7.48-7.07 (m, 3, ArH), 3.08-2.45 (m, 3, ArCH₂ and ArCOCH), 2.38-1.66 (m, 2, ArCOCH and ArCH₂CH), 0.98 (s, 9, tert-butyl).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.24; H, 8.91.

The red-orange 2,4-dinitrophenylhydrazone of 14c melted at 223-224°.

Anal. Calcd for $C_{20}H_{22}N_4O_4$: C, 62.81; H, 5.80. Found: C, 62.99; H, 5.79.

15b: bp 102° (0.2 mm); ir (neat) 1680 cm^{-1} (C=O); mass spectrum (70 eV) m/e (rel intensity) 202 (24), 187 (100), 131 (18), 115 (13), 91 (9), 41 (11); pmr (CCl_4) δ 7.83 (d, 1, ArH peri to carbonyl), 7.30-7.10 (m, 2, ArH), 2.88 (t, 2, $ArCH_2$), 2.49 (t, 2, $ArCOCH_2$), 2.04 (p, 2, $ArCH_2CH_2$), 1.30 (s, 9, tert-butyl).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.99; H, 8.94.

The red 2,4-dinitrophenylhydrazone melted at 241-243°.

Anal. Calcd for $C_{20}H_{22}N_4O_4$: C, 62.81; H, 5.80. Found: C, 62.74; H, 5.85.

15c: mp 99-100° [lit.^{22c} 101-102.5°]; mass spectrum (70 eV) m/e (rel intensity) 202 (19), 188 (15), 187 (100), 159 (6), 131 (11), 115 (9); pmr (CCl_4) δ 7.94 (d, 1, ArH peri to carbonyl), 7.46-6.98 (m, 2, ArH), 2.88 (t, 2, $ArCH_2$), 2.53 (t, 2, $ArCOCH_2$), 2.08 (p, 2, $ArCH_2CH_2$), 1.33 (s, 9, tert-butyl).

16b: bp 86-90° (0.2 mm); mp 49-51° [lit.²³ 50°]; mass spectrum (70 eV) m/e (rel intensity) 174 (85), 146 (100), 118 (71), 117 (30), 115 (28); pmr (CCl_4) δ 7.56 (s, 1, ArH peri to carbonyl), 7.04 (s, 1, ArH), 2.73 (t, 2, $ArCH_2$), 2.27-2.22 (two s, 6, $ArCH_3$), 2.6-1.9 (m, 4, $ArCOCH_2CH_2$). The red 2,4-dinitrophenylhydrazone became dark at 230° and melted at 272°.

16c:¹⁴ bp 105° (0.6 mm); mass spectrum (70 eV) m/e (rel intensity) 174 (46), 146 (100), 118 (19), 117 (18), 115 (15); pmr (CCl₄) δ 6.77 (s, 2, ArH), 2.82 (t, 2, ArCH₂), 2.52 (s, 3, ArCH₃ peri to carbonyl), 2.25 (s, 3, ArCH₃), 2.6-1.8 (m, 4, ArCOCH₂CH₂).

Anal. Calcd for C₁₂H₁₄O: C, 82.72; H, 8.10. Found: C, 82.83; H, 8.35.

The red 2,4-dinitrophenylhydrazone melted at 202-203°.

17b and 17c: bp of 2.0:1.0 mixture, 83-85° (0.2 mm). The ratio of the mixture was established by glc^{12a,c} and by integration of the two pmr (CCl₄) doublets centered at δ 1.14 and 1.04 respectively. Mass of 17b:17c (2.0:1.0) (70 eV) m/e parent ion (rel intensity) 174, M⁺ (50).

18b and 18c: bp of 1.0:8.0 mixture, 93-95° (0.3 mm). The ratio of this mixture was established by glc^{12a,c} and by integration of the two pmr (CCl₄) doublets centered at δ 1.13 and 1.00; mass spectrum of 18b:18c (1.0:8.0) (70 eV) m/e, parent ion (rel intensity) 174, M⁺ (49).

19b and 19c: bp of 1.0:3.0 mixture, 128-131° (0.2 mm). The ratio of this mixture was established by glc^{12c} and by integration of the two pmr (CCl₄) singlets at δ 1.05 and 0.94; mass spectrum of 19b:19c (1.0:3.0) (70 eV) m/e, parent ion (rel intensity) 258, M⁺ (20).

20c: mp 84-86°; ir spectrum (CCl₄) 1670 cm⁻¹ (C=O); mass spectrum (70 eV) m/e (rel intensity) 258 (28), 243 (45), 202 (59), 201 (39), 187 (36), 57 (100); pmr spectrum (CCl₄) δ 7.81 (d, 1, ArH peri to carbonyl), 7.30-7.10 (m, 2, ArH), 2.94-2.50 (m, 3, ArCH₂ and ArCOCH), 2.32-1.82 (m, 2, ArCOCH and ArCH₂CH), 1.33 (s, 9, tert-butyl attached at C-6), 0.98 (s, 9, tert-butyl attached at C-3).

Anal. Calcd for C₁₈H₂₆O: C, 83.66; H, 10.14. Found: C, 83.59; H, 10.14.

The red 2,4-dinitrophenylhydrazone melted at 244-245°.

Anal. Calcd for $C_{24}H_{30}N_4O_4$: C, 65.73; H, 6.90. Found: C, 65.71; H, 6.96.

21b:¹⁴ bp 95-100° (0.2 mm); mp 20° from isopropyl alcohol; ir (neat) 1675 cm^{-1} (C=O); mass spectrum (70 eV) m/e (rel intensity) 188 (41), 146 (100), 118 (27), 117 (25), 115 (19); pmr (CCl_4) δ 6.95, 6.79 (AB q, 2, ArH), 2.46 (s, 3, ArCH₃ peri to carbonyl), 2.10 (s, 3, ArCH₃), 2.9-1.2 (envelope, 5, ArCH₂CH₂CH), 1.08 (d, 3, CH₃); uv max (95% C₂H₅OH) 213 nm (log ϵ 4.73), 254 (4.18), and 300 (3.62).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.89; H, 8.43.

The 2,4-dinitrophenylhydrazone, mp 183-184°, was prepared.

21c:¹⁴ mp 71-72°; mass spectrum (70 eV) m/e (rel intensity) 188 (65), 173 (25), 146 (100), 118 (31), 117 (27); pmr (CCl_4) δ 7.01, 6.81 (AB q, 2, ArH), 2.49 (s, 3, ArCH₃ peri to carbonyl), 2.17 (s, 3, ArCH₃), 2.1-1.7 (envelope, 5, ArCH₂CHCH₃CH₂), 1.07 (d, 3, CH₃); uv max (95% C₂H₅OH) 213 nm (log ϵ 4.67), 254 (4.08), and 306 (3.42).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.90; H, 8.65.

The 2,4-dinitrophenylhydrazone melted at 249-250°.

22b and 22c: bp of 1.0:6.1 mixture, 96-99° (0.3 mm). The ratio of this mixture was established by glc.^{12c} and by integration of the two pmr (CCl_4) singlets at δ 1.09 and 0.98; mass spectrum of 22b:22c (1.0:6.1) (70 eV) m/e, parent ion (rel intensity) 202, M⁺ (36).

PART II

HYDROGENOLYSIS AND DEUTERIUMOLYSIS OF KETONES

RELATED TO ACETOPHENONE

CHAPTER IV

INTRODUCTION AND HISTORICAL

The use of hydrogen and catalyst for bench-scale conversions in organic synthesis has recently received increased attention.²⁴ Hydrogenolysis, molecular cleavage with hydrogen and noble-metal catalyst, is in many cases the preferred technique for removing oxygen at the benzylic position. In addition, there are several other methods available for such conversions.²⁵ Linstead²⁶ in 1940 first pointed out the potential of catalytic hydrogenolysis of 1-tetralones to tetralins. Newman²⁷ in 1943 clearly demonstrated that β -arylpropionic acids may be converted to γ -arylbutyric acids. Baker²⁸ in 1946 also used the technique and called attention to its utility. More recently, Rylander^{29a} has demonstrated that the product composition from catalytic reduction of acetophenone is dependent on choice of catalytic metal. Palladium was shown to catalyze reduction and hydrogenolysis with no ring hydrogenation. Rhodium, on the other hand, reduces the aromatic ring with retention of the oxygen attached at the benzylic position. Platinum gives both hydrogenolysis of the carbonyl and reduction of the aromatic ring in a nonselective fashion. Horning^{29b} used Pd/C and hydrogen in the conversion of benzoin (23) to 1,2-diphenylethane (24).

In this laboratory, we were confronted with the need to conveniently deoxygenate organic compounds to hydrocarbons in good yield and at times on a large laboratory scale as part of our synthesis program.

for the American Petroleum Institute. An early study was to improve a conventional synthesis of alkyl-substituted naphthalenes, in this case hydrocarbons analogous to cadalene (1,4-dimethyl-6-isopropyl-naphthalene) (25). A common textbook synthesis required seven steps and provided an 18% overall yield.^{29c} We verified this synthesis and concluded it was not practical for large-scale work. Through use of Pd/C in hydrogenation and hydrogenolysis and with other modern reagents, the total yield was increased to 65% and the number of steps reduced to those shown in Figure 3. A considerable reduction in time and effort was also realized

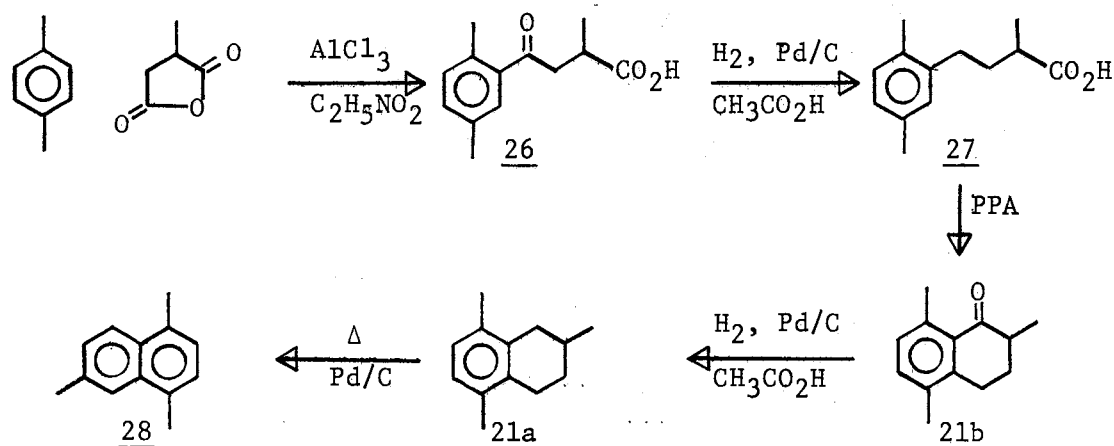


Figure 3. Use of Hydrogenolysis in the Synthesis of Polymethylnaphthalenes

so that it is now possible to prepare substituted naphthalenes in good yield in days rather than weeks.¹⁴ Hydrogenolysis of the keto acid **26** to **27** and the tetralone **21b** to **21a** is aided by acidic solvents, in this case, acetic acid. In neutral organic solvents containing an alkali

metal hydroxide, hydrogenolysis does not occur.^{29,30} Van Bekkum has demonstrated the presence of a steric effect in the hydrogenation of ketones.³⁰

An obvious extension of hydrogenolysis would be to replace the reactant, hydrogen gas, with deuterium gas. This technique could be used as a convenient method for selective labeling of appropriate compounds with deuterium. Surprisingly, little has been done to utilize deuteriumolysis in this capacity. A possible limitation of the procedure would be unwanted incorporation of deuterium in the starting ketone, as a result of enolization prior to deuteriumolysis.

