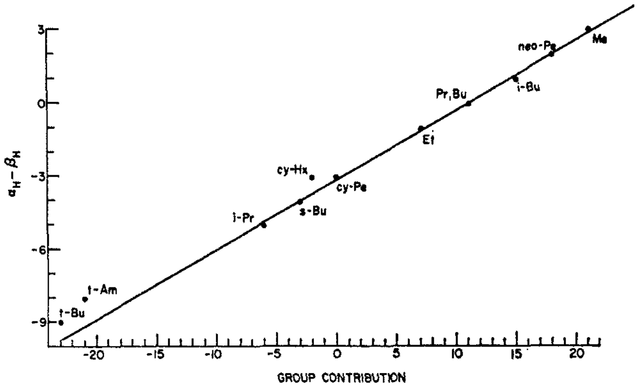


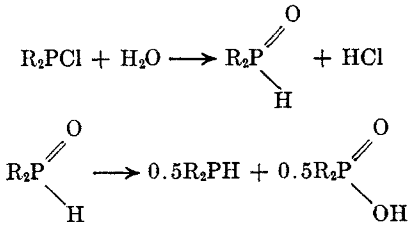
Figure 1.—The number of $\alpha - \beta$ hydrogens of an alkyl group *vs.* the group contribution of the alkyl group to the ^{31}P chemical shift of a tertiary phosphine.

The actual relationship between ($\alpha_H - \beta_H$) and β and γ carbons of an alkyl group is

$$\alpha_H - \beta_H = 3 - 4\beta_C + \gamma_C$$

which agrees substantially with eq 4.

The formation of diphenylphosphine (see the Experimental Section) in the preparation of *t*-butyldiphenylphosphine is also of interest. A similar product was observed in a recent report[23] on the preparation of various *t*-butylphosphines and it was suggested that the secondary phosphine arises by disproportionation of the phosphinous acid formed on hydrolysis of unreacted phosphorus halide, *viz.*



$$R_2PCl + H_2O \longrightarrow R_2P(=O)H + HCl$$

$$R_2P(=O)H \longrightarrow 0.5R_2PH + 0.5R_2P(=O)OH$$

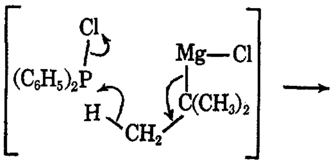
or possibly by hydrolysis of a magnesium phosphide which forms by halogen-metal exchange.

$$R_2PCl + t\text{-BuMgX} \longrightarrow R_2PMgX + t\text{-BuCl}$$

$$R_2PMgX + H_2O \longrightarrow R_2PH + 0.5MgX_2 + 0.5Mg(OH)_2$$

Our results show that isobutylene is given off in the reaction only during the addition of chlorodiphenylphosphine to the *t*-butyl Grignard reagent and not during the preparation of the Grignard reagent nor during the hydrolysis of the reaction mixture. Hence, it is strongly suggested that the secondary phosphine arises by partial reduction of the chlorophosphine with *t*-butyl Grignard reagent.

$$(C_6H_5)_2PCl + (CH_3)_3CMgCl \longrightarrow$$



$$(C_6H_5)_2PH + CH_2{=}C(CH_3)_2 + MgCl_2$$

Registry No.—Neo-PePh$_2$P, 7660-85-7; *i*-BuPh$_2$P, 5952-47-6; *i*-Bu$_2$PhP, 7650-78-4; *sec*-BuPh$_2$P, 7650-79-5; *sec*-Bu$_2$PhP, 7650-80-8; *c*-PePh$_2$P, 7650-81-9; *c*-Pe$_2$PhP, 7650-82-0; *n*-PrPhP, 7650-83-1; *n*-PrPh$_2$P, 7650-84-2; *i*-Bu$_3$P, 4125-25-1; *t*-BuPh$_2$P, 6002-34-2; *t*-AmPh$_2$P, 7650-87-5; *c*-Pe$_3$P, 7650-88-6; Bz$_3$P, 7650-89-7; Bz$_2$PhP, 7650-90-0; BzPh$_2$P, 7650-91-1; vinyl Ph$_2$P, 2155-96-6; allyl Ph$_2$P, 2741-38-0.

Acknowledgments.—We thank the National Science Foundation for support of this work under Grant No. GP4483 and for the purchase of a Varian Associates A-60A nmr spectrometer. We also thank Drs. J. E. Huheey, G. R. Miller, and W. Reeve for helpful criticism of this work.

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[23] H. Hoffmann and P. Schellenbeck, *Chem. Ber.*, **99**, 1134 (1966).

The Synthesis of Substituted 1,8-Diphenylnaphthalenes[1]

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Received August 23, 1966

1-(3-Substituted phenyl)naphthalene **10**–**12** and 1,8-bis(3-substituted phenyl)naphthalene derivatives **5**, **14**, and **15** have been prepared from the appropriate tetralone and octalone precursors. Since only a single stereoisomer of each of the 1,8-diarylnaphthalenes was isolated, no definitive information was obtained concerning the barrier to rotation about the arylnaphthalene bonds. Nitration of either 1-phenylnaphthalene (**20**) or 1,8-diphenylnaphthalene (**6**) yielded the corresponding 4-nitro derivatives (**21** and **22**). Carbonation of the anion radicals derived from these two hydrocarbons (**6** and **20**) yielded the diacids (**25a**, **26a**, and **27a**) accompanied by the starting hydrocarbons (**6** and **20**).

To continue our study of the 1,8-diphenylnaphthalene system,[2,3] we wished to find synthetic routes to derivatives in which the phenyl rings carried substituents. It is our plan to use such derivatives to test the hypotheses[2b] that a substantial energy barrier exists to free rotation of the phenyl rings and that substituents in one phenyl ring may transmit their electronic influence to the second phenyl ring. Since the two

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[1] This work has been supported by research grants from the National Institutes of Health (Grant No. GM-08761) and the National Science Foundation (Grant No. GP-5685).

