*trans* isomer are 43 and 64% changed at 10°, 40 and 70% at 20°, and 48 and 69% at 30°. The number of points used to characterize the straight lines was between six and nine.

The following molar concentrations ($a$ = KI, $b$ = chloride) were used. Allyl chloride: $a$ = 0.2871 (20°), 0.1968 (30°), 0.09543 (40°); $b$ = 0.03904 (20°), 0.03933 (30°), 0.01999 (40°). *cis*-Crotyl chloride: $a$ = 0.1962 (10°, 20°), 0.07730 (30°); $b$ = 0.03923 (10°, 20°), 0.02000 (30°). *trans*-Crotyl chloride: $a$ = 0.3849 (10°), 0.1962 (20°), 0.1496 (30°); $b$ = 0.03849 (10°), 0.03923 (20°), 0.02000 (30°). *cis*-1-Chloro-2-pentene: $a$ = 0.1961 (10°), 0.1955 (20°), 0.1010 (30°); $b$ = 0.04000 (10°), 0.03989 (20°), 0.02040 (30°). *trans*-1-Chloro-2-pentene: $a$ = 0.3824 (10°), 0.1961 (20°), 0.1996 (30°); $b$ = 0.03900 (10°), 0.04000 (20°), 0.02040 (30°). *cis*-1-Chloro-4-methyl-2-pentene: $a$ = 0.2000 (10°, 20°), 0.1020 (30°); $b$ = 0.04000 (10°, 20°), 0.02000 (30°). *trans*-1-Chloro-4-methyl 2-pentene: $a$ = 0.4000 (10°), 0.2000 (20°), 0.2120 (30°); $b$ = 0.04000 (10°, 20°), 0.02000 (30°).

**Reaction with Sodium Ethoxide in Ethanol.**—A plot of log $b(a - x)/a(b - x)$ *vs.* time for allyl chloride gave a straight line between 19 and 57% changed at 30°, 28 and 56% at 35° and 13 and 52% at 40°. *cis*-Crotyl chloride gave a straight line between 42 and 68% changed at 40°, 31 and 61% at 50°, and 37 and 68% at 60°. Similar data for the *trans* isomer are 47 and 66% changed at 40°, 36 and 60% at 50°, and 37 and 58% at 60°. *cis*-1-Chloro-2-pentene gave a straight line between 48 and 66% changed at 40°, 38 and 56% at 50°, and 44 and 59% at 60°. Similar data for the *trans* isomer are 41 and 58% changed at 40°, 37 and 49% at 50°, and 35 and 55% at 60°. *cis*-1-Chloro-4-methyl-2-pentene gave a straight line between 45 and 68% changed at 40°, 25 and 60% at 50°, and 40 and 64% at 60°. Similar data for the *trans* isomer are 45 and 68% changed at 40°, 42 and 62% at 50°, and 50 and 64% at 60°. The number of points used to characterize the straight lines was between six and nine.

The following molar concentrations ($a$ = chloride, $b$ = $CH_3CH_2ONa$) were used. *cis*-Crotyl chloride: $a$ = 0.1020 (40°), 0.05183 (50°), 0.05174 (60°); $b$ = 0.04833 (40°, 50°, 60°). *trans*-Crotyl chloride: $a$ = 0.1016 (40°), 0.05147 (50°), 0.05180 (60°); $b$ = 0.04833 (40°, 50°, 60°). *cis*-1-Chloro-2-pentene: $a$ = 0.1032 (40°), 0.05182 (50°), 0.05281 (60°); $b$ = 0.04926 (40°, 50°, 60°). *trans*-1-Chloro-2-pentene: $a$ = 0.1042 (40°), 0.05009 (50°), 0.05283 (60°); $b$ = 0.04926 (40°, 50°, 60°). *cis*-1-Chloro-4-methyl-2-pentene: $a$ = 0.1063 (40°), 0.05279 (50°), 0.05335 (60°); $b$ = 0.05076 (40°, 50°, 60°). *trans*-1-Chloro-4-methyl-2-pentene: $a$ = 0.1103 (40°), 0.05480 (50°), 0.05278 (60°); $b$ = 0.05076 (40°, 50°, 60°).