This problem is expected to exist in acidic solvents, particularly acetic acid-0-d. However, attempted deuterium exchange between acetic acid-0-d and the methyl hydrogens of acetophenone in the absence of deuterium gas has been shown to be negligible at 65°.³¹ Exchange of aromatic protium with the deuterated solvent was also shown to be unimportant.³¹ Thus, there is a good indication that deuteriumolysis of benzylic ketones can occur with selective placement of deuterium.

CHAPTER V

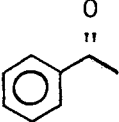
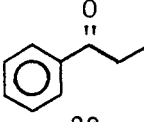
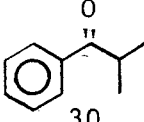
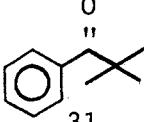
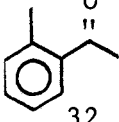
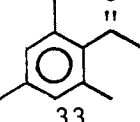
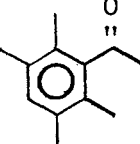
DISCUSSION AND RESULTS

The author undertook a study of the Pd/C-catalyzed hydrogenolysis of ketones related to acetophenone to test for the presence of a steric limitation of the reaction.³² The ketones used in the study are shown in Table II. It is evident from the data shown that reduction to the alcohol is retarded by a steric effect in the side chain of the ketone. However, this effect is minor compared to the dramatic retardation from the steric effect obtained by substituting the aromatic ring of the ketone with alkyl groups.

In a like manner, hydrogenolytic removal of the hydroxyl group (Table III), the final step of conversion to hydrocarbon, is retarded by increasing the steric requirements of the side chain.

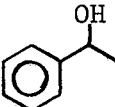
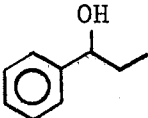
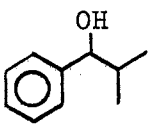
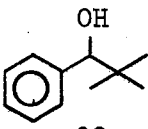
In the absence of steric effects such as the extreme cases cited in Table II,^{31,34} most ketones related to acetophenone respond nicely to deoxygenation via catalytic hydrogenolysis and this is a superior method of hydrocarbon synthesis. However, in some cases, the available ketone and/or the resulting hydrocarbon could not be brought to the required purity and it became necessary to resort to preparation of carbonyl derivatives for purification.³³ But since the hydrocarbon was the desired product and the purified ketone was not required, we decided to investigate direct hydrogenolysis of carbonyl derivatives to hydrocarbons.³⁴

TABLE II
 HYDROGENOLYSIS OF KETONES RELATED TO ACETOPHENONE

	Hydrogenation Time (seconds)		
	For 10% of Theoretical H ₂	For 25%* of Theoretical H ₂	Completion
 <u>40a</u>	390	1011	1.38 hr
 <u>29</u>	385	998	2.42 hr
 <u>30</u>	463	1199	1.55 hr
 <u>31</u>	607	1594	1.07 hr (to alcohol)
 <u>32</u>	380	1357	1.90 hr
 <u>33</u>	Too Slow To Measure	TSTM	
 <u>34</u>	TSTM	TSTM	

*GLC data show that only the alcohol is present at this point.

TABLE III
 HYDROGENOLYSIS OF ALCOHOLS RELATED TO
 α -METHYLBENZYL ALCOHOL

	Hydrogenation Time (seconds)		
	For 10% of Theoretical H ₂	For 25% of Theoretical H ₂	Completion ^a
 <u>35</u>	196	484	1.22 hr
 <u>36</u>	314	780	1.78 hr
 <u>37</u>	1576 ^b	4348	7.40 hr
 <u>38</u>	TSTM	TSTM	TSTM

^a Monitored by comparison of GLC peaks.

^b Duplicate result. In one run, an equal molar amount of conc. HCl was added at 25% theoretical H₂. The reaction quickly proceeded to completion (1.65 hr.).

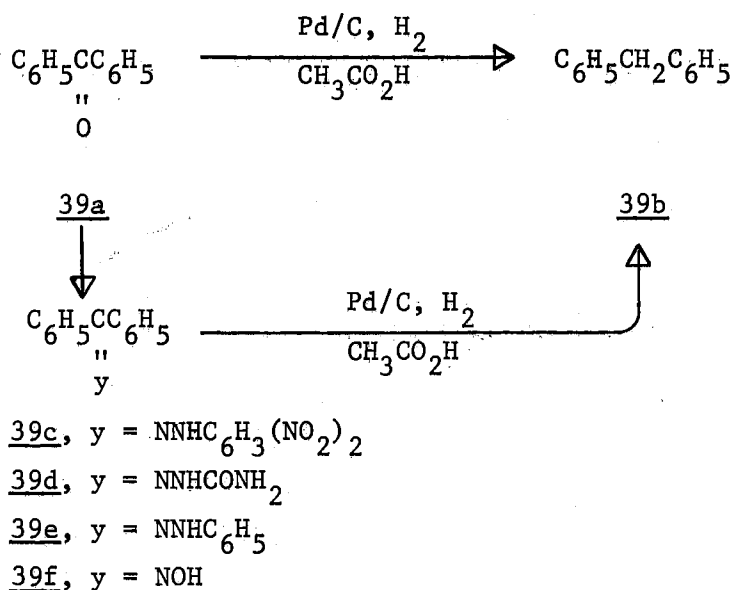


Figure 4. Hydrogenolysis of Carbonyl Derivatives of Benzophenone

As applied to benzophenone (39a) of Figure 4 or acetophenone (40a) of Figure 5, which were used to screen for the most suitable derivative, the 2,4-dinitrophenylhydrazone appears to be the most effective derivative for hydrogenolysis to pure 39b and 40b. The results of hydrogenolysis experiments applied to several carbonyl derivatives (Figure 5) are shown in Table IV.

Gas-liquid chromatography (glc) studies were used to determine the extent of hydrogenolysis and hydrogenation. For example, acetophenone phenylhydrazone (40e) gave some phenethylamine as well as cyclohexylamine. Additional hydrogenolysis converted the former to ethylbenzene and extraction with aqueous hydrochloric acid removed the latter. Glc studies were also used to identify the hydrocarbons resulting from hydrogenolysis and to determine the yield of 39b, 40b, 41b, 42b, and

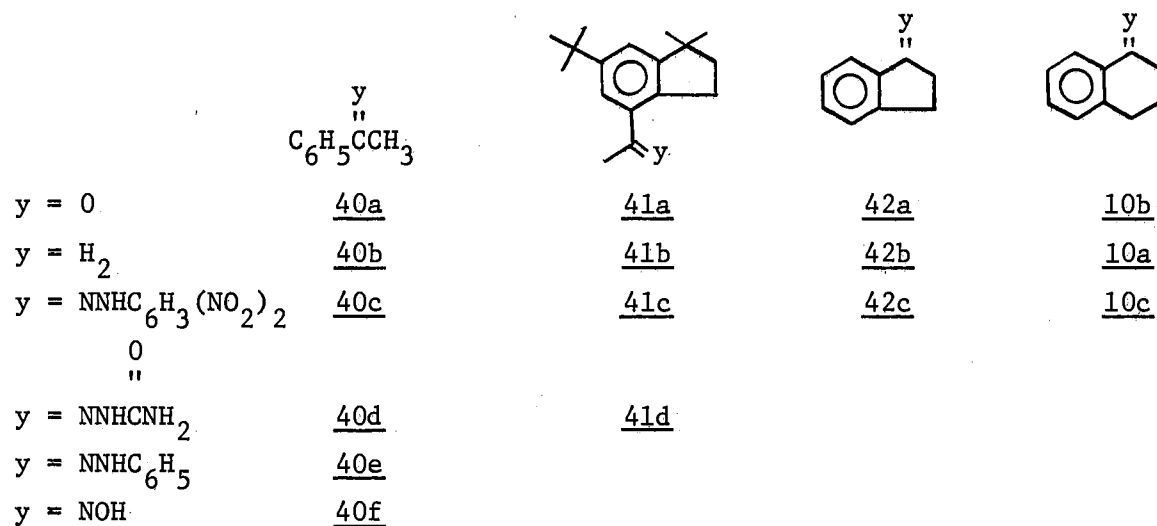


Figure 5. Compounds Used in Hydrogenolysis Studies

10a. The nitrogenous hydrogenolysis-hydrogenation products of oximes, semicarbazones and 2,4-dinitrophenylhydrazones were not investigated.

In general, the hydrogenolyses could be brought to completion in 3-7 hours. However, 41a and its derivatives 41c and 41d were resistant to hydrogenolysis as compared to 39a and 40a and their derivatives. As a result of prolonged treatment, "overhydrogenation" was observed for 41a and 41d but surprisingly, the 2,4-dinitrophenylhydrazone 41c cleanly hydrogenolyzed to the corresponding hydrocarbon 41b. Overhydrogenation may result from prolonged or severe treatment of 39a or 40a and their derivatives. This was absent in 42a and 10b and their 2,4-dinitrophenylhydrazones.

Since catalytic hydrogenolysis may be used to convert benzylic ketones, ketone derivatives, and alcohols to hydrocarbons, it seems reasonable that deuteriumolysis of ketones, at least in principle, would be an elegant and economical means for introducing deuterium at the

TABLE IV
HYDROGENOLYSIS OF CARBONYL DERIVATIVES

Compound ^a	Reaction Hrs	% Yield ^b
<u>39a</u>	1.5	95
<u>39c</u>	7	92 ^c
<u>39d</u>	6	93 ^c
<u>39e</u>	6	96 ^c
<u>39f</u>	4	96 ^c
<u>40a</u>	1.5	95
<u>40c</u>	6	81
<u>40d</u>	5	97
<u>40e</u>	5	94
<u>40f</u>	3	82
<u>41a</u>	2.5	92
<u>41c</u>	21	84
<u>41d</u>	10	75
<u>42a</u>	1	87
<u>42c</u>	3	71
<u>10b</u>	1	94
<u>10c</u>	4	95

^aFor preparation and melting points of these derivatives except as noted, see R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 5th Ed., 1964, pp. 147, 253, 289, 363, and 364. The melting points of these derivatives agreed with literature values.

^bGlc comparison with standards.

^cGravimetrically determined as well.

benzylic position. A possible limitation is the exchange of aromatic protium by deuterium.^{35,36}

To determine whether this was a suitable method for synthesis of hydrocarbons labelled with deuterium at the benzylic position and to ascertain whether exchange of aromatic protium would take place, the deuteriolysis of benzophenone (39a) was studied.