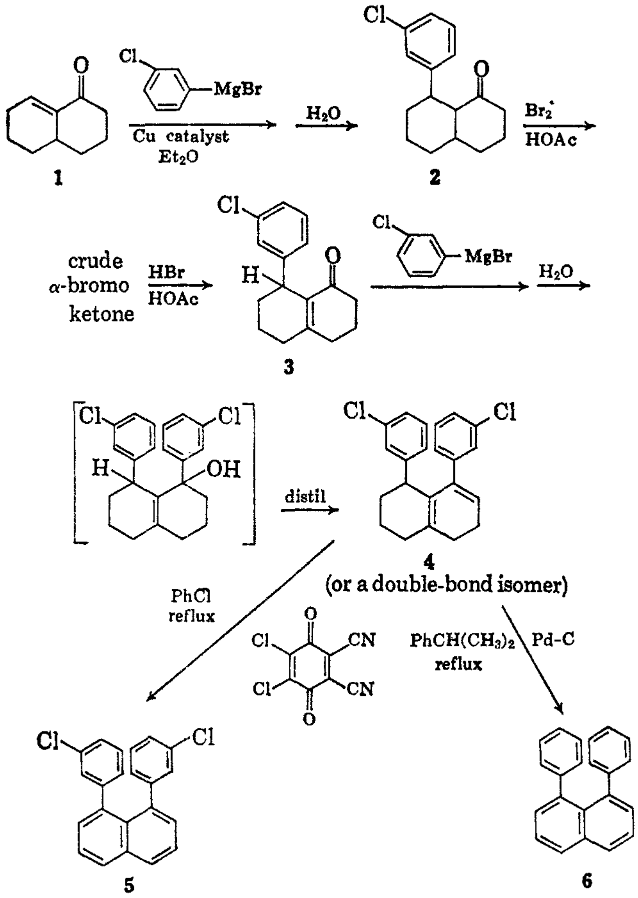
[2] (a) H. O. House and H. W. Thompson, *J. Org. Chem.*, **28**, 360 (1963); (b) H. O. House, R. W. Magin, and H. W. Thompson, *ibid.*, **28**, 2403 (1963); (c) H. O. House and R. W. Bashe, II, *ibid.*, **30**, 2942 (1965).

[3] For other studies and discussion of this system and relatives, see (a) A. S. Bailey, G. A. Dale, A. J. Shuttleworth, and D. P. Weizmann, *J. Chem. Soc.*, 5110 (1964); (b) E. D. Bergmann, S. Blumberg, P. Bracha, and S. Epstein, *Tetrahedron*, **20**, 195 (1964); (c) C. Dufraisse and Y. Lepage, *Compt. Rend.*, **258**, 1507, 5447 (1964); (d) Y. Lepage and O. Pouchot, *Bull. Soc. Chim. France*, 2342 (1965); (e) S. C. Dickerman, D. deSouza, and P. Wolf, *J. Org. Chem.*, **30**, 1981 (1965); (f) H. H. Jaffé and O. Chalvet, *J. Am. Chem. Soc.*, **85**, 1561 (1963); (g) E. Harnik, F. H. Herbstein, G. M. J. Schmidt, and F. L. Hirshfeld, *J. Chem. Soc.*, 3288 (1954); (h) M. Rabinovitz, I. Agranat, and E. D. Bergmann, *Tetrahedron Letters*, 4133 (1965); (i) Z. A. Akopyan, R. L. Aboyan, and Yu. T. Struchkov, *Zh. Struk. Khim.*, **3**, 602 (1962); (j) V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

phenyl rings are believed to lie parallel to one another and perpendicular to the plane of the naphthalene ring, any transmission of electronic effects would presumably be by mechanisms not requiring overlap of the π orbitals of the phenyl rings with the adjacent naphthalene ring π orbital.

The previously described[2] synthetic route was utilized to prepare the bis-3-chlorophenyl derivative (**5**) as illustrated in Scheme I. Although dehydration of the intermediate alcohol and dehydrogenation of the diene (**4**) with 2,3-dichloro-5,6-dicyanobenzoquinone yielded the desired bis-3-chlorophenyl derivative (**5**), an attempt to effect the same change catalytically with palladium on carbon resulted in concommitant hydrogenolysis to form 1,8-diphenylnaphthalene (**6**). This latter change, while not synthetically useful, does establish that the present synthesis is not complicated by unanticipated rearrangements.[4]

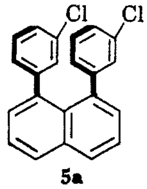
SCHEME I



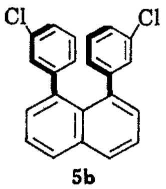
The initial conjugate addition of the organometallic reagent[5] to the octalone (**1**) yielded, after chromatography, a mixture from which two crystalline stereoisomers of ketone **2** were isolated. The major product, stereoisomer **2a**, was not epimerized by treatment with methanolic sodium methoxide and was catalytically hydrogenolyzed to yield the known phenyl ketone (**7**).[2a] Both these observations and analogy with the previously studied phenyl series[2a] indicate that this isomer should be assigned the stereochemistry indicated in structure **2a**. We presume, in consideration of previous work,[2a] that the initial product from the organometallic addition and subsequent hydrolysis was the stereoisomer (**2b**) which was epimerized during the chromatographic separation to the more stable isomer (**2a**). The second, minor, crystalline isomer (**2c**) isolated was epimerized to give mainly a third stereoisomer (**2d**) by a refluxing solution of sodium methoxide in methanol. These two isomers are tentatively assigned the stereochemistry indicated in structures **2c** and **2d**, based on the previous observation that the analogous *trans*-fused 8-phenyl-1-decalone is the more stable epimer.[2a] In further work, only the major stereoisomeric product **2a** was employed (see Scheme II).

As model compounds for comparison of spectra and other physical properties, the monoarylnaphthalene derivatives (**10–13**) were prepared as indicated in Scheme III. A similar reaction sequence (Scheme IV) was utilized to convert the dichloro derivative (**5**) to the dinitrile (**14**) and the diester (**15**). A number of attempts to convert the corresponding dicarboxylic acid (**16**) to the cyclic anhydride (**17**) were unsuccessful. The diacid (**16**) could be heated above its melting point (350°) and then sublimed without evidence of formation of the monomeric anhydride (**17**). Treatment of the diacid (**16**) with acetic anhydride yielded a crude product with spectroscopic properties corresponding to the mixed anhydride (**18**).

In the foregoing synthetic work each of the diarylnaphthalene products (**5**, **14**, and **15**) proved to be a single, crystalline substance contrary to our expectation that the aromatization of diene **4** would yield a mixture of the *cis* **5a** and *trans* **5b** dichloro compounds (**5**).