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# The Synthesis of 1,8-Diphenylnaphthalene

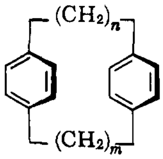
HERBERT O. HOUSE, RALPH W. MAGIN,[1a] AND HUGH W. THOMPSON[1b]

*Department of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Massachusetts*

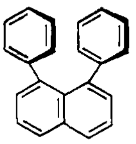
*Received April 8, 1963*

1,8-Diphenylnaphthalene (**2**) has been prepared by reaction of 8-phenyl-$\Delta^{9,10}$-octal-1-one (**5**) with phenylmagnesium bromide followed by dehydration and dehydrogenation. 1,7-Diphenylnaphthalene (**8**) has been similarly obtained by reaction of 7-phenyl-1-tetralone (**9**) with phenylmagnesium bromide followed by dehydration and dehydrogenation. The physical properties of 1,8-diphenylnapthalene (**2**) are consistent with the hypothesis that this molecule exists in a ground state conformation in which the two benzene rings are parallel to one another and perpendicular to the plane of the naphthalene ring.

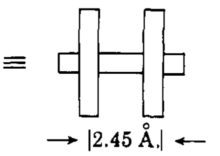
A number of interesting properties of the paracyclophanes **1**[2] have been ascribed to existence of these molecules in conformations in which the two benzene rings lie parallel to one another. The possibility of a transannular electron delocalization (or at least a polarization) between the two benzene rings has been suggested[2] to explain the ability of substituents in one ring of these materials to influence the reactivity of the second benzene ring. From a consideration of the geometry of naphthalene (C-1 and C-8 bonds parallel and separated by 2.45 Å.),[3] it appeared probable that the same face-to-face arrangement of two benzene rings could be achieved in 1,8-diphenylnaphthalene (**2**) as illustrated in the top view **2b**. Presumably the phenyl rings in this molecule **2** would be incapable of free rotation[4] and would be constrained to conformations in which both benzene rings are perpendicular to the plane of the naphthalene ring with the consequence that conventional π-orbital overlap (*i.e.*, resonance interaction) between each benzene ring and the naphthalene system would be prevented. Since it appeared that the preparation of 1,8-diphenylnaphthalenes with a variety of substituents on the phenyl rings might offer synthetic advantages over the preparation of the corresponding paracyclophanes and since it was clear from the preparation of compounds such as **3**,[5] **4**,[6] and **5**[7] that 1,8-diphenylnaphthalene (**2**) was capable of existence, we have explored possible synthetic paths to this hydrocarbon and report here its synthesis.



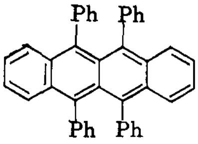
**1**



**2a**



**2b**



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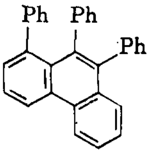
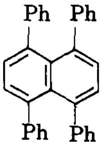


**4**



**5**

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[1] (a) Union Carbide Corporation Predoctoral Fellow in Chemistry, 1962–1963; (b) Allied Chemical Corporation Fellow, 1960–1962.

[2] (a) For a review of earlier work see D. J. Cram, *Rec. Chem. Progr.*, **20**, 71 (1959); (b) for more recent studies see D. J. Cram and D. I. Wilkinson, *J. Am. Chem. Soc.*, **82**, 5721 (1960).

[3] "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc.* (London), *Spec. Publ.*, No. **11**, (1958).

[4] For example, an optically active form of the much less hindered 1-(2-carboxyphenyl)naphthalene has been obtained by D. M. Hall, S. Ridgwell, and E. E. Turner, *J. Chem. Soc.*, 2498 (1954).