The reduction of 39a was studied in acetic acid and acetic acid-0-d, Figure 6, at atmospheric pressure with Pd/C using hydrogen and deuterium. The deuterium content of the phenyl rings of 43 was determined by pmr integration of the aromatic absorption signal using cyclohexane as the internal standard.³⁷

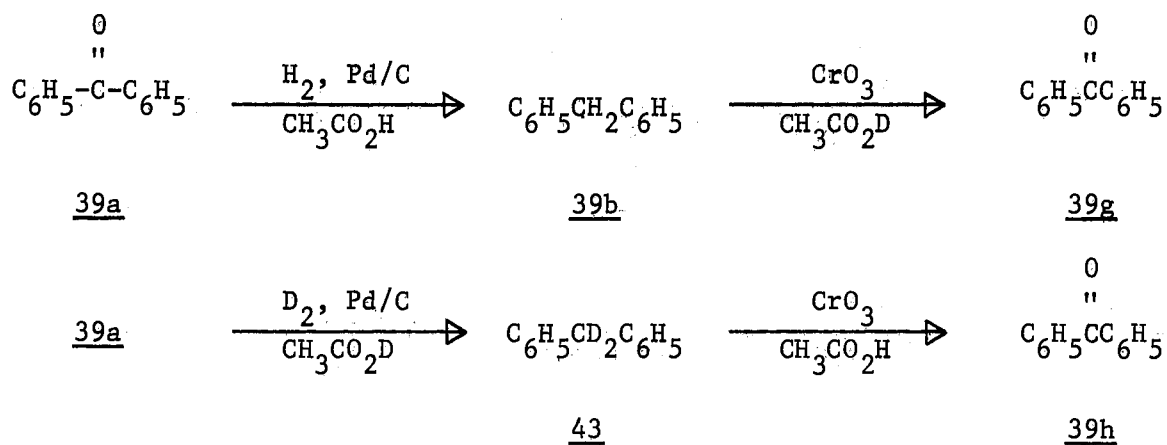


Figure 6. Hydrogenolysis and Deuteriumolysis of Benzophenone

TABLE V
 NORMALIZED AROMATIC PROTON RATIOS
 FOR 39b AND 43

Sample	Compound in Cyclohexane	Molar Ratio ^a	Number of Phenyl Protons ^b	
			A-60	HR-60
1	Diphenylmethane	1.1619	10.499 ± 0.101 ^c 10.607 ± 0.096 ^d	
2		1.1470	10.469 ± 0.118 ^c 10.574 ± 0.103 ^d	10.150 ± 0.146
3		1.3018	10.456 ± 0.097 ^c 10.467 ± 0.091 ^d	10.201 ± 0.109
4		1.2587	10.457 ± 0.091 ^c 10.521 ± 0.136 ^d	10.153 ± 0.109
AV			10.498 ± 0.036	10.171 ± 0.068
5	Diphenylmethane- $\alpha, \alpha\text{-}d_2$	1.1566	10.717 ± 0.142 ^c 10.491 ± 0.088 ^d	10.029 ± 0.098
6		1.0735	10.465 ± 0.096 ^c 10.623 ± 0.091 ^d	10.086 ± 0.104
7		1.1562	10.540 ± 0.114 ^c 10.652 ± 0.091 ^d	10.139 ± 0.092
AV			10.569 ± 0.041	10.087 ± 0.056

^a Molar ratio of 39b:cyclohexane or 43:cyclohexane was chosen so that the absorptions of the phenyl:cyclohexyl protons were $\alpha\alpha$. equal.

^b Normalized to a cyclohexane value of 12 with an average of 15-20 integrations of each sample at two different amplitudes. A 5% error in sample preparation was assumed in calculating standard deviations.

^{c, d} Data obtained at different integral amplitudes.

averages were weighted in proportion to the reciprocals of the squares of their standard deviations.³⁸ The atom fraction of hydrogen in the aromatic rings of 43 is $10.569/10.498$ or 1.0068 ± 0.0052 , yielding 10.07 ± 0.05 atoms of aromatic hydrogen. These results were verified by use of the HR-60 spectrometer. As seen in Table V, the deviation from 10 for the number of aromatic protons of 39b is less for HR-60 data than for A-60 data. The HR-60 data yields an atom fraction of aromatic hydrogen for 43 of $10.087/10.171$ or 0.9918 ± 0.087 . The atoms of aromatic protium are thus 9.92 ± 0.09 .

The determination of the deuterium content of the aromatic rings of 43 by mass spectrometry is complicated by the observation that both methylene and aromatic hydrogens are involved in the loss of C_6H_5 from the molecular ion of 39b in forming m/e 91.³⁹

This problem was resolved by reoxidation of 43 to benzophenone 39h with chromium trioxide in acetic acid. To establish the absence of exchange accompanying oxidation, 39b was oxidized to benzophenone 39g with chromium trioxide in acetic acid-0-d. The presence of an M-1 ion at all values of the ionizing voltage great enough to produce a useful molecule ion intensity precluded determination of the deuterium content in 39g and 39h from the molecular ion region of its spectrum. The intense fragment ion at m/e 105 in the spectrum of 39a was chosen because of the absence of peaks (a) at lower mass, (b) at m/e 106 and 107 in excess of natural abundance isotope peaks for m/e 105, and (c) ions from m/e 108 through 110. Since any isotope effect on loss of C_6H_5 should be negligible, the atom % deuterium in the m/e 105 ion will be equal to that in the molecular ion.

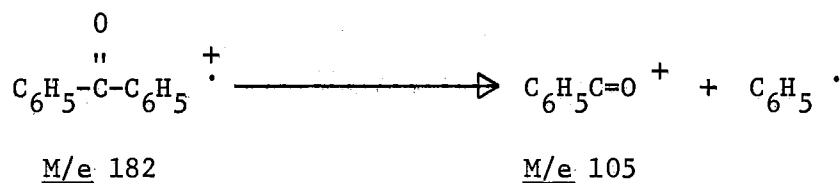


Figure 7. Fragmentation of Benzophenone

Comparison of the intensities of m/e 106 and 107 from the spectra of 39a and 39g (Table VI) shows that within experimental error, the oxidation of 39b in acetic acid-0-d proceeds without incorporation of deuterium in the aromatic ring.

TABLE VI

ION INTENSITIES IN THE SPECTRA OF 39a AND 39g

<u>M/e</u>	Intensities ^a	
	<u>39a</u>	<u>39g</u>
105	100.0	100.0
106	8.15	8.00
107	0.70	0.69

^a Average of data from ten each 15 and 16 eV Spectra

In the mass spectrum of 39h, Table VII, small residual intensities, which may be within experimental error equal to zero, are observed at m/e 106 and 107. From these average values, the percentages of species containing 0, 1, and 2 atoms of D were calculated (Table VII). The atom percent of aromatic hydrogen in 43 and 39h is calculated to be $99.9 \pm 0.4\%$.

TABLE VII
RESIDUAL ION INTENSITIES IN THE MASS
SPECTRUM OF 39h^a

<u>M/e</u>	Intensities ^b	Species	Percent of Total
105	100.0	d_0	99.65
106	0.287 ± 0.470	d_1	0.29 ± 0.47
107	0.0645 ± 0.0499	d_2	0.06 ± 0.05

^aBased upon data from ten scans each at 15.0 and 16.0 eV and corrected for naturally occurring heavy isotopes.

^bDerived by comparing spectra of 39a and 39g.

Thus, both methods of analysis indicate that no more than 0.05% deuterium becomes incorporated in the aromatic rings of 39a during deuteriolysis or in the aromatic rings of 39b during oxidation with chromic acid. Because of the relative low cost of gaseous deuterium and the simplicity of the procedure, this method promises to be a useful

technique for specific introduction of deuterium at the benzylic position. The general applicability of this process is under study.

CHAPTER VI

EXPERIMENTAL¹²

General Hydrogenolysis Procedure.— A water-jacketed glass reaction vessel (300 ml) is charged with 0.5 g of 10% Pd/C^{40a} and 75 ml of acetic acid. The glass hydrogenation system is evacuated and flushed with hydrogen twice, and the catalyst saturated with hydrogen over a period of 30 minutes. The reaction temperature is maintained at $30^{\circ} \pm 0.5$ using a circulating water bath. A sample (0.0125 mol) of the ketone or alcohol is then introduced by means of a sample inlet on the reaction vessel. A record of hydrogen consumption versus time³² at one atmosphere hydrogen pressure is taken. A mercury reservoir is used for hydrogen storage. See Table II or Table III.

Hydrogenolysis of Ketone Derivatives.— The purified carbonyl derivative (0.03 mol) is introduced into a 300-ml stainless steel hydrogenation vessel containing 50 ml of acetic acid and 0.6 g of 10% Pd/C catalyst.^{40a} The vessel is evacuated, hydrogen is introduced, and the vessel is shaken at 30-50 psi and 50-60° C until the pressure drop ceases.^{40b} Excess hydrogen is vented, and the vessel contents are filtered through Dicalite to remove the catalyst. The filtrate is diluted with 200 ml of water and extracted with ether (2 x 100 ml), and the extract is washed with 10% NaOH (2 x 100 ml), dried (MgSO₄), and concentrated by distillation or evaporation under reduced pressure. Other details are given in Table IV.

Preparation of Carbonyl Derivatives.— The carbonyl derivatives used were prepared according to published procedures (Table IV) and were purified by recrystallization from 95% ethanol except for 41c, (2,4-DNP), which was best purified by successive recrystallization from nitroethane⁴¹ and isopropyl alcohol.

GLC Studies of Hydrogenolysis Products.— A standard solution of the product hydrocarbon in ether (ca. 2%) was prepared and the glc curve was obtained^{42a} with duplicate or more injections (4 μ l) onto a 1/4 in. x 11 ft. column of 5% UC W-98 coated on 80-100 mesh, acid-washed, DMCS-treated Chromosorb G heated at 190°. The peak areas of average injections were used to compare with peak areas obtained for each hydrogenolysis product. The yields (Table IV) were derived from these data and also gravimetrically for benzophenone derivatives.

Reduction of Benzophenone (39a). (a) Deuteriumolysis to Diphenylmethane- α,α - d_2 (43).— To a dry 300 ml hydrogenation flask containing 10 ml of $\text{CH}_3\text{CO}_2\text{D}$ and 1.82 g of 10% Pd/C catalyst, saturated with 60 ml of D_2 , was added 9.1 g (0.05 mol) of 39a dissolved in 50 ml of $\text{CH}_3\text{CO}_2\text{D}$. Reduction at atmospheric pressure was continued for 5.4 hr until 2535 ml (0.105 mol) of D_2 was consumed. The catalyst was filtered out with Dicalite and the filtrate was made basic with 10% NaOH. Extracting with ether (2 x 200 ml), drying (MgSO_4), concentrating by rotary evaporation under reduced pressure, dissolving in 100 ml petroleum ether, bp 60-68°, and filtering through a 0.5-in. (OD) combination column (2 in. silica gel on top and 1 in. basic alumina at bottom) gave a colorless solution which was concentrated to yield 8.2 g of 43.

(b) Hydrogenation of Diphenylmethane (39b).— The procedure described under part (a) was repeated using H_2 to give 39b.

Chromic Acid Oxidation of Diphenylmethane (39b) in Acetic Acid-

0-d.— A 0.84-g sample of 39b was added to 21 ml of $\text{CH}_3\text{CO}_2\text{D}$. A solution of 0.66 g CrO_3 in 0.33 ml D_2O and 5.8 ml $\text{CH}_3\text{CO}_2\text{D}$ was added dropwise over 18 min to the magnetically stirred solution. The temperature of the mixture, cooled with a water bath, rose from 20° to 25° . After a 21-hr period of stirring, a second identical portion of the oxidizing mixture was added. The temperature rose 1° . After 24 additional hours, a third portion of oxidizing agent was added and the temperature rose 1° . After a total of 52 hr, the reaction mixture was diluted with 100 ml H_2O and made basic with 10% NaOH.