5a



5b

Comparison of the dipole moment (2.42 D.)[6] for our dichloro derivative **5** with the value (1.70 D.) for monochloro compound **10** does not offer any clear-cut distinc-

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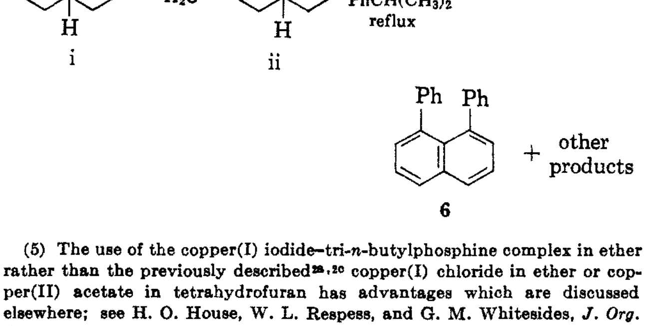
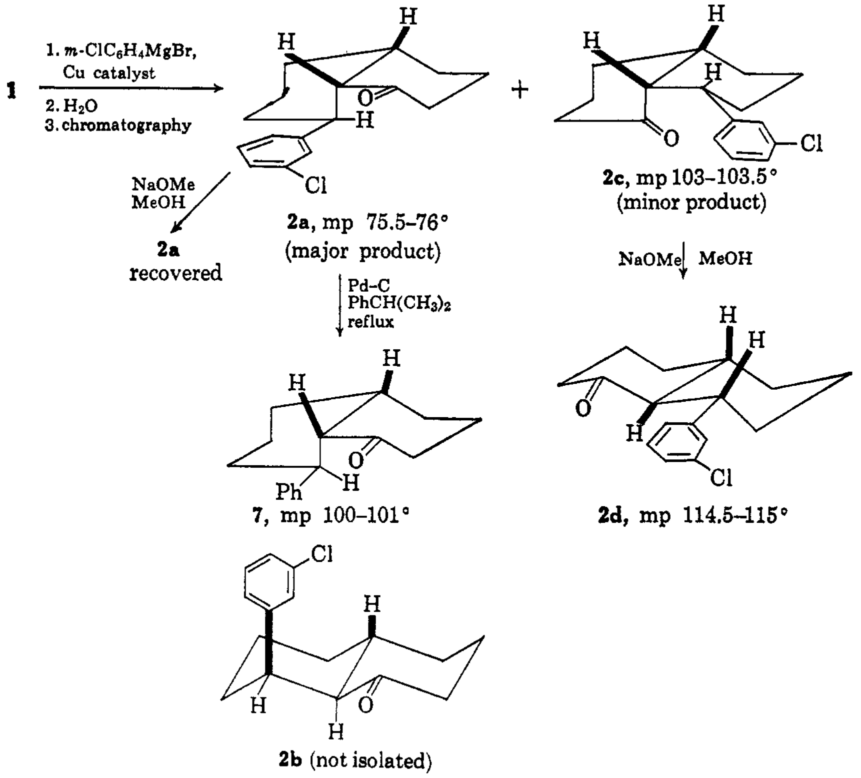
[4] We had found previously[2c] that dehydration and dehydrogenation of the alcohol (i) over palladium on carbon at temperatures in excess of 300° led to substantial amounts of rearranged products as well as the desired 1,8-diphenylnaphthalene (**6**) in poor yield. By use of the milder conditions (palladium on carbon in refluxing cumene) it has been possible to effect the dehydrogenation of the olefin (ii) to 1,8-diphenylnaphthalene (**6**) in 54% yield with less contamination by rearranged products.



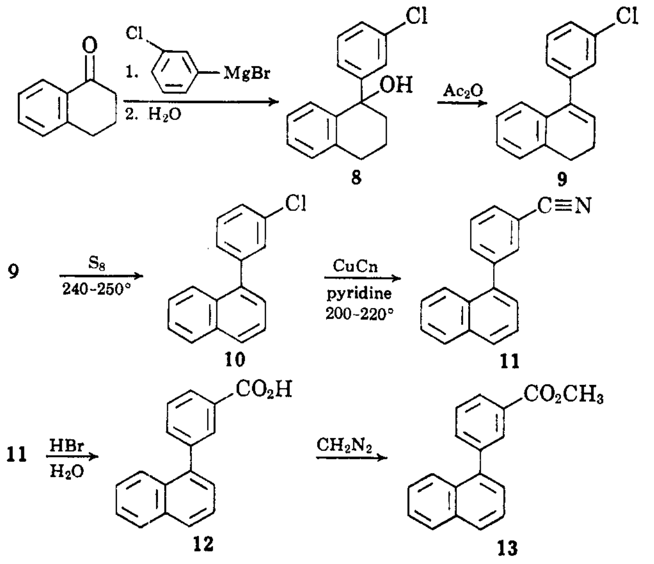
[5] The use of the copper(I) iodide–tri-*n*-butylphosphine complex in ether rather than the previously described[2a,2c] copper(I) chloride in ether or copper(II) acetate in tetrahydrofuran has advantages which are discussed elsewhere; see H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966).

[6] We are indebted to Professor N. L. Allinger for determining these dipole moment values.

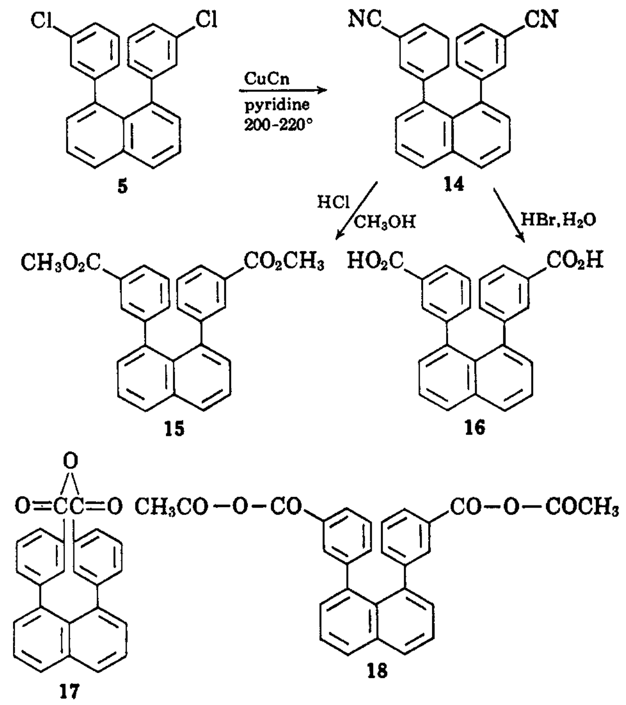
SCHEME II



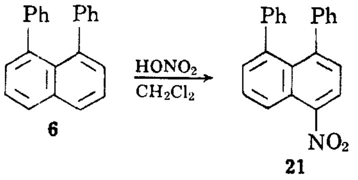
SCHEME III



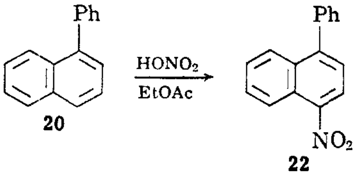
SCHEME IV



tion between stereoisomers **5a** and **5b**. If the diarylnaphthalene system **5** possesses the normal geometry expected of naphthalene, *trans* isomer **5b** would be expected to have a dipole moment comparable in magnitude with monochloro derivative **10** while *cis* isomer **5a** would be expected to have a moment about twice as large. The intermediate value found could either reflect the fact that the diarylnaphthalene system is deformed from the normal naphthalene geometry or indicate that the *cis* and *trans* forms are interconverting in solution at room temperature. In an effort to learn something of the latter possibility, the O-methyl nmr signal of dimethyl ester **15** was examined in the temperature range 5 to 54°. The resulting spectra indicated that an equilibration among at least two different conformations was slowed sufficiently at temperatures below 20° so that two different, closely spaced O-methyl signals were apparent. Unfortunately, this observation is not unambiguous since, even without free rotation about the phenylnaphthalene bonds, several different conformations are possible for either the *cis* or *trans* isomer. Until we have obtained definitive data concerning the ease of rotation about the phenyl naphthalene bonds of the 1,8-diphenylnaphthalene system, we prefer not to draw conclusions from the aforementioned observations.