[5] (a) C. Moureu, C. Dufraisse, and P. M. Dean, *Compt. rend.*, **182**, 1440 (1926); (b) C. F. H. Allen and L. Gilman, *J. Am. Chem. Soc.*, **58**, 937 (1936); (c) I. Gillet, *Bull. soc. chim. France*, 1135, 1141 (1950).

[6] R. C. Fuson and P. Tomboulian, *J. Am. Chem. Soc.*, **79**, 956 (1957).

[7] E. Harnick, F. H. Herbstein, G. M. J. Schmidt, and F. L. Hirshfeld, *J. Chem. Soc.*, 3288 (1954). The description of the synthesis of this material has apparently not been published.

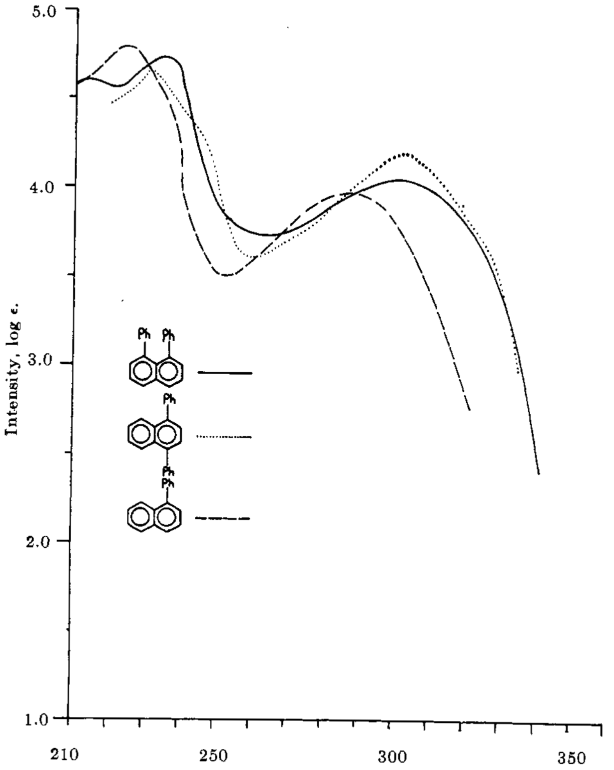


Fig. 1.—Ultraviolet spectra in 95% ethanol.

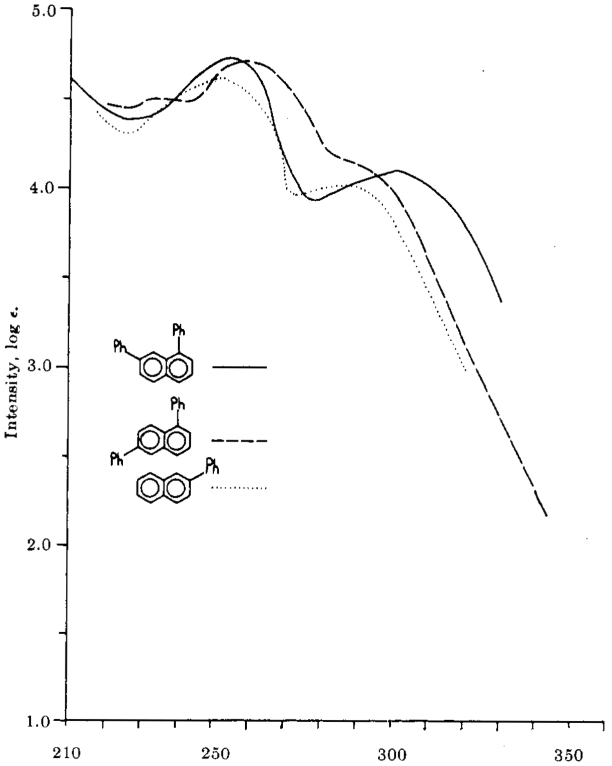
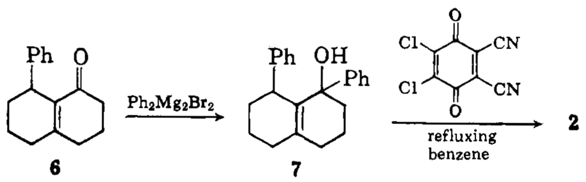


Fig. 2.—Ultraviolet spectra in 95% ethanol.