Extraction (2 x 100 ml ether), drying (MgSO_4), and concentrating gave 0.5 g of a 70:30 (39g:39b) mixture. The mixture was separated by chromatography with petroleum ether, bp $60-68^\circ$, on a 0.5-in (OD) combination column (2 in. silica gel, 1 in. basic alumina, and 1 in. acidic alumina - top to bottom). Elution of 39b and 39g was accomplished with petroleum ether and ether, respectively.

Oxidation of Diphenylmethane- $\alpha,\alpha\text{-d}_2$ (43).— A 1.7-g (0.01 mol) sample of 43 was oxidized as described in the preceding experiment except that sufficient oxidizing agent (5.28 g, 0.053 mol CrO_3) was added over 81 hr to convert 43 to 39h, which was obtained as 1.3 g (72%) of colorless crystals free of 43. Recrystallization from petroleum ether, bp $60-68^\circ$, gave 39h: mp $47-48^\circ$.

PART III
SYNTHESIS AND PURIFICATION
OF HYDROCARBONS

CHAPTER VII

INTRODUCTION

The American Petroleum Institute (API) initiated the API Hydrocarbon Research Project (API HRP) in 1938.⁴³ The primary objective of the program was to synthesize and/or purify gasoline-range hydrocarbons for engine testing, instrument calibration, and thermodynamic studies. More recent emphasis under API Research Project 58A has been on the synthesis of hydrocarbons to serve as standards⁴⁴ for the petroleum industry and for use in continuing thermodynamics studies at the Bureau of Mines Energy Research Center, Bartlesville, Oklahoma. In addition, a need has developed for pure polynuclear aromatic (PNA) hydrocarbons⁴⁵ for use by the petroleum industry in such areas as pollution, attendant health hazards, and refining operations. Because of these needs for PNA hydrocarbons the API hydrocarbon synthesis project at Oklahoma State University, Stillwater, Oklahoma, is currently involved in the synthesis of several specific fused-ring hydrocarbons.⁴⁵

CHAPTER VIII

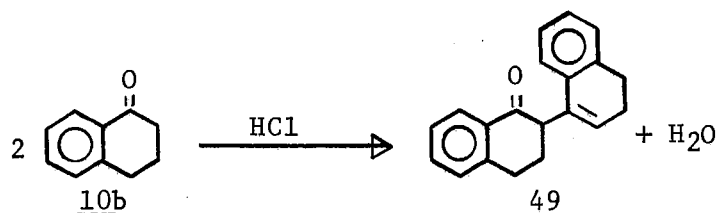
HISTORICAL

Alkylnaphthalenes as a whole have received considerable attention because of their occurrence in petroleum. Bailey¹⁶ et al. have described syntheses of the ten possible dimethylnaphthalenes; however, for 1,8-dimethylnaphthalene (44) the synthesis involved a chain-lengthening step which is unsatisfactory for large-scale preparation. Ried⁴⁶ utilized reduction of 1,8-bis(chloromethyl)naphthalene (45) with lithium aluminum hydride as a route to 44. The former requires preparation of 45 obtained by treatment of 1,8-naphthalenedimethanol (46) with gaseous hydrogen chloride. A more desirable preparation of 44 would be direct catalytic hydrogenolysis of the diol 46. Sarett⁴⁷ and Plakhov⁴⁸ have used the hydrogenolysis of 46 as a source of 44 but experimental details are meager and the side products of the reaction were not mentioned.

Procedures have been developed that provide pure alkylnaphthalenes from petroleum sources. Separation of hydrocarbon fractions has been achieved using dehydrated zeolitic metallic aluminosilicates⁴⁹ and molecular sieves.^{50a,b} Of particular interest^{50a} is the separation of 2,6-dimethylnaphthalene (47) from 2,7-dimethylnaphthalene (48). Mixtures of 47 and 48 form a binary eutectic which cannot be broken by distillation or solvent crystallization. The separation is achieved by selective adsorption of 48 with sodium type Y molecular sieves. The unadsorbed raffinate then yields pure 47.

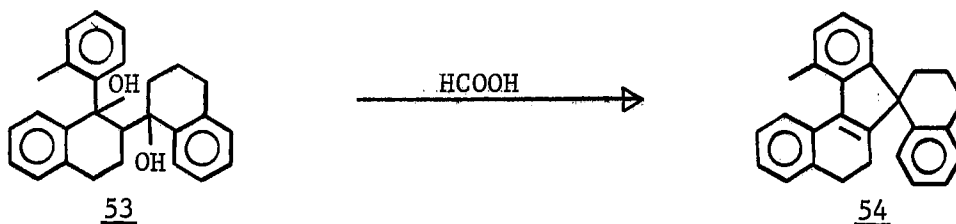
The purification of aromatic hydrocarbons has also been achieved via picrate formation, purification of the derivative and regeneration of the hydrocarbon. The cleavage of arene picrates to the hydrocarbons may be accomplished by extraction of picric acid from a benzene solution of the picrate with ammonium hydroxide^{50c} or aqueous sodium carbonate.^{50d} The separation of arenes from picric acid may also be done by adsorption of the latter on a column of alumina.^{50e} The arenes are then recovered from the benzene eluate. These techniques are adequate for small-scale isolations, but they become cumbersome, tedious, and expensive when larger quantities are involved.

Hydrocarbons containing more than two rings may be synthesized with 1-tetralone (10b) as starting material. Orchin⁵¹ has used 10b in the preparation of 2-(3',4'-dihydro-1'-naphthyl)-3,4-dihydro-1(2H)-naphthalenone (49). The latter synthesis involves using gaseous hydrogen chloride as a catalyst to dimerize 10b and dehydrate the resulting



alcohol. The position of the double bond in 49 was originally in doubt,⁵¹ but recent work⁵² has shown it to be β,γ to the carbonyl function. Dehydrogenation of 49 with Pd/C provided a low yield of 1,2'-

binaphthyl (50). 1-Tetralone (10b) was also used in the synthesis of 1-(o-tolyl)-3,4-dihydronaphthalene (51) and 1-(o-tolyl)naphthalene (52). However, in the course of this synthesis, a crystalline side product was isolated in 19% yield from the reaction mixture of 10b with o-tolylmagnesium bromide. Analysis of the side product showed it to be $C_{27}H_{28}O_2$, and its structure was shown to be 1-(o-tolyl)-1,1'-dihydroxy-1,2,3,4,1',2',3',4'-octahydro-2,1'-binaphthyl (53). Treatment of 53 with boiling formic acid yielded a hydrocarbon $C_{27}H_{24}$. Structure assignment for this compound was made on the basis of ultraviolet adsorption data. The spiro hydrocarbon 54 was suggested as the most likely structure.⁵³



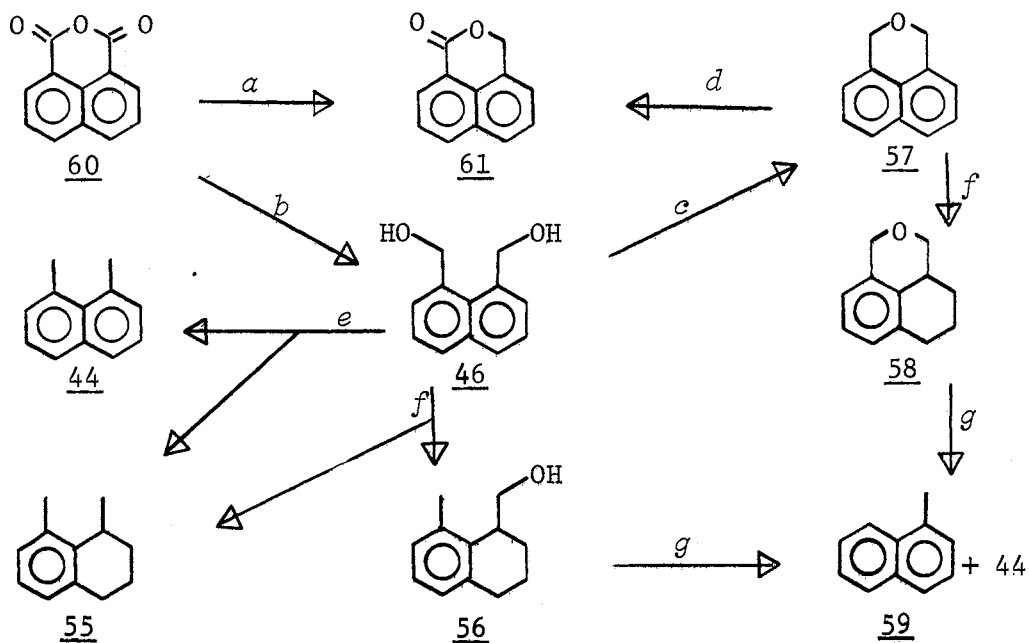
CHAPTER IX

DISCUSSION AND RESULTS

The synthesis of 1,8-dimethylnaphthalene (44) was undertaken to provide the Bureau of Mines Energy Research Center, Bartlesville, Oklahoma, with a substantial quantity of high-purity 44 for thermodynamic studies. Earlier syntheses of 44 have utilized 1,8-naphthalenedimethanol (46)^{47,48} or the corresponding dichloride.⁴⁶ We chose Pd/C hydrogenolysis of 46 for the preparation of 44 and found the reaction to be remarkably simple. We have found that depending upon reaction conditions,⁵⁴ 46 may be converted to a mixture of 44 and 55 or of 55 and 1,2,3,4-tetrahydro-8-methyl-1-naphthalenemethanol (56). The diol 46 may be hydrogenated to a mixture of 55:56 (55:45) in ethanol and in the absence of mineral acid.

Since traces of 57 were observed as a product in all hydrogenations of 46, it became of interest to prepare 57 and subject it to the same hydrogenation conditions to determine whether it may serve as an intermediate to 44, 55, or 56. Under hydrogenation condition *e* of Figure 8, there was no apparent reaction and 57 was recovered unchanged. However, more vigorous conditions (*f* of the Figure) gave the hexahydronaphtho-[1,8-*cd*]pyran (58) in 84% yield. Therefore, we do not consider 57 to be a significant hydrogenation or hydrogenolysis intermediate in the formation of 44, 55, or 56. Also, the rapidity with which 46 is reduced (*f*

of the Figure) to 55 and 56 militates against regarding 57 as an intermediate.



^aDIBAH:60 (2:1) in toluene.

^bDIBAH:60 (4:1) in benzene or $\text{NaAl}(\text{C}_2\text{H}_5)_2\text{H}_2$:60 (2:1) in xylene.

^cAmberlyst-15 in benzene at reflux.

^dDilute CrO_3 in acetic acid.

^e H_2 , Pd/C in acetic acid and hydrochloric acid at room temperature and one atmosphere.

^f H_2 , Pd/C in 95% ethanol at 50 psi at 60° .

^gPd/C, Δ .

Figure 8. Synthesis of 1,8-Dimethylnaphthalene

It is of interest that dehydrogenation of 56 provides the expected 44 but in addition, 59 is formed as the major product, the 44:59 ratio being 7:93. It is assumed that dehydrogenation of 56 to an aldehyde takes place and then decarbonylation ensues.⁵⁵ We have no evidence that 56 may be intermediate in the dehydrogenation of 58 to 59.