6 → 21



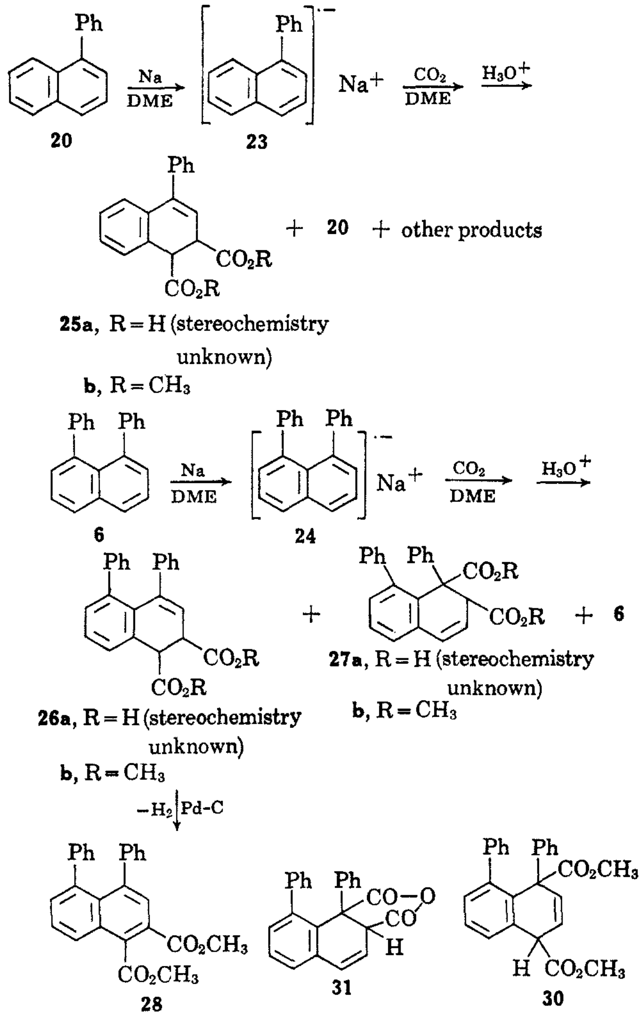
20 → 22

We have also explored direct substitution reactions with 1,8-diphenylnaphthalene (**6**) as well as the model compound 1-phenylnaphthalene (**20**). In each case nitration yielded a single, crystalline mononitro derivative (**21** and **22**) in which the nitro group was located at the 4 position of the naphthalene nucleus. The orientation of the nitro group in these products was readily discernible from examination of their nmr spectra, an observation in agreement with the previous structural assignment for the phenylnaphthalene derivative (**22**).[7]

Each of hydrocarbons **6** and **20** could be converted to the corresponding radical anion (**23** and **24**) by reaction with sodium in 1,2-dimethoxyethane. Carbonation of radical anion **23** produced a mixture of products from which crystalline dihydro diacid **25a** and starting hydrocarbon **20** were isolated.[8] Two dihydro diacid derivatives (**26** and **27**) were isolated along with starting hydrocarbon **6** from the carbonation of radical anion **24** derived from 1,8-diphenylnaphthalene (see Scheme V). Although the structure of diester **26b** was apparent from its nmr spectrum (see the Experimental Section), the spectroscopic data for the second diester did not offer a clear distinction between structures **27b** and **30**. To resolve this question the corresponding diacid **27a** was treated with acetic anhydride. The resulting product had infrared absorption corresponding to the five-membered cyclic anhydride **31**.

We found no products from this carbonation reaction in which substituents had been introduced at the phenyl groups. Thus, it would appear that neither electrophilic substitution reactions nor anion radical reactions offer routes for the introduction of substituents into the phenyl rings of 1,8-diphenylnaphthalene.

Scheme V



25a, R = H (stereochemistry unknown)
b, R = CH_3

26a, R = H (stereochemistry unknown)
b, R = CH_3

27a, R = H (stereochemistry unknown)
b, R = CH_3

Experimental Section[9]

Reaction of $\Delta^{8,9}$-Octal-1-one (1) with *m*-Chlorophenylmagnesium Bromide.—Reaction of 2.692 g (17.8 mmoles) of octalone 1 and 346.6 mg (1.92 mmoles) of anhydrous $Cu(OAc)_2$ in 25 ml of tetrahydrofuran with 25.4 mmoles of *m*-chlorophenylmagnesium bromide[10] in 20 ml of ether for 5 hr at room temperature followed by the usual isolation procedure yielded 5.132 g of a viscous liquid which was chromatographed on Woelm alumina (activity II). The early fractions, eluted with hexane, were recrystallized from hexane to separate 114 mg (2.3%) of chloro ketone **2c** as white prisms, mp 102–103°. Recrystallization raised the melting point to 103–103.5°; infrared[12] 1720 cm^{-1} (C=O); ultraviolet[13] series of maxima in the region 260–280 mμ (ε 237–302); nmr[14] δ 6.9–7.4 (4 H, multiplet, aryl CH), 3.0 (1 H multiplet, benzylic CH), and 1.0–2.8 (14 H multiplet, aliphatic CH).

Anal. Calcd for $C_{16}H_{19}ClO$: C, 73.13; H, 7.29; Cl, 13.49; mol wt, 262. Found: C, 73.02; H, 7.36; Cl, 13.32; mol wt, 262 (mass spectrum for ^{35}Cl isotope).