The starting material for this synthesis, 8-phenyl-$\Delta^{9,10}$-octal-1-one (6),[8] was converted to the crude alcohol 7 which was dehydrated and dehydrogenated with 2,3-dichloro-5,6-dicyanobenzoquinone[9] in boiling benzene to produce 1,8-diphenylnaphthalene (2). Although the mild conditions employed in the synthesis of this hydrocarbon 2 led us to expect that no isomerization had occurred during its synthesis, the existence of precedents for rearrangement in quinone dehydrogenations[9] and the reported conversion of 1-phenylnaphthalene to 2-phenylnaphthalene at high temperatures[10] prompted us to consider other possible structures for our hydrocarbon product. The reported properties for the possible diphenylnaphthalenes are summarized in Table I.[12–30] All of these materials had been described previously except for the 1,8-isomer 2 and the 1,7-isomer 8 which we synthesized from the known 7-phenyl-1-tetralone (9)[11] by the procedure indicated in the accompanying equations.

TABLE I

PROPERTIES OF THE DIPHENYLNAPHTHALENES

| Diphenyl-naphthalene | M.p., °C. | $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (log ε) | Ref. |
|---|---|---|---|
| 1,2 | 109.5–110, 114 | ... | 12, 13 |
| 1,3 | 70–71, 77–78 | ... | 12, 14 |
| 1,4 | Within the range 134–137° | 231 (4.66), 300 (4.20) [minimum at 257 (3.61)] | 5b, 5c<br>15, 16<br>18–20 |
| 1,5 | 220–222, 223–224 | 228 (4.68), 297 (4.15) | 21, 22 |
| 1,6 | 86–87 | 235 (4.50), 258 (4.73), 300 (4.00) | 17, 23, 24 |
| 1,7 (8) | 93–94 | 254 (4.74), 300 (4.11) | This study |
| 1,8 (2) | 149.5–150.5 | 235.5 (4.73), 300 (4.06) | This study |
| 2,3 | 86–87, 92–93 | ... | 12, 25 |
| 2,6 | 230, 233–234 | ... | 26–28 |
| 2,7 | 142–143 | ... | 29, 30 |

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(8) H. O. House and H. W. Thompson, *J. Org. Chem.*, **28**, 360 (1963).

(9) For a review of dehydrogenations using this reagent see L. M. Jackman in R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., "Advances in Organic Chemistry, Methods, and Results," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1960, p. 329.

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(25) H. M. Crawford and H. B. Nelson, *J. Am. Chem. Soc.*, **68**, 134 (1946).

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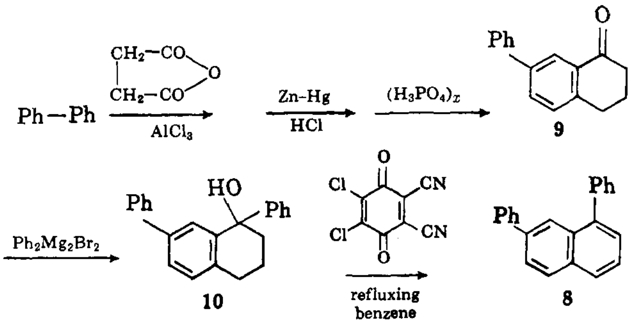
(27) C. C. Price and A. J. Tomisek, *J. Am. Chem. Soc.*, **65**, 439 (1943).

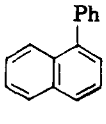
(28) N. P. Buu-Hoï and P. Cagniant, *Compt. rend.*, **220**, 326 (1945).