The preparation of the diol 46 precursor to 44 is carried out by reduction of 1,8-naphthalic anhydride (60) with diisobutylaluminum hydride (DIBAH).⁵⁶ DIBAH is a remarkably versatile reagent.⁵⁶ We have found that addition of DIBAH to a slurry of 60 in toluene at 10° gives the lactone 61 in 86% yield as the sole product. It is of interest that reduction of 60 with sodium borohydride in dimethylformamide, a reagent reported to convert anhydrides selectively to lactones, gave a complex mixture of products.⁵⁷ 1H,3H-Naphtho[1,8-*cd*]pyran-1-one (61) has been prepared as a mixture of products by high-pressure copper chromite hydrogenation of 60 in an unspecified yield.⁵⁸ Chromic acid oxidation of the pyran 57 produces 61 in 59% yield.⁵⁹

The purification of 44 is achieved by repeated recrystallization of its picrate from 95% ethanol. This is a convenient procedure for the purification of hydrocarbons which form stable picrates, but regeneration of the arene after purification is often troublesome.^{50c,d,e,}

A procedure has been devised for dissociation of picrates of arenes that depends upon the leaching action of petroleum ether, which dissolves the arene but essentially no picric acid; this permits recovery of picric acid for reuse and considerably reduces the amount of hydrocarbon solvent and alumina needed for the separation. Most of the picric acid remains undissolved and out of contact with the alumina. The arene is then recovered by removing the solvent by rotary evaporation or distillation.^{50f}

We describe in detail the application of this procedure to 2,7-dimethylnaphthalene because of the attention its isolation and purification have received.^{49,50a,b} We have also applied purification via the picrate to 1,8- and 2,6-dimethylnaphthalene. Our glc data^{60a} show that a 2% impurity of 2,6-dimethylnaphthalene^{60b} was removed from 2,7-dimethylnaphthalene by this procedure.^{60d} It is of interest that a 0.2% impurity (m/e 170) in zone-refined 2,6-dimethylnaphthalene was also removed.

We sought to extend the technique for cleavage of hydrocarbon picrates to those of more complex arenes. The picrates of phenanthrene, fluoranthene, and pyrene were prepared and tested. Of these, the picrate of phenanthrene was readily cleaved as described for that of 2,7-dimethylnaphthalene. However, the picrates of fluoranthene and pyrene are more stable and less soluble in petroleum ether and therefore require more time (double or triple) for cleavage. As expected, with prolonged reflux the liberated picric acid is dissolved and penetrates the alumina column. Consequently, there is no advantage in using the extraction apparatus of Figure 9. For this type of picrate, the previously described procedure^{50e} of using alumina to adsorb picric acid from a benzene solution of the picrate may be used; it is rapid and effective but more solvent and alumina are required, for example, the cleavage of 1 g of fluoranthene picrate requires 500 ml of benzene and at least 15 g of basic alumina.

The choice between benzene and petroleum ether for cleavage of the hydrocarbon picrate may be made by testing the solubility in boiling petroleum ether and observing a change in appearance⁶¹ or a loss in weight due to extraction of hydrocarbon. The petroleum ether extraction

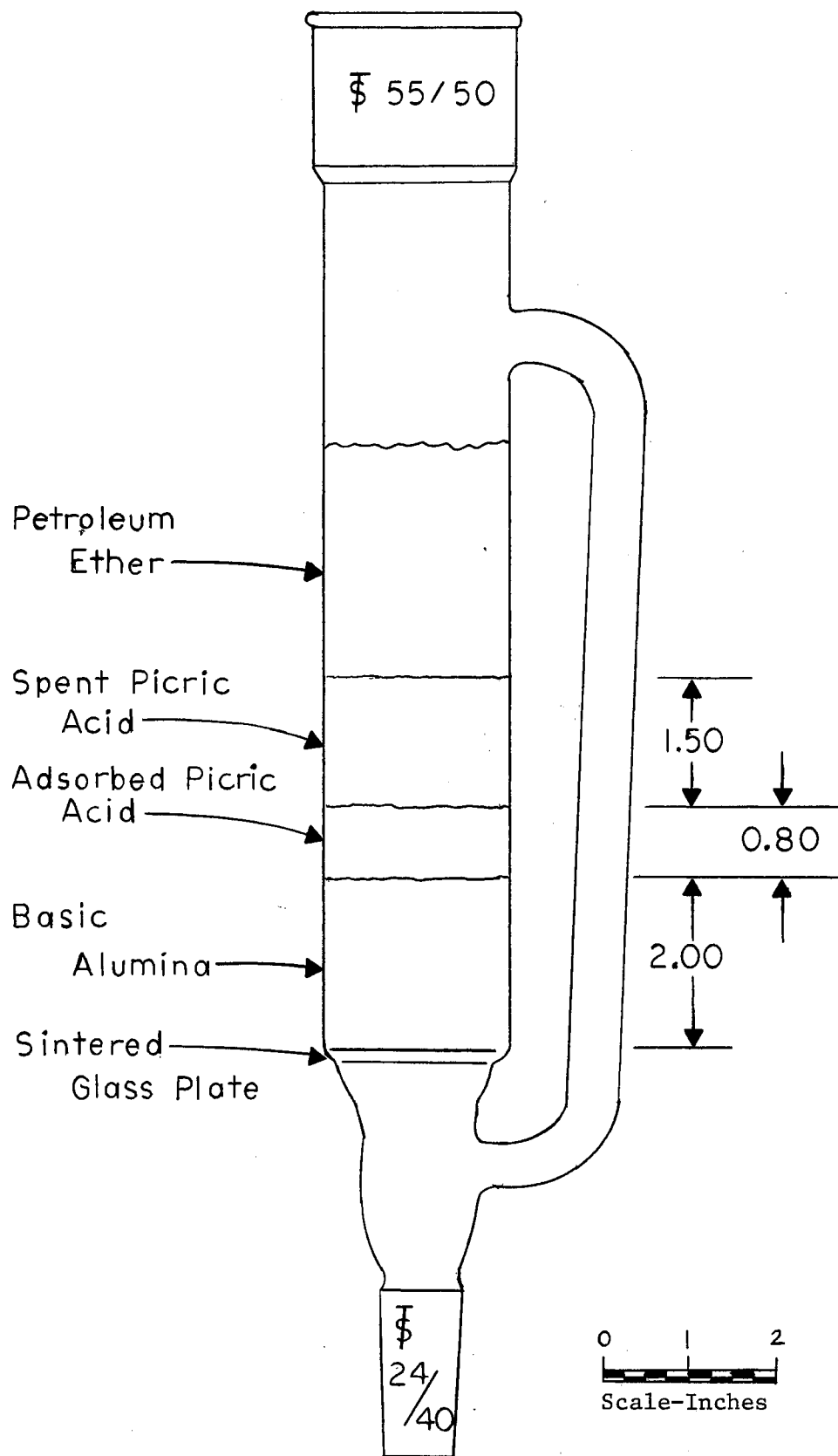


Figure 9. Apparatus for Cleavage of Arene Picrates

of an equivalent weight of picric acid serves as a good comparison. It should be noted that the number of rings and molecular weight of the hydrocarbon are not always reliable criteria in judging whether a hydrocarbon picrate will readily decompose in petroleum ether; for example, the picrate of 1',2',3',4'-tetrahydro-1,2'-binaphthyl (4 rings, C₂₀H₁₈) is readily cleaved by petroleum ether in the extraction apparatus.⁶²

The current emphasis on pollution and pollution control has created a demand for high-purity standards for use in detection and characterization of potentially harmful chemicals. The presence of polynuclear aromatic (PNA) hydrocarbons in engine exhaust gases and products of combustion is an established fact.⁴⁵ Many PNA hydrocarbons are recognized carcinogens. As a result, emphasis is currently being placed on the synthesis of selected fused-ring hydrocarbons to serve as standards for the petroleum industry.⁴⁵

1-Tetralones are valuable starting materials in the synthesis of PNA hydrocarbons. Of particular interest is the unsaturated ketone 49,^{51,52} obtained from the smooth self-condensation of 1-tetralone 10b in the presence of Amberlyst-15 sulfonic acid resin⁶³ in boiling toluene. The 2,1' linkage of 49 was substantiated by conversion to 1,2'-binaphthyl (50) via 62 in 80% yield from 10b.

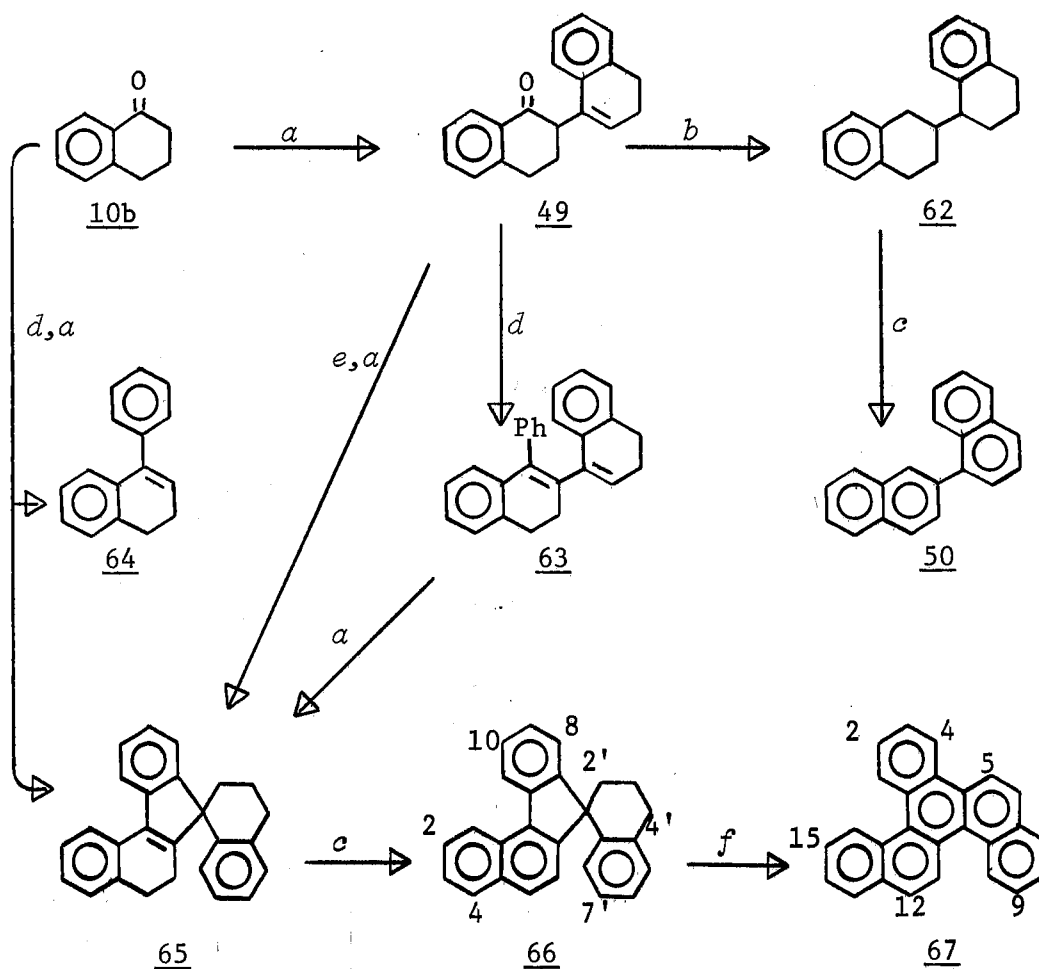
The β,γ -unsaturated ketone 49 was also treated with phenylmagnesium bromide to learn whether it and the diene 63 are possible intermediates in the formation of the spiro hydrocarbon 65. We first obtained the latter as a low-yield side product in the preparation of 1-phenyl-naphthalene^{64a} via 10b and 64. The formation of 65 during preparation of 64 appears to be dependent upon order of addition^{64b} and judicious use of acid during work-up.⁶⁵ Thus, addition of 10b to a stirred

solution of phenylmagnesium bromide followed by acid treatment during work-up provided the maximum yield of 64 (67%) and a small pot residue^{64b} from which 65 was isolated in 2-3% yield. Inverse addition^{64b} gave 12% of 65. We also noted that the reaction of 49 with phenylmagnesium bromide, regardless of mode of addition, was incomplete with at least 30% recovery of 49.