Later fractions, eluted with hexane, were recrystallized from hexane to separate 1.053 g (22.5%) of ketone **2a** as white plates, mp 73.5–74.5°. An additional recrystallization gave pure ketone **2a**: mp 75.5–76°; infrared[12] 1715 cm^{-1} (C=O); ultraviolet[13] maxima in the region 260–280 mμ (ε 251–316); nmr[14] δ 6.9–7.3 (4 H multiplet, aryl CH), 1.2–2.3 (13 H multiplet, aliphatic CH), 3.06 [1 H, broadened triplet (J = 10 cps) of doublets (J = 4 cps), benzylic CH], and 2.57 [1 H, broadened doublet (J = 10 cps) of doublets (J = 3 cps), C_9H]. This nmr pattern resembles very closely the pattern observed[2a] for phenyl analog **7**.

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[7] R. Weiss and K. Wodich, *Monatsh.*, **46**, 453 (1925).

[8] For comparison, the carbonation of sodium naphthalenide is reported to yield a mixture of 1,4-dicarboxy-1,4-dihydronaphthalene and 1,2-dicarboxy-1,2-dihydronaphthalene as well as one-half of the starting naphthalene; see J. F. Walker and N. D. Scott, *J. Am. Chem. Soc.*, **60**, 951 (1938).

[9] 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 a Perkin-Elmer, Model 237, infrared recording spectrophotometer fitted with a grating. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 14. The nmr spectra were determined at 60 Mc with a Varian, Model A-60, nmr spectrometer. The chemical shift values are expressed either in cycles per second (cps) or as δ values in parts per million (ppm) relative to a tetramethylsilane internal standard. The mass spectra were obtained with a CEC, Model 21-130, a CEC, Model 21-103, or a Perkin-Elmer-Hitachi, Model RMU-6D, mass spectrometer. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory. All reactions involving organometallic reagents were performed under a nitrogen atmosphere.

[10] When an aliquot of this reagent was hydrolyzed, the organic products consisted of ether and chlorobenzene along with a trace of benzene; no bromobenzene was detected.[11]

[11] A gas chromatography column packed with silicone fluid no. SE-30, suspended on Chromosorb P was employed for this analysis.

[12] Determined as a solution in carbon tetrachloride.

[13] Determined as a solution in 95% ethanol.

[14] Determined as a solution in deuteriochloroform.

Anal. Calcd for $C_{16}H_{19}ClO$: C, 73.13; H, 7.29; Cl, 13.49; mol wt, 262. Found: C, 72.88; H, 7.12; Cl, 13.31; mol wt, 262 (mass spectrum for ^{35}Cl isotope).

In a subsequent run 40 mmoles of *m*-chlorophenylmagnesiumbromide in 32 ml of ether was treated with 5.00 g (33.3 mmoles) of octalone **1** and 314 mg (0.8 mmole) of tri-*n*-butylphosphine–copper(I) iodide complex in 20 ml of ether. Ketone **2a** [mp 73–75°, yield 3.544 g (40%)] was isolated by direct crystallization after the crude product had been treated with a refluxing solution of methanolic NaOMe to isomerize any unstable epimers present.

After a solution of 20 mg of ketone **2a** and NaOMe (from 101 mg of sodium) in 3 ml of methanol had been refluxed under a nitrogen atmosphere for 3 hr, the crude ketone (19 mg), recovered in the usual manner, was identified with starting ketone by comparison of infrared spectra and gas chromatographic retention times.[15] (Stereoisomeric ketone **2c** is eluted before ketone **2a** on this gas chromatography column.[15]) Crystallization of this crude material afforded 5 mg of ketone **2a**, mp 71–72°, which was identified by a mixture melting point determination. Similar treatment of 20.7 mg of ketone **2c** with NaOMe (from 137 mg of sodium) in 3 ml of methanol yielded a crude product (23 mg, mp 112–113.5°) which was recrystallized from hexane to separate 16 mg of ketone **2d** as white needles: mp 114.5–115°, infrared[12] 1720 cm^{-1} (C=O), ultraviolet maxima[13] in the region 260–280 mμ (ε 281–353), nmr[12] δ 7.0–7.4 (4 H multiplet, aryl CH) and 1.1–3.0 (15 H multiplet, aliphatic CH).

Anal. Calcd for $C_{16}H_{19}ClO$: C, 73.13; H, 7.29; mol wt, 262. Found: C, 73.17; H, 7.39; mol wt, 262 (mass spectrum for ^{35}Cl isotope).

A mixture of 112.6 mg (0.455 mmole) of chloro ketone **2a**, 120.5 mg of 5% Pd–C catalyst, and 4.0 ml of cumene was heated under reflux with stirring in a nitrogen atmosphere for 19 hr. The crude product crystallized from hexane to separate 41.5 mg of needles (mp 84–88°) which contained[16] 92% of phenyl ketone **7** and 8% of starting chlorophenyl ketone **2a**. Several additional recrystallizations from hexane separated 15 mg of phenyl ketone **7** as white needles (mp 97–98°) which was identified with a previously described sample[2a] by comparison of infrared spectra and by a mixture melting point determination.

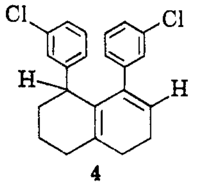
Preparation of Unsaturated Ketone 3.—Reaction of 1.946 g (7.42 mmoles) of ketone **2a** with 0.396 ml (7.42 mmoles) of bromine in 24 ml of acetic acid containing 1% aqueous 48% HBr at room temperature for 1 hr followed by the usual isolation procedure yielded the crude bromo ketone.[17] A solution of this bromo ketone, a yellow oil, in a mixture of 16 ml of acetic acid and 12 ml of aqueous 48% HBr was refluxed under a nitrogen atmosphere for 24 hr and then subjected to the previous isolation procedure.[2c] Chromatography of the residual yellow oil (2.036 g) on 100 g of silicic acid separated several unidentified preliminary fractions followed by crude unsaturated ketone **3** (1.1491 g or 60%), eluted with a benzene (200 volumes)–chloroform (5 volumes)–methanol (2 volumes) mixture. A sample of this ketone (**3**) was further purified by distillation in a short-path still [140–160° (2 mm)]: infrared[19] 1660 (conjugated C=O) and 1630 cm^{-1} (conjugated C=C); ultraviolet maximum[13] at 241 mμ (ε 13,100); nmr[14] δ 6.9–7.3 (4 H multiplet, aryl CH), 3.9–4.2 (1 H multiplet, benzylic CH), and 1.2–2.6 (12 H multiplet, aliphatic CH).

Anal. Calcd for $C_{16}H_{17}ClO$: C, 73.70; H, 6.57; Cl, 13.60; mol wt, 260. Found: C, 73.62; H, 6.43; Cl, 13.67; mol wt, 260 (mass spectrum for ^{35}Cl isotope).