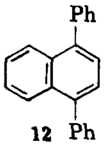
(29) D. H. Hey and S. E. Lawton, *J. Chem. Soc.*, 374 (1940).

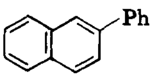
(30) N. P. Buu-Hoï, P. Cagniant, and C. Mentzer, *Bull. soc. chim. France*, **11**, 127 (1944).

The ultraviolet spectra of 1-phenylnaphthalene (**11**), 1,4-diphenylnaphthalene (**12**, data from ref. 20), and 1,8-diphenylnaphthalene (**2**) are reproduced in Fig. 1. The corresponding spectra for 2-phenylnaphthalene (**13**, data from ref. 24), 1,6-diphenylnaphthalene (**14**, data from ref. 17), and 1,7-diphenylnaphthalene (**8**) are reproduced in Fig. 2 and the spectra of naphthalene (data from ref. 17), 1-phenylnaphthalene (**11**), and 7*H*-benz[*de*]anthracene (**15**, data from ref. 17) are compared in Fig. 3. It will be noted that all of the naphthalenes **2**, **11**, and **12**, containing phenyl substituents at only the alpha positions of the naphthalene ring (Fig. 1) have similar ultraviolet spectra which differ from the spectrum of naphthalene and from the spectra of naphthalenes **8**, **13**, and **14** having a $\beta$-phenyl substituent (Fig. 2). The similarity in the ultraviolet spectra of 1,8-diphenylnaphthalene (**2**) and the 1-phenylnaphthalenes **11** and **12** coupled with the fact that all of these systems have more intense absorption at longer wave lengths than naphthalene, indicates that in the electronically excited state the electronic systems in the phenyl rings and the naphthalene ring of 1,8-diphenylnaphthalene (**2**) can interact. That this electronic interaction does not necessarily imply coplanarity of at least one of the phenyl rings and naphthalene rings in **2**, **11**, and **12** may be seen by reference to Fig. 3 which shows the spectra of 1-phenylnaphthalene (**11**) and the necessarily copolanar analog **15** to differ substantially. Similarly, even 2,2-bridged biphenyls which are certainly not coplanar[31] have ultraviolet absorption very different from the ultraviolet absorption of simple benzene derivatives.




**11**


**12**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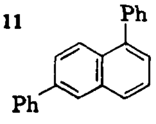
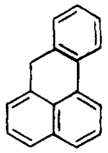

**14**


**15**

Comparison of the n.m.r. spectra of **2**, **8**, and **11** is provided in Fig. 4. Of special interest is the fact that the resonance signal at 3.15 $\tau$ from the 10 protons on the phenyl rings of 1,8-diphenylnaphthalene (**2**) are all essentially equivalent and are shifted upfield from the signal for the phenyl protons of **8** (at 2.51 $\tau$) and **11** (at 2.62 $\tau$) by approximately 0.5 p.p.m. This upfield shift is comparable in magnitude and direction to the