The best preparation of 65 (55%) resulted from addition of phenyllithium to 49 (cf. e,a of Figure 10). The latter was completely consumed.

In our opinion, the sequence leading to 65 during the addition of a solution of 10b to phenylmagnesium bromide (Figure 10) involves base-catalyzed formation of 49 or a related species which in turn reacts with Grignard reagent to give an alcohol precursor of 63. The diene 63 may be isolated when 49 is treated with phenylmagnesium bromide and acidification is accomplished with cold aqueous hydrochloric acid.^{65a} The sequence leading to 65 is completed by cyclization of 63 using Amberlyst-15.^{63,65b}

To establish the structure of 65, it was dehydrogenated to the spiro hydrocarbon 66 by heating in the presence of Pd/C. The strongest argument for the structure of these spiro hydrocarbons is the anisotropy exhibited by the C-1, C-11, and C-8' protons in the pmr spectra (100 MHz) of both hydrocarbons 65 and 66. Dreiding models of 65 and 66 indicate that the C-1 and C-11 protons should experience deshielding.^{66a} For 65, this strong interaction results in a downfield triplet at 7.88 δ for both protons. For 66 the C-1 and C-11 protons give separated signals (pair of doublets) shifted to 8.79 and 8.37 δ respectively. Strong shielding is observed for the C-8' proton of 65 and 66. These



a Amberlyst-15, toluene, Δ .

b Pd/C, H₂, CH₃CO₂H.

c Pd/C, Δ .

d C₆H₅MgBr, H₃O⁺.

e C₆H₅Li.

f Pd/C, S, Δ .

Figure 10. Spiro Hydrocarbons and Dibenzo[c,p]Chrysene From 1-Tetralone.

high-field shifts appear as doublets centered at 6.49 and 6.25 δ respectively. Dreiding models of 65 and 66 also show that the C-8' proton is

situated above the aromatic rings of the fluorene system and hence should be influenced by aromatic ring currents.^{66b}

Aromatization of 66 to dibenzo[c,p]chrysene (67) was accomplished by heating it in the presence of Pd/C and sulfur.^{66c} The structure of 67 is supported by its high-resolution mass spectrum, which shows a molecular ion peak (m/e 328), peaks resulting from loss of 1, 2, and 4 H atoms, and the formation of doubly charged ions m/e 164 (M)⁺⁺, 163 (M-2H)⁺⁺, and 162 (M-4H)⁺⁺. The m/e 326 ion apparently loses CH and C₂H₂ to yield doubly charged ions m/e 156.5 and 150. These fragmentations are characteristic of condensed polynuclear aromatic hydrocarbons.^{67a,b} The pmr spectrum of 67 shows a multiplet of 6 aromatic protons at δ 9.56-8.19. This corresponds to the bay protons at positions C-1, 4, 5, 10, 11, and 16. The remaining 10 protons give rise to an upfield multiplet centered at δ 7.93. A similar spectrum was reported^{67c} for dibenzo[g,p]chrysene.

CHAPTER X

EXPERIMENTAL^{12,60}

DIBAH Reduction of Naphthalic Anhydride (60). A: To 61.— To a 22-1. vessel⁶⁸ fitted with stirrer and a dropping funnel with wide-bore Teflon stopcock and equalizing sidearm was added 4 l. of dry toluene and 400 g (2 mol) of 60. The reaction mixture was cooled in an ice bath to 5-10° and held in this temperature range during addition of 579 g (4.1 mol) of neat DIBAH⁵⁶ over 2 hr. The direct addition of DIBAH from 1-1. storage bottles to the dropping funnel was readily accomplished through use of a simple adapter.⁶⁹ The reaction mixture was then poured onto 4 kg of ice and water. The salts were decomposed with 2 l. of conc. hydrochloric acid. Three l. of ether were added and the resulting mixture was filtered through Dicalite to remove a small amount of suspended material. A second 2-1. ethereal extract was combined with the first extract and these were dried (MgSO₄), filtered, and concentrated to 362 g of crude solid, yellow lactone (98%). It was purified by dissolving in 10% sodium hydroxide and extracting with ether to remove neutral material. On acidification to pH 8-9, the lactone crystallized as colorless 61 (316 g, 86%): mp 154-157° [lit.⁵⁸ 152-155°]; mass spectrum (70 eV) m/e (rel intensity) 184 (66), 183 (38), 156 (19), 155 (100), 127 (70), 126 (22); pmr (CDCl₃) δ 8.30 (d, 1, ArH ortho to carbonyl), 8.13-7.21 (m, 5, ArH), 5.72 (s, 2, ArCH₂).

B: To 1,8-Naphthalenedimethanol (46).— The apparatus mentioned in part A was used for reduction of 60 to 46. A slurry of 600 g (3 mol) of 60 in 2.5 l. benzene was added over 2 hr to 1850 g (13 mol) of neat DIBAH⁵⁶ in 1.5 l. of dry benzene. During addition, the reaction temperature rose until reflux resulted (20 min) and was held at this temperature by addition of the remainder of 60. After addition was complete, reflux was maintained for 17 hr at which time a sample was withdrawn. Glc studies^{12c,70} showed that 60 had been consumed. Ethyl acetate (2 mol) was added to consume excess DIBAH. The reaction mixture was added to ice and water. Concentrated hydrochloric acid (2.2 l.) was added to the gel-like suspension. The white crystals which formed were filtered and dried and then added to 3.5 l. of 95% ethanol. The boiling ethanol suspension was diluted with 10 l. of water and allowed to cool to room temperature, then the layer of crystals (546 g) was skimmed from the solution. These were recrystallized from 2 l. of hot 95% ethanol to give 525 g (94%) of colorless 46: mp 154.5–155° [lit.⁴⁷ 158°]; mass spectrum (70 eV) m/e (rel intensity) 188 (M⁺, 15), 170 (96), 169 (100), 153 (26), 142 (36), 141 (92), 115 (39). A pmr analysis was attempted but a suitable solvent was not found. Compound 46 is very insoluble in common solvents at room temperature. Reduction of 60 to 46 may also be conveniently carried out with NaAl(C₂H₅)₂H₂ in xylene.⁵⁶

Cyclization of 46 to 1H,3H-Naphtho[1,8-cd]pyran (57) with Amberlyst-15.— The dehydration of 46 to 57 was carried out by azeotropic distillation of water from a magnetically stirred mixture of 47 g (0.25 mol) of 46, 500 ml of benzene and 5 g of Amberlyst-15⁶³ during 2 hr. The catalyst was filtered out, the filtrate concentrated to 250 ml, and 250 ml of petroleum ether^{12d} was added. The mixture was passed

through a basic alumina column (2 cm x 17 cm). The colorless filtrate was further concentrated and on cooling, the filtrate gave 39 g (92%) of 57: mp 81-82° [lit.⁷¹ 80-81°]; mass spectrum (70 eV) m/e (rel intensity) 168 (72), 167 (29), 142 (55), 141 (100), 139 (28), 115 (41); pmr (CCl₄) δ 7.72-6.98 (m, 6, ArH), 4.95 (s, 4, ArCH₂O).

Chromic Acid Oxidation of 57 to 61.— To a stirred mixture of 13.6 g (0.08 mol) of 57 in 750 ml of acetic acid at 11° was added 107 ml of oxidizing mixture (190 ml acetic acid, 10 ml water, and 21 g CrO₃) at one time.⁷² The temperature ranged from 11° to 19°. The reaction mixture was stirred for 100 min, poured into 5 l. of water, and extracted with 2 x 750 ml of ether. The combined extracts were filtered to remove 0.6 g of 60. The filtrate was stirred with 500 ml of 10% NaOH to remove 61 (as the salt of the hydroxy acid). The ethereal layer yielded 4.6 g of 57. The alkali layer was acidified with conc. hydrochloric acid (cyclization back to 61) and extracted to give 6.1 g (63%) of crude 61 which was purified by dissolving in benzene-petroleum ether (1:1) and then filtering through basic alumina to give 5.7 g (59%) of 61: mp 155-157° [lit.⁵⁸ 152-155°].

Pd/C Hydrogenolysis of 46 to 1,8-Dimethylnaphthalene (44) and 1,8-Dimethyl-1,2,3,4-tetrahydronaphthalene (55).— A 94-g (0.5-mol) sample of 46 in 750 ml of acetic acid and 2 ml of conc. hydrochloric acid in the presence of 1.6 g of 10% Pd/C was hydrogenated at atmospheric pressure for 4 hr at 25° using a Parr Model 3920 hydrogenation apparatus. The catalyst was filtered through a bed of Dicalite. Water (2 l.) was added to the filtrate and the mixture was extracted with ether (2 x 500 ml). The extract was washed with water and 10% sodium hydroxide, dried (MgSO₄), and concentrated by rotary evaporation to give 77 g of a

mixture of dark crude solid 44:55 (9:1) containing less than 1% of 56. These crystals were dissolved in 400 ml of petroleum ether^{12d} and the solution was decolorized by elution through a 1.5 x 5 in. column of basic alumina. The petroleum ether was removed to give 70 g (88%) of a colorless mixture of 44 and 55. The mixture was dehydrogenated at 265° in the presence of 2 g of 10% Pd/C to give after filtration 69 g (82% from 60) of 44:^{50f} mp 63.5-64° [lit.⁴⁷ 62-63.5°]; mass spectrum (70 eV) m/e (rel intensity) 156 (M⁺, 100), 155 (29), 153 (15), 141 (65), 115 (16), 76 (13); pmr (CCl₄) δ 7.67-7.46 (m, 2, ArH peri), 7.30-7.08 (m, 4, ArH), 2.28 (s, 6, ArCH₃).

Pd/C Hydrogenolysis of 46 to 55 and 1,2,3,4-Tetrahydro-8-methyl-1-naphthalenemethanol (56).— A 47 g (0.25 mol) sample of 46 in 750 ml of 95% ethanol in the presence of 1.2 g of 10% Pd/C was hydrogenated at 50 psi and 60° for 4 hr. Filtration through Dicalite and concentration by rotary evaporation gave 41 g of yellow oil which was shown by glc^{12c} to be 55:56 (1.2:1.0). Addition of 50 ml of petroleum ether,^{12d} refrigeration and filtration gave 16 g (35%) of 56 free of 55: mp 72.5-73°; mass spectrum (70 eV) m/e (rel intensity) 176 (M⁺, 12) 146 (14), 145 (100), 130 (13), 129 (12), 128 (12); pmr (CDCl₃) δ 7.20-6.82 (m, 3, ArH), 3.74-3.42 (m, 2, ArCHCH₂OH), 3.28-2.98 (m, 1, CH₂OH), 2.89-2.67 (m, 2, ArCH₂), 2.33 (s, 3, ArCH₃), 2.29-1.46 (envelope, 5, ArCH₂CH₂CH₂CH).