Crude, unsaturated ketone **3** (51 mg) gave 60 mg of the **2,4-dinitrophenylhydrazone of ketone 3** as orange crystals from ethanol, mp 157–158°. Recrystallization raised the melting point to 163.5–164.5°; ultraviolet maxima[13] at 256 mμ (ε 17,600) and 386 mμ (ε 29,500); nmr[14] δ 11.27 (1 H, broad, NH), 9.22 [1 H, doublet (*J* = 2.5 cps), aryl CH], 8.33 [1 H, doublet of doublets (*J* = 10 and 2.5 cps), aryl CH], 4.22 (1 H, broad, benzylic CH), 7.1–7.7 (5 H multiplet, aryl CH), and 1.3–2.9 (12 H multiplet, aliphatic CH).

Anal. Calcd for $C_{22}H_{21}ClN_4O_4$: C, 59.93; H, 4.80; Cl, 8.04; N, 12.71. Found: C, 59.60; H, 4.83; Cl, 8.00; N, 12.80.

Preparation of Diene 4.—Reaction of 1.313 g (4.84 mmoles) of ketone **3** and 9.80 mmoles of *m*-chlorophenylmagnesium bromide in 27 ml of ether followed by the previously described isolation procedure[2c] gave 1.793 g of neutral oil which was chromatographed on silicic acid. The crude liquid alcohol (1.280 g or 71%) was eluted in the early fractions (benzene–chloroform–methanol eluent), infrared[19] 3560 cm^{-1} (OH) with no absorption in the 6-μ region attributable to a C=O function. Later fractions from the chromatography contained starting ketone **3** (389 mg or 29%). A sample of the crude alcohol was distilled in a short-path still [160–200° (2.5 mm)] to separate diene **4** as a viscous, fluorescent liquid which was redistilled [170–180° (0.02 mm)] for characterization: infrared[12] no absorption in the 3- or 6-μ regions attributable to OH or C=O functions; ultraviolet[13] shoulder at 258 mμ (ε 11,100) as well as intense end absorption; nmr[12] δ 6.4–7.5 (8 H multiplet, aryl CH), 1.3–2.8 (10 H multiplet, aliphatic CH), 5.59 (1 H broad singlet, vinyl CH), and 3.52 (1 H, broad singlet, benzylic CH). These nmr data are compatible with the formulation of the diene as either structure **4** or structure **29**. Although the ultraviolet absorption of our product would appear to be inconsistent with its formulation as a 1-aryl-1,3-butadiene derivative such as **29**, there is a very real possibility that the ultraviolet spectrum of structure **29** would be abnormal because of lack of planarity in the chromophore.



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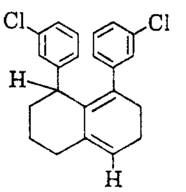

29

Anal. Calcd for $C_{22}H_{20}Cl_2$: C, 74.37; H, 5.67; Cl, 19.96; mol wt, 354. Found: C, 74.18; H, 5.67; Cl, 20.40; mol wt, 354 (mass spectrum for ^{35}Cl isotope).

Preparation of Diarylnaphthalene 5.—A solution of 20.0 g (0.0565 mole) of diene **4** and 39.0 g (0.17 mole) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 900 ml of chlorobenzene was refluxed for 16 hr under a nitrogen atmosphere and then concentrated under reduced pressure. The hexane extract of residual solid was filtered through a column of alumina (activity grade II) and then concentrated to deposit 2.680 g (13.5%) of desired naphthalene derivative **5** as white needles, mp 98–99°. The solid remaining after the hexane extraction was partitioned between methylene chloride and aqueous Na_2CO_3. The crude material obtained from the methylene chloride solution was subjected to a series of chromatographic separations on silicic acid and recrystallizations from hexane to separate an additional fraction of diarylnaphthalene **5**: mp 97–98.5°, total yield 6.288 g (32%). Recrystallization separated pure dichloro compound **5**: mp 98–98.5°, infrared[19] no infrared absorption in the 3- or 6-μ regions attributable to OH or C=O functions, ultraviolet maxima[13] at 234 mμ (ε 58,400) and 300 mμ (ε 21,500),[20] nmr[14] δ

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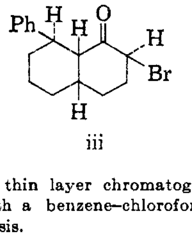
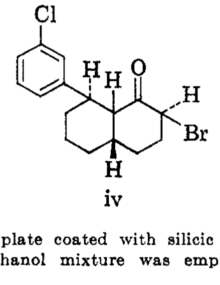
(15) A gas chromatography column packed with Versamid 900 resin suspended on Chromosorb P was employed for this analysis.

(16) A gas chromatography column packed with silicone fluid no. SE52, suspended on Chromosorb P was employed for this analysis.

(17) In another preparation, the crude bromo ketone was chromatographed on silicic acid. The crude, major component[18] was a liquid: infrared[19] 1720 (C=O) with minor peaks at 1780 and 1680 cm^{-1}; nmr[14] δ 6.9–7.3 (4 H multiplet, aryl CH), 2.9–4.9 (3 H multiplet, protons α to phenyl and carbonyl groups), and 1.2–2.9 (11 H multiplet, aliphatic CH). The δ 2.9–4.9 region of this nmr spectrum resembles closely the spectrum of the previously described[2a] bromo ketone (iii) suggesting that the crude bromo ketone should be formulated as iv.



iii



iv

(18) A thin layer chromatographic plate coated with silicic acid and eluted with a benzene–chloroform–methanol mixture was employed for this analysis.

(19) Determined as a solution in chloroform.

(20) The ultraviolet maxima for 1,8-diphenylnaphthalene are at 235.5 mμ (ε 54,500) and 300 mμ (ε 11,500).[2b]

6.8–8.3 multiplet attributable to aryl protons. The lower filed portion (δ 7.3–8.3) of this multiplet, attributable to the six naphthyl protons, resembles closely the corresponding region in the spectrum of 1,8-diphenylnaphthalene (**6**), but the higher portion (δ 6.8–7.3) attributable to the eight *m*-chlorophenyl protons is a broad, partially resolved multiplet. The dipole moment of dichloro compound **5**, determined in benzene solution, is 2.42 ± 0.01 D.[6]

Anal. Calcd for $C_{22}H_{14}Cl_2$: C, 75.66; H, 4.04; Cl, 20.30; mol wt, 348. Found: C, 75.88; H, 4.04; Cl, 20.36; mol wt, 348 (mass spectrum for ^{35}Cl isotope).