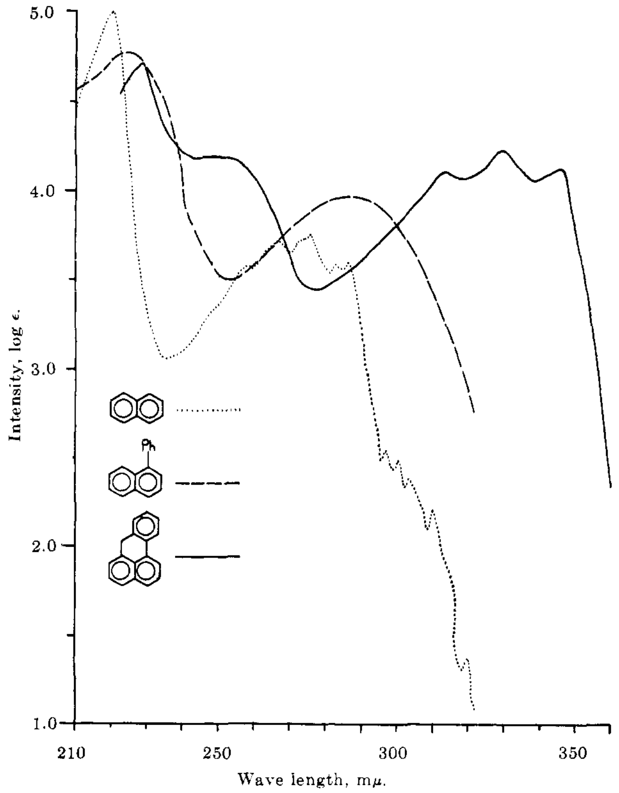


Fig. 3.—Ultraviolet spectra in 95% ethanol.

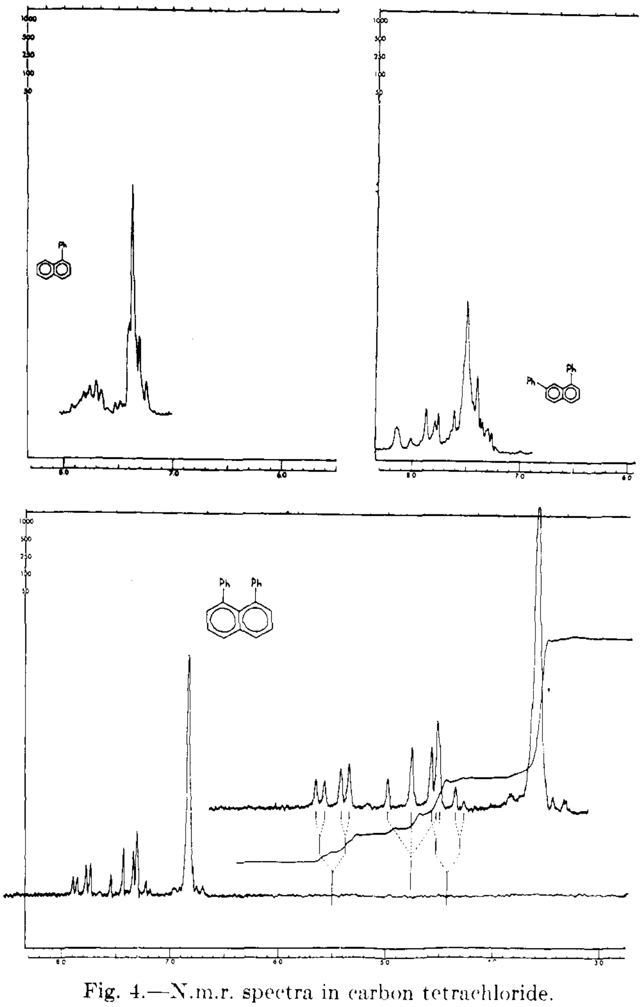


Fig. 4.—N.m.r. spectra in carbon tetrachloride.

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[31] See A. C. Cope and R. D. Smith, *J. Am. Chem. Soc.*, **78**, 1012 (1956), and references therein.

difference between the aryl proton signal in (2,2)-paracyclophane (**1**, m = n = 2, *ca.* 3.63 $\tau$)[32] and *p*-xylene (2.95 $\tau$)[33] and is of the correct order of magnitude to be accounted for by having each set of phenyl protons shielded by an adjacent, parallel benzene ring.[34]

As illustrated in Fig. 4, the splitting pattern observed (with $J$ = 2.5 and 7 c.p.s.) for the naphthalene protons in 1,8-diphenylnaphthalene (**2**) is in accord with the structure assigned to this hydrocarbon. Thus, the n.m.r. data are in agreement with the existence of 1,8-diphenylnaphthalene in a conformation corresponding to **2b**. Experiments designed to learn the energy barrier to rotation of the phenyl rings and to learn the extent of electronic interaction between the phenyl rings of the 1,8-diphenylnaphthalene system are in progress.