Anal. Calcd for C₁₂H₁₆O: C, 81.77; H, 9.15. Found: C, 81.74; H, 9.06.

The filtrate containing 55:56 (46:1) was distilled to give 20 g (40%) of 55: bp 60° (0.5 mm); mass spectrum (70 eV) m/e (rel intensity) 160 (M⁺, 20), 146 (12), 145 (100), 129 (9), 128 (11), 115 (13); pmr

(CCl₄) δ 6.94-6.74 (m, 3, ArH), 3.20-2.87 (m, 1, ArCHCH₃), 2.86-2.58 (m, 2, ArCH₂), 2.27 (s, 3, ArCH₃), 1.98-1.58 (m, 4, CH₂CH₂CH₂), 1.16 (d, 3, ArCHCH₃).

Anal. Calcd for C₁₂H₁₆: C, 89.94; H, 10.05. Found: C, 90.14; H, 10.17.

Pd/C Hydrogenation of 57 to 58.— An 8.5-g (0.05 mol) sample of 57 was hydrogenated in the presence of 0.85 g of 10% Pd/C in 75 ml of 95% ethanol at 50 psi and 60° for 7 hr. The product was 8.5 g of crude 58 which contained about 2% 56. Recrystallization from cold petroleum ether^{12d} gave 7.4 g (84%) of 58: mp 40-42°, bp 105° (1.1 mm); mass spectrum (70 eV) m/e (rel intensity) 174 (21), 145 (28), 144 (100), 129 (59), 128 (27), and 115 (24); pmr (CCl₄) δ 7.06-6.51 (m, 3, ArH), 4.66 (s, 2, ArCH₂O), 4.04-3.04 (m, 2, ArCH₂OCH₂), 2.96-2.38 (m, 3, ArCH₂CH₂CH₂CH), 2.04-0.78 (m, 4, ArCH₂CH₂CH₂).

Anal. Calcd for C₁₂H₁₄O: C, 82.72; H, 8.10. Found: C, 82.60; H, 8.12.

Pd/C Dehydrogenation of 56 to 44 and 1-Methylnaphthalene (59).— A 1.76-g (0.01-mol) sample of 56 under an N₂ atmosphere was dehydrogenated at 260° in the presence of 0.3 g of 10% Pd/C for 2 hr. Filtration and distillation gave 1.3 g of a mixture of 44 and 59 (7:93).

The identity of 59, obtained by preparative glc, was established by comparing the pmr and ir spectra with those of an authentic sample.

Pd/C Dehydrogenation of 58 to 57, 44, and 59.— The above procedure was applied to 58, which gave 1.3 g of 57:44:59 (3:1:21).

Preparation and Recrystallization of Dimethylnaphthalene Picrates.— To a 4-l., wide-mouth, Pyrex crystallizing bottle (Corning No. 1597) was added 78 g (0.5 mol) of 2,7-dimethylnaphthalene, mp 92-95°, of

approximately 98% purity,^{60a,b} 126 g (0.55 mol) of picric acid,^{60c} and 2 l. of 95% ethanol. The suspension was boiled with a mantle (Glascol No. 0-636) until solution was complete. The solution was allowed to cool to room temperature and the picrate of 2,7-dimethylnaphthalene crystallized spontaneously as bright yellow needles. After overnight refrigeration, the crystals were filtered and dried to give 165 g (85%), mp 136-138°. Successive recrystallizations from 1.8 to 2 l. of 95% ethanol gave 140 g (72%); 130 g (67%); 105 g (54%) based on dried^{60e} wt. The final mp was 136-137° [lit.¹⁶ 135.5-136°].

The melting point, dried^{60e} wt. of picrate, and percent yield for the similarly prepared yellow-orange picrate of 1,8-dimethylnaphthalene at each step were: 153-156°, 132 g (68%); 154.5-156°, 125 g (65%); 155-156.5°, 115 g (50%); and 155-157°, 100 g (52%) [lit.⁷³ 154.5-155.5°]. Likewise, the picrate of 2,6-dimethylnaphthalene was prepared in 75% yield and recrystallized from 95% ethanol to give a 60% yield of yellow-orange crystals, mp. 141-143.5° [lit.¹⁶ 141-142°].

The Regeneration of Arenes from their Picrates.— A dried^{74a} 72 g (0.18 mol) sample of the purified picrate was added to the glass filtration apparatus⁷⁴ (Figure 9) fitted with reflux condenser and containing 80 g of basic alumina (2.2 in. x 2.7 in.). A 5 cm Teflon-coated magnetic stirring bar was placed on the picrate crystals and a 1-l. recovery flask containing 500 ml petroleum ether^{74c} was attached to the apparatus. The contents of the flask were refluxed at a rate which kept a level of condensed solvent above the picrate as shown in the drawing. At intervals, the picrate crystals were agitated by manually manipulating the Teflon-covered magnetic stirring bar to reduce channeling. The extraction was continued for 5-6 hr until the yellow-

orange color of the picrate had changed to the pale yellow color of anhydrous picric acid. The height of the picrate layer in the apparatus shrank from 2.7 in. to 1.5 in. during the extraction. At the end of the extraction period, an orange-colored band (ca. 0.8 in.) had penetrated the alumina charge. The remainder of the alumina was colorless. The contents of the recovery flask were concentrated (rotary evaporation) to give 27 g of 2,7-dimethylnaphthalene: mp 96-97° [lit.¹⁶ 96-97°]. A second extraction for 2 hr yielded an additional 1.5 g of hydrocarbon (98% total yield for the regeneration).

The yields of 1,8-dimethylnaphthalene, mp 63-64.5° [lit.⁷³ 62.5-64°], and 2,6-dimethylnaphthalene, mp 109.5-111° [lit.¹⁶ 110-111°], obtained by regeneration from their picrates were 95% and 97% respectively.

Phenanthrene, mp 97-99°, fluoranthene, mp 106-108.5°, and pyrene, mp 148.5-152.5°, were used to prepare the respective picrates. Recrystallization in each case from 95% ethanol gave yellow crystals, mp 144-146.5° [lit.⁷⁵ 145°]; orange needles, mp 186-188° [lit.^{76a} 186.8-188.1°]; and fine red needles, mp 226-227.5° [lit.^{76b} 219-220°] respectively. Decomposition of phenanthrene picrate as described for 2,7-dimethylnaphthalene gave 90% of colorless phenanthrene, mp 98-99.5° [lit.⁷⁵ 100°], while similar decomposition required 15-20 hr for 19 g of picrate using petroleum ether, bp 60-68°, and 65 g of basic alumina to give 80% of colorless fluoranthene, mp 109.5-110.5° [lit.^{76a} 110.6-111°]. A similar experiment with pyrene picrate gave pyrene, mp 150-153° [lit.^{76b} 149-150°].

In a separate regeneration, a 1-g sample of fluoranthene picrate dissolved in 100 ml benzene was added to a 2.5 x 15 cm (50 g) column of

basic alumina. Four additional 100-ml portions of benzene were passed through the column. Only a trace amount of fluoranthene was observed in the last portion of effluent. The benzene was removed by rotary evaporation to leave crystalline fluoranthene. The color due to picric acid extended about 5 cm into the alumina column.

Conversion of 1-Tetralone (10b) to 2-(3',4'-Dihydro-1'-naphthyl)-3,4-dihydro-1(2H)-naphthalenone (49).— 1-Tetralone (292 g, 2 mol), 30 g Amberlyst-15⁶³ and 750 ml of dry toluene were combined in a 2-l. one-neck flask equipped with a Dean-Stark trap. The mixture was heated at reflux for 4.5 hr with magnetic stirring until production of water (4 ml) ceased. The reaction mixture was cooled, filtered, and concentrated with a rotary evaporator. The concentrated oil was mixed with 100 ml of ether, and the yellow-white crystals of 49 (37 g) that formed after refrigeration for two days were filtered out. The mother liquor was distilled at 80° (0.1 mm) to give 193 g of recovered 10b. A small forerun containing naphthalene was collected. Ether (150 ml) was added to the cooled viscous pot residue, which then crystallized on seeding. An additional 45 g of 49 was obtained as brown crystals. The combined yield of crude 49 was 91% based on recovered 10b. This mixture was washed with ether and recrystallized from acetone to give 49 as colorless crystals: mp 132.5-135° [lit.⁵¹ 132.5-134.2°]; orange 2,4-dinitrophenylhydrazone mp 249-250° (dec) [lit.⁵¹ 247-248°]; mass spectrum (70 eV) m/e (rel intensity) 274 (77), 146 (75), 129 (100), 43 (97), 29 (91); pmr (CDCl₃) δ 8.24 (m, 1, isolated ArH at C-8), 7.63-7.24 (m, 7, ArH), 5.88 (t, 1, vinylic), 3.89 (t, 1, C=CCH and adjacent to C=O), 3.21-2.02 (m, 8, -CH₂-); uv as previously recorded.⁷⁷

Pd/C-Catalyzed Hydrogenation of 49 to 1,2,3,4,1',2',3',4'-Octahydro-1,2'-binaphthyl (62).— A 100-g (0.36-mol) sample of 49 in 400 ml of acetic acid in the presence of 5 g of 10% Pd/C was hydrogenated at 50 psi and 65° for 12 hr. The catalyst was filtered out with Dicalite. Water (1.5 l.) was added to the filtrate and the mixture was extracted with ether (2 x 500 ml). The extract was washed with water and 100 ml of 10% sodium hydroxide, dried (MgSO₄), filtered, and distilled to give 89 g (95%) of 62: bp 165° (0.1 mm) [lit.⁷⁷ 175-180° (0.2 mm)]; mass spectrum (70 eV) m/e (rel intensity) 262 (8), 132 (21), 131 (100), 130 (30), 129 (17), 115 (15), 91 (22); pmr (CCl₄) δ 7.32-6.72 (m, 8, ArH), 3.08-1.12 (envelope, 14, ArCH, ArCH₂ and -CH₂-); uv as previously recorded.⁷⁷

Pd/C-Catalyzed Dehydrogenation of 62 to 1,2'-Binaphthyl (50).— A 89-g (0.34-mol) sample of 62 and 5 g of 10% Pd/C were heated together at 300° under nitrogen for 2.5 hr. The cooled mixture was dissolved in benzene and filtered through Dicalite to remove catalyst. An equal portion of petroleum ether^{12d} was added and the solution decolorized by elution through a 1 x 4 in. column of basic alumina. The solvents were removed by rotary evaporation to give 86 g of crystalline 50. Recrystallization from petroleum ether^{12d} gave 80 g (93%) of 50 free of impurity by glc:^{12c} mp 76-78° [lit.⁷⁷ 76.5-77.5°]; mass spectrum (70 eV) m/e (rel intensity) 254 (100), 253 (72), 252 (53), 250 (13), 127 (10), 126 (27); pmr (CDCl₃) δ 8.05-7.18 (m, ArH).