A comparable reaction of 1.280 g (3.43 mmoles) of the crude unsaturated alcohol (before distillation with concurrent dehydration to diene **4**) with 2.455 g (10.8 mmoles) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone yielded 408 mg (35%) of dichloro compound **5**, mp 98–98.5°. A mixture of 196.4 mg of diene **4**, 124.1 mg of a 5% Pd–C catalyst, and 5.0 ml of cumene was refluxed under a nitrogen atmosphere for 31 hr and then filtered and concentrated. The crude product (107.6 mg, mp 141–142°) was recrystallized from hexane to separate 70.5 mg (44%) of 1,8-diphenylnaphthalene (**6**, mp 148–149°) identified with previously described[2] samples by a mixture melting point determination and comparison of nmr and infrared spectra. Similarly, a mixture of 77.5 mg (0.27 mmole) of 1,8-diphenyl-$\Delta^{1,2}$-octalin (structure **10** in ref 2c), 52.7 mg of a 5% Pd–C catalyst, and 5.0 ml of cumene was refluxed for 42.5 hr and then subjected to the previously described isolation procedure to yield 40.6 mg (54%) of 1,8-diphenylnaphthalene (**6**), mp 148–149°. A recrystallized sample (mp 150–150.5°) was identified by a mixture melting point determination and comparison of infrared spectra. Although the gas chromatogram[11] of the original, crude product exhibited only one major peak corresponding to 1,8-diphenylnaphthalene (**6**), examination of the mother liquors by gas chromatography[11] revealed the presence of minor amounts of two more rapidly eluted components as well as a peak corresponding in retention time to 1,6-diphenylnaphthalene.[2c]

Preparation of 1-(3-Chlorophenyl)naphthalene (10).—The reaction of 30.0 g (0.205 mole) of α-tetralone with 0.280 mole of *m*-chlorophenylmagnesium bromide in 220 ml of ether yielded a crude liquid (56.315 g) which was steam distilled to remove chlorobenzene and any unchanged tetralone. The remaining crude alcohol (**8**, 46.792 g) was an orange liquid, infrared[12] 3600 and 3450 (broad) cm^{-1} (unassociated and associated OH). A solution of this crude alcohol (**8**) in 20 ml of acetic anhydride was heated on a steam bath for 40 min and then fractionally distilled in a 90-cm spinning-band column. Fractions boiling in the range 125–135° (0.08 mm), which contained[21] **olefin 9**, amounted to 31.171 g (64%): ultraviolet maximum[13] at 257 mμ (ε 7500), shoulder 236 mμ (ε 11,300), and intense end absorption; nmr[12] δ 6.8–7.6 (8 H multiplet, aryl CH), 2.1–3.0 (4 H multiplet, aliphatic CH), and 6.02 [1 H triplet (*J* = 4.5 cps), vinyl CH].

Anal. Calcd for $C_{16}H_{13}Cl$: C, 79.83; H, 5.44; Cl, 14.73; mol wt, 240. Found: C, 79.68; H, 5.46; Cl, 15.01; mol wt, 240 (mass spectrum for ^{35}Cl isotope).

A mixture of 27.943 g (0.116 mole) of olefin **9** and 3.870 g (0.120 mole) of sulfur was heated to 240–250° for 45 min at which time the evolution of H_2S had ceased. The residual orange yellow liquid was fractionally distilled through a 40-cm spinning-band column to separate 18.687 g (68%) of chlorophenylnaphthalene **10**: bp 95–110° (*ca.* 0.01 mm), $n^{25}D$ 1.6628–1.6650, ultraviolet maxima[13] at 220 mμ (ε 61,600) and 286 mμ (ε 9800), nmr multiplet[12] δ 7.1–8.0 (aryl CH). The dipole moment of monochloro compound **10**, determined in benzene solution, is 1.70 ± 0.04 D.[6]

Anal. Calcd for $C_{16}H_{11}Cl$: C, 80.50; H, 4.64; Cl, 14.85; mol wt, 238. Found: C, 80.70; H, 4.65; Cl, 14.95; mol wt, 238 (mass spectrum for ^{35}Cl isotope).

Preparation of Nitrile 11.—A mixture of 515.6 mg (2.15 mmoles) of monochloro compound **10**, 239.2 mg (2.68 mmoles) of CuCN, and 0.23 ml of pyridine was heated to 200–220° in a sealed tube for 4 days. During the reaction period the sealed tube was slowly rotated to ensure mixing of the contents. The resulting mixture was cooled, mixed with an aqueous solution of $FeCl_3$ and HCl, warmed to 60° for 20 min, and then cooled and extracted with methylene chloride. The crude, neutral product (497.6 mg, mp 72–73°) was recrystallized from hexane to separate pure nitrile **11** as white needles: mp 76–77°, yield 342 mg (69%), infrared[19] 2225 cm^{-1} (C≡N), ultraviolet maxima[13] at 222 mμ (ε 90,000) and 286 mμ (ε 9900), nmr multiplet[14] δ 7.2–8.2 (aryl CH).

Anal. Calcd for $C_{17}H_{11}N$: C, 89.05; H, 4.84; N, 6.11; mol wt, 229. Found: C, 88.85; H, 4.97; N, 6.27; mol wt, 229 (mass spectrum).

Preparation of Monoacid 12.—A mixture of 162.7 mg (0.720 mmole) of nitrile **11** and 4.0 ml of aqueous 48% HBr was heated under reflux in a nitrogen atmosphere for 24 hr and then subjected to the usual isolation procedure. The crude acid (154.9 mg, mp 184–186°) was recrystallized from ethyl acetate to separate 119.4 mg (67%) of acid **12** as white needles: mp 187–188°, infrared[14] 1695 cm^{-1} (carboxyl C=O), ultraviolet maxima[13] at 222 mμ (ε 74,500) and 287 mμ (ε 10,100), nmr multiplet[22] δ 7.3–8.3 (aryl CH). The sample has a pK^*_{MCS} value[23] of 6.56.

Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87; mol wt, 248. Found: C, 82.32; H, 4.64; mol wt, 248 (mass spectrum).

An ethereal solution of 124.5 mg of acid **12** was esterified with excess diazomethane. The crude product (130 mg, mp 64–66°) was recrystallized from hexane to separate 55.3 mg (41.6%) of **pure ester 13** as white needles: mp 70–70.5°, infrared[19] 1720 cm^{-1} (conjugated ester C=O), ultraviolet maxima[13] at 222 mμ (ε 79,100) and 288 mμ (ε 10,500), nmr[14] δ 7.1–8.3 (11 H multiplet, aryl CH) and 3.91 (3 H singlet, OCH_3). The O-methyl singlet remained sharp with no evidence of line separation at −47.5°.

Anal. Calcd for $C_{18}H_{14}O_2$: 82.42; H, 5.38; mol wt, 262. Found: C, 82.20; H, 5.45; mol wt, 262 (mass spectrum).