## Experimental[35]

**1,8-Diphenylnaphthalene** (**2**).—A solution of 1.017 g. (4.5 mmoles) of the octalone **6**[8] in 7 ml. of ether was treated with 5.0 ml. of an ethereal solution containing 9.0 mmoles of phenylmagnesium bromide. The resulting mixture was stirred for 12 hr. at room temperature and then treated with an aqueous ammonium chloride-ammonium hydroxide solution. After the ether layer had been separated and the inorganic phase had been washed with ether, the combined organic layers were dried and concentrated. Chromatography of the residual brown oil on 80 g. of Woelm, activity no. III, alumina separated biphenyl (eluted with hexane) followed by 870 mg. of the crude alcohol **7** (a pale yellow viscous oil eluted with hexane) and then 365 mg. of the crude starting ketone **6** from which 200.3 mg. (19.7% recovery) of the ketone **6**, m.p. 72–75.5°, was obtained by sublimation. The recovered ketone **6** was identified by a mixture melting point determination and comparison of infrared spectra. The crude alcohol **7** has infrared absorption[36] at 3580 cm.$^{-1}$ (O—H) with no absorption in the 6-$\mu$ region attributable to a carbonyl function and complex n.m.r. absorption in the regions 2.5–3.5 $\tau$ (aryl C—H) and 7.6–9.2 $\tau$ (aliphatic C-H) as well as a broad peak centered at 6.84 $\tau$ (1H, C=C—CH—Ar). A solution of 104 mg. (*ca.* 0.33 mmole) of this crude alcohol **7** and 232 mg. (1.02 mmoles) of 2,3-dichloro-5,6-dicyanobenzoquinone in 16 ml. of benzene was refluxed, under a nitrogen atmosphere, for 3.75 hr. at which time gas chromatographic analysis[37] of the reaction mixture indicated that the bulk of the starting material was gone and one major product was present. After a total reflux period of 11.5 hr., the reaction mixture was cooled, filtered, and concentrated. The residue was extracted with boiling hexane and, after the hexane extract had been filtered through 3 g. of alumina and concentrated, the residual solid (63.5 mg.) was recrystallized from hexane to separate 43.8 mg. of **2** as pale yellow, flat needles, m.p. 149.5–150.5°. The product has ultraviolet maxima[38] at 235.5 m$\mu$ ($\epsilon$ 54,500) and 300 m$\mu$ ($\epsilon$ 11,500). From a second, comparable dehydrogenation employing the remaining 655 mg. of the crude alcohol **7**, 299.6 mg. of the hydrocarbon **2**, m.p. 149–150°, was isolated corresponding to a total yield of 343.4 mg. of **2** or 27% based on the starting octalone **6**.

*Anal.* Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75; mol. wt., 280. Found: C, 94.26; H, 5.78; mol. wt., 280 (mass spectrum).