Conversion of 1-Tetralone (10b) to 3,4-Dihydro-1-phenylnaphthalene (64) and Spiro[5,6-dihydro-7H-benzo[c]fluorene-7,1'-(1',2',3',4'-tetrahydronaphthalene)] (65).— The preparation of 64 from 584 g (4 mol) of 10b and 4.8 mol of phenylmagnesium bromide was carried out as

described^{64a} except that commercial Grignard reagent⁷⁸ was substituted and Amberlyst-15⁶³ in boiling toluene was used for dehydration. Glc studies^{12c} at 240° of this reaction mixture showed the presence of 1-phenyl-1,2,3,4-tetrahydronaphthalene:64:1-phenylnaphthalene in a ratio of 5:80:15. The hydrocarbon mixture was distilled at 95-99° (0.01 mm) through an 18 in. vacuum-jacketed Vigreux column to give 486 g (67%) of crude 64 and 32 g of distillation pot residue. Redistillation⁷⁹ gave pure 64: bp 91° (0.01 mm) [lit.⁸⁰ 130.5-135.5° (0.3 mm)]; mass spectrum (70 eV) m/e (rel intensity) 206 (100), 205 (29), 202 (18), 191 (38), 128 (25), 91 (22); pmr (CCl₄) δ 7.36-6.97 (m, 9, ArH), 5.96 (t, 1, vinylic), 2.91-2.59 (m, 2, ArCH₂) 2.44-2.03 (m, 2, allylic); uv max (95% ethanol) 205 nm (log ε 4.39), 220 (4.36), 267 (3.91).

The identity of the glc peaks assigned to 1-phenyl-1,2,3,4-tetrahydronaphthalene and 1-phenylnaphthalene in the reaction product mixture was established by glc^{12c} comparison at 225° with authentic materials. Samples of these hydrocarbons were obtained from 64 by catalytic hydrogenation and catalytic dehydrogenation in the presence of 10% Pd/C catalyst.

The pot residue (32 g) was recrystallized twice from benzene to give colorless crystals of 65: mp 189-190°; mass spectrum (70 eV) m/e (rel intensity) 334 (100), 305 (12), 303 (12), 289 (10), 229 (11), 215 (21); pmr (CDCl₃) δ 7.88 (t, 2, isolated ArH at C-1 and C-11), 7.42-6.72 (m, 9, ArH), 6.49 (d, 1, ArH at C-8'), 3.08-2.56 (m, 4, ArCH₂), 2.50-1.61 (m, 6, ArCH₂CH₂ and ArCH₂CH₂CH₂); uv max (95% ethanol) 203 nm (log ε 4.75), 238 (4.46), 266 (3.87), 294 (3.86).

Anal. Calcd for C₂₆H₂₂: C, 93.37; H, 6.63. Found: C, 93.23; H, 6.79.

Inverse Addition of Phenylmagnesium Bromide to 10b to Form 64 and 65.— To a mechanically stirred solution of 44 g (0.3 mol) of 10b in 500 ml of dry ether at 10° was added 200 ml (0.6 mol) of 3-molar phenylmagnesium bromide⁷⁸ over a 15-min period. Reflux was established after 5 min and the mixture was stirred for 1.5 hr. The reaction mixture was then added to 500 g of ice and 200 ml of conc. hydrochloric acid. The ether extract was dried (MgSO₄) and concentrated to give 63 g of red-brown oil. The oil was dissolved in 350 ml of toluene and stirred at reflux for 1.5 hr with 3 g of Amberlyst-15.⁶³ Filtration and steam distillation gave 41 g of volatile hydrocarbon and 20 g of non-steam-volatile material. The non-volatiles were dissolved in petroleum ether^{12d} and percolated through a 2 x 3 in. column of basic alumina; concentration of the effluent and crystallization from petroleum ether^{12d} gave 6 g (12%) of 65.

Inverse Addition of Phenylmagnesium Bromide to 49 to Form 1-Phenyl-3,3',4,4'-tetrahydro-2,1'-binaphthyl (63).— To a stirred mixture of 27.4 g (0.1 mol) of 49 in 500 ml dry ether was added 67 ml (0.2 mol) of a 3-molar phenylmagnesium bromide⁷⁸ solution during five minutes. There was no apparent temperature change; the mixture was then heated at reflux for 24 hr. The reaction mixture was added to 500 g of ice and 50 ml conc. hydrochloric acid. Extraction with benzene (250 ml), drying (MgSO₄), and concentration gave 37 g of yellow oil. Petroleum ether^{12d} (150 ml) was added and 10 g of 49 was recovered on cooling and filtering. The filtrate was percolated through two 2 x 3 in. columns of Merck basic alumina to give 16 g of concentrated oil. This oil crystallized from 25 ml of cold acetone after 3 days to give 8.5 g (40%) of 65: mp 95–97°; mass spectrum (70 eV) m/e (rel intensity) 334 (100), 333 (12),

332 (11), 305 (11), 215 (10), 117 (11); pmr (CCl_4) δ 7.26-6.62 (m, 13, ArH), 5.54 (t, 1, vinylic), 3.04-2.76 (m, 2, ArCH_2 at C-4), 2.70-2.28 (m, 4, ArCH_2CH_2 and ArCH_2 at C-3 and C-4' respectively), 2.10-1.81 (m, 2, ArCH_2CH_2 at C-3'); uv max (95% ethanol) 205 nm ($\log \epsilon$ 4.65), 267 (3.97).

Anal. Calcd for $\text{C}_{26}\text{H}_{22}$: C, 93.37; H, 6.63. Found: C, 93.18; H, 6.68.

Amberlyst-15-Catalyzed Cyclization of 63 to 65.— Three g of 63 were cyclized over 30 min by heating in 150 ml of boiling toluene containing 2 g of Amberlyst-15.⁶³ The reaction mixture was cooled, filtered, and concentrated and the crude product crystallized from 50 ml of petroleum ether^{12d} to give 2.7 g (90%), mp 189-190°, found to be identical with 65 from other experiments.

Conversion of 49 to 65 using Phenyllithium.— Phenyllithium (0.4 mol) was prepared as described⁸¹ from 63 g bromobenzene and 3 g of Li. To the stirred reagent was added, during 40 min at 25-30°, 27.4 g (0.1 mol) of 49 dissolved in 300 ml of dry benzene. The mixture was heated at reflux for 10 hr. During this period the temperature rose from the boiling point of ether to that of benzene. The reaction mixture was cooled and added to ice and 300 ml of 10% HCl. Extraction with ether gave 34 g of concentrated oil; ir (neat) 3460 cm^{-1} (OH). The oil was dehydrated and cyclized with 3 g of Amberlyst-15⁶³ in 300 ml of toluene heated at reflux temperature for 1 hr. Two ml of water were collected. The filtered and concentrated product was dissolved in 200 ml of toluene:petroleum ether (1:1) and the mixture was passed through a 1.5 x 3 in. column of Merck basic alumina. Removal of the solvent and crystallization from 75 ml of toluene gave 18 g (55%) of colorless 65: mp 188-190°. This sample was found to be identical with other samples of 65.

Pd/C Catalyzed Dehydrogenation of 65 to Spiro[7H-benzo[c]fluorene-7,1'-(1',2',3',4'-tetrahydronaphthalene)] (66).— A 18.3-g sample of 65 and 3 g of 10% Pd/C were heated together at 310° (bath temperature) for 20 min under a blanket of N₂. The cooled product mixture was dissolved in chloroform and filtered through Dicalite, the chloroform removed by rotary evaporation, and 50 ml of petroleum ether were added to the oil. Refrigeration and filtration gave 16.9 g (92%) of 66 as white plates: mp 157–159°; mass spectrum (70 eV) m/e (rel intensity) 332 (100), 304 (17), 303 (52), 302 (6), 300 (8), 151 (13); pmr (CDCl₃) δ 8.79 (d, 1, isolated ArH at C-1), 8.37 (d, 1, isolated ArH at C-11), 7.98–6.95 (m, 10, ArH), 6.76 (t, 1, isolated ArH at C-7'), 6.25 (d, 1, isolated ArH at C-8'), 3.24–3.01 (m, 2, ArCH₂), 2.41–1.95 (m, 4, ArCH₂CH₂CH₂); uv max (95% ethanol) 204 nm (log ε 4.70), 237 (4.69), 252 (4.49 sh), 306 (3.97 sh), 317 (4.10), 326 (4.05), 342 (4.16).

Anal. Calcd for C₂₆H₂₀: C, 93.94; H, 6.06. Found: C, 93.79; H, 6.14.

The Pd/C and Sulfur Dehydrogenation of 66 to Dibenzo[c,p]chrysene (67).— A 2-g sample of 66 was heated under nitrogen at 325° in the presence of 0.75 g of 10% Pd/C and 0.75 g sulfur for 10 min. The mixture was cooled, dissolved in benzene and filtered through Dicalite to give a green solution. This solution was diluted with an equal volume of petroleum ether^{12d} and passed through a 1.5 x 2.5 in. column of Merck acidic alumina. Concentration and trituration with petroleum ether^{12d} gave 1.2 g of yellow 67: mp 200–202° (dec); mass spectrum (70 eV) m/e (rel intensity) 328 (100), 327 (33), 326 (40), 324 (15). Accurate mass values (±0.003 theoretical) were obtained for the doubly charged ions 164 (7), 163 (14), and 162 (15); pmr (CDCl₃) δ 9.56–8.19 (m, 6, ArH),

8.19-7.66 (m, 10, ArH); uv max (95% ethanol) 213 nm (log ϵ 4.64), 276 (4.84), 295 (4.71), 305 (4.79), 334 (4.09), 350 (3.87).

Anal. Calcd for $C_{26}H_{16}$: C, 95.09; H, 4.91. Found: C, 95.03; H, 4.91.

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12. (a) 10-ft x 0.25-in. column of 25% Carbowax 20M on acid-washed Chromosorb W; (b) Preparative separations were made on a Carbowax 20M column, 10-ft. x 0.375-in.; (c) 11-ft. x 0.25-in. 5% Silicone rubber UC W-98 on acid-washed, DMCS-treated Chromosorb W; (d) Petroleum ether, bp 60-68°; (e) Pmr spectra were determined on Varian XL-100 and A-60 spectrometers; mass spectra were obtained with a Consolidated Electro-dynamics Corp. Model 21-103C mass spectrometer; (f) Ir spectra were obtained with a Beckman IR5A spectrometer. (g)

Elemental analyses were determined by Galbraith Laboratories, Knoxville, Tennessee.

13. (a) Correspondence regarding samples of 12a, 13a, 14a, 15a, 16a, 17a, 18a, 19a, 20a, 21a, and 22a should be directed to A. J. Streiff, American Petroleum Institute, Carnegie-Mellon University, Pittsburgh, Pa. 15213; (b) We thank Ashland Oil and Chemical Company for a hydrocarbon sample from which 12a was obtained by preparative glc.^{12b}
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0.25-in. x 10-ft. column of 80-100 mesh Chromosorb G (acid-washed and DMCS-treated) coated with a mixture of 15% Bentone-34 and 5% SE-52 was used for the glc analyses; (b) The 2,6-dimethylnaphthalene used for glc comparison with pure and impure 2,7-dimethylnaphthalene studies showed a purity in excess of 99.9% by calorimetric mp. determination. We thank D. R. Douslin, H. Finke, and J. Messerly, API Research Project 62, Bureau of Mines, Bartlesville, Okla., for this information; (c) The Picric acid was previously covered with anhydrous ethanol and isolated by filtration to remove the water (15%) present in commercial material; (d) Usually 4-5 recrystallizations afforded the pure picrate as determined by glc^{60a} of regenerated hydrocarbon; (e) The dried wt. was obtained by drying a portion of free flowing crystals at 1 mm. at room temperature.

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