**1,7-Diphenyl-1-hydroxy-1,2,3,4-tetrahydronaphthalene** (**10**).—Following previously described directions,[11] 3-(4-phenylbenzoyl)-propionic acid, m.p. 184–185° (lit.[11] m.p. 185°), $\bar{\nu}_{max}^{KBr}$ 1709 cm.$^{-1}$ ($CO_2H$) and 1676 cm.$^{-1}$ (conj. C=O), $\lambda_{max}^{EtOH}$ 282 m$\mu$ ($\epsilon$ 23,500), was converted to 4-(*p*-biphenylyl)butyric acid, m.p. 119–121° (lit.[11] m.p. 118–119°), $\bar{\nu}_{max}^{CHCl_3}$ 1708 cm.$^{-1}$ ($CO_2H$), $\lambda_{max}^{EtOH}$ 253 m$\mu$ ($\epsilon$ 20,800), and subsequently to 7-phenyl-1-tetralone (**9**), m.p. 67–68.5° (lit.[11] m.p. 69°), $\bar{\nu}_{max}^{CCl_4}$ 1680 cm.$^{-1}$ (conj. C=O), $\lambda_{max}^{EtOH}$ 245 m$\mu$ ($\epsilon$ 34,300) and 314 m$\mu$ ($\epsilon$ 1640). To a cold (0°) solution of phenylmagnesium bromide, prepared from 9.74 g. (0.062 mole) of bromobenzene, 2.24 g. (0.093 g.-atom) of magnesium and 50 ml. of ether was added, dropwise and with stirring under nitrogen, a solution of 6.85 g. (0.031 mole) of the tetralone **9** in 100 ml. of ether. The resulting mixture was stirred overnight and then treated with an aqueous solution of ammonium chloride and ammonium hydroxide. The ethereal solution was separated, dried, and concentrated to leave 8.61 g. (89%) of the crude tetralol **10**, m.p. 85–90°. A portion of this material was recrystallized from hexane to give the pure tetralol **10** as white needles, m.p. 95.3–96.2°, with infrared absorption[36] at 3620 and 3460 cm.$^{-1}$ (O—H) but no absorption in the 6-$\mu$ region attributable to a carbonyl function. The material has an ultraviolet maximum[38] at 255 m$\mu$ ($\epsilon$ 22,800) with complex n.m.r. absorption[36] in the region 2.4–3.2 $\tau$ (aryl C—H) as well as a triplet ($J$ ~6 c.p.s.) centered at 7.18 $\tau$ (2H, benzylic $CH_2$), a singlet at 7.76 $\tau$ (1H, O—H, position dependent on temperature), and a multiplet in the region 7.8–8.5 $\tau$ (4H, $CH_2$).

*Anal.* Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.94; H, 6.91.

**1,7-Diphenylnaphthalene** (**8**).—A solution containing 5.0 g. (17 mmoles) of the crude tetralol **10** described before and 4.35 g. (19.2 mmoles) of 2,3-dichloro-5,6-dicyanobenzoquinone in 50 ml. of benzene was refluxed, under nitrogen and with stirring, for 12 hr. and then cooled, filtered, and concentrated. After the residue had been extracted with boiling hexane, the resulting hexane solution was chromatographed on 150 g. of Woelm, activity no. III, alumina to separate 4.12 g. (88%) of the crude naphthalene **8**, m.p. 78–83°. Recrystallization from hexane gave 2.49 g. (53%) of the pure hydrocarbon **8** as white needles, m.p. 93–94°, with no infrared absorption[36] in the 3- or 6-$\mu$ region attributable to hydroxyl or carbonyl functions and ultraviolet maxima[38] at 254 m$\mu$ ($\epsilon$ 54,800) and 300 m$\mu$ ($\epsilon$ 12,200).

*Anal.* Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75; mol. wt., 280. Found: C, 94.25; H, 5.74; mol. wt., 280 (mass spectrum).

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[32] (a) J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957); (b) D. J. Cram, C. K. Dalton, and G. R. Knox, *ibid.*, **85**, 1088 (1963).

[33] "Varian N.M.R. Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, no. 203.

[34] C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958). If normal bond angles and distances are assumed for the 1,8-diphenylnaphthalene system in a conformation corresponding to **2b** an up-field shift of *ca.* 0.35 p.p.m. would be predicted from the data of Johnson and Bovey.

[35] All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated magnesium sulfate was employed as a drying agent. The infrared spectra were determined with either a Baird, Model B, or a Perkin-Elmer, Model 21, infrared recording spectrophotometer fitted with a sodium chloride prism. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 14. The n.m.r. spectra were determined at 60 Mc. with a Varian, Model A-60, n.m.r. spectrometer. The mass spectra were obtained with a CEC, Model 21-103, mass spectrometer. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory.

[36] Determined in carbon tetrachloride solution.

[37] A column packed with General Electric silicone gum, SE 30, suspended on ground firebrick was employed.

[38] Determined in 95% ethanol solution.