Preparation of Dinitrile 14.—A mixture of 1.605 g (4.57 mmoles) of dichloro compound **5**, 1.728 g (19.1 mmoles) of CuCN, and 2.09 ml of pyridine was divided into portions, each of which was heated to 210–220° in a sealed tube for 7 days following the reaction and isolation procedures described earlier. The crude, solid product (1.450 g) contained[18] primarily dinitrile **14** accompanied by a small amount of the monochloromononitrile. Chromatography on silicic acid separated 172.7 mg of liquid in early fractions which contained[18] mainly the minor reaction product. This product, which crystallized on standing, was recrystallized from ethyl acetate to separate 150 mg (9.6%) of **1-(3-chlorophenyl)-8-(3-cyanophenyl)naphthalene** as white prisms: mp 120–121°, infrared[19] 2230 cm^{-1} (C≡N), ultraviolet maxima[13] at 227 mμ (ε 51,500) and 300 mμ (ε 12,100). The nmr spectrum[14] of the product resembles the spectra of other disubstituted 1,8-diphenylnaphthalenes in having low-field (δ 7.3–8.1) multiplets partially resolved from the multiplet in the region δ 6.6–7.3 attributable to the phenyl protons.

Anal. Calcd for $C_{23}H_{14}ClN$: C, 81.29; H, 4.15; Cl, 10.43; N, 4.12; mol wt, 339. Found: C, 81.55; H, 4.07; Cl, 9.99; N, 4.21; mol wt, 339 (mass spectrum for ^{35}Cl isotope).

The later fractions from the chromatograph contained[18] dinitrile **14** (932.2 mg, 61.5%), mp 188–189°, Recrystallization from an ethyl acetate–hexane mixture afforded dinitrile **14** as white needles: mp 188–189°, infrared[19] 2240 cm^{-1} (C≡N), ultraviolet maximum[13] at 300 mμ (ε 12,100) and shoulder 225 mμ (ε 57,500). The nmr spectrum[14] has a complex multiplet in the region δ 7.0–8.3 (aryl CH). The lower field portion of this nmr spectrum also resembles the spectrum of 1,8-diphenylnaphthalene although the protons of the cyanophenyl rings overlap part of the naphthalene pattern.

Anal. Calcd for $C_{24}H_{14}N_2$: C, 87.25; H, 4.27; N, 8.48; mol wt, 330. Found: C, 87.09; H, 4.28; N, 8.34; mol wt, 330 (mass spectrum).

Preparation of Diester 15.—A suspension of 323.2 mg (0.98 mmole) of dinitrile **14** in 50 ml of methanol was saturated with gaseous HCl and the resulting solution was refluxed for 5.5 hr, allowed to stand for 12 hr, and then concentrated. The residual solid was chromatographed on alumina and the crude diester (190.7 mg, mp 124–131°) was collected in fractions eluted with a benzene (200 volumes)–chloroform (5 volumes)–methanol (2 volumes) mixture. Two recrystallizations from methanol afforded 75 mg (19%) of pure diester **15** as white needles: mp 143–144°, infrared[19] 1720 cm^{-1} (conjugated ester C=O), ultra-

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[21] A thin layer chromatography plate coated with silicic acid and eluted with hexane was employed for this analysis.

[22] Determined as a solution in perdeuteriodimethyl sulfoxide.

[23] The value of pK^*_{MCS}, the apparent pK_a value in a mixture of 80% Methyl Cellosolve and 20% water, were determined by Dr. W. Simon. For discussion and leading references, see W. Simon, *Angew. Chem., Intern. Ed. Engl.*, **3**, 661 (1964).

violet maximum[13] at 300 mμ (ε 13,300) and shoulder 225 mμ (ε 60,700). The nmr spectrum[14] has a complex multiplet in the region δ 6.7–8.1 (14 H, aryl CH) with a singlet at 3.75 (6 H OCH_3). As the solution is cooled, the O-methyl singlet separates into two lines separated by 1.8 cps at temperatures below 4.5°. Following a procedure to be described elsewhere,[24] approximate Arrhenius parameters, $E_a \sim 8$ kcal/mole, $A \sim 10^7$, were calculated for these temperature-dependent spectra.

Anal. Calcd for $C_{26}H_{20}O_4$: C, 78.77; H, 5.09; mol wt, 396. Found: C, 78.56; H, 5.02; mol wt, 396 (mass spectrum).

After a mixture of 56.0 mg (0.169 mmole) of dinitrile **14** and 4.0 ml of aqueous 48% HBr had been refluxed under a nitrogen atmosphere and with stirring for 12 hr, the mixture was cooled, diluted with water, and filtered. The residual solid diacid (**16**, 58 mg or 94% of a gray-white powder) melted without apparent decomposition at 350–353°, was relatively insoluble in all solvents tried, and exhibited broad infrared absorption[25] in the 3-μ region (associated OH) with a peak at 1690 cm^{-1} (carboxyl C=O). A mixture of 6.0 mg of crude diacid **16**, 0.10 ml of Me_2SO_4, 0.15 ml of dicyclohexylethylamine, and 0.25 ml of acetone[26] was heated on a steam bath for 5 min and then diluted with aqueous 2 *M* HCl. Diester **15**, collected as 4.0 mg of white crystals (mp 142.5–143.5°) was identified with the previously described sample by comparison of infrared spectra. A 42.4-mg sample of crude diacid **16** was heated above its melting point (to 345–365°) under a nitrogen atmosphere for 40 min and then the crude melt was sublimed [240–260° (0.1 mm)]. The infrared spectrum of the crude sublimate corresponded to the spectrum of diacid **16** and lacked absorption in the region 1750–1850 cm^{-1} which might be attributable to an anhydride. The crude sublimate was treated with Me_2SO_4, dicyclohexylethylamine, and acetone as previously described to yield, after recrystallization, 10.2 mg of diester **15** (mp 143–144.5°) which was identified with the previous sample by comparison of infrared spectra.

A mixture of 58 mg (0.16 mmole) of diacid **16** and 2.0 ml of acetic anhydride was refluxed with stirring for 1 hr. After the resulting solution had been concentrated under reduced pressure, the residual, oily solid was taken up in a hexane–benzene mixture and allowed to stand. The product separated as a poorly defined, crystalline solid which softened at 119° and melted at 122–123.5. This material appeared to be contaminated with small amounts of a less soluble acid: infrared[19] 1740 and 1820 cm^{-1} (anhydride C=O), nmr (CD_3COCD_3-CCl_4 mixture) δ 6.8–8.2 (14 H multiplet, aryl CH) and 2.32 (6 H singlet, CH_3COO). The composition of this crude product (Found: C, 75.33, 75.69; H, 5.03, 5.09,) corresponded much more closely to the composition of mixed anhydride **18** (Calcd for $C_{28}H_{20}O_6$: C, 74.33; H, 4.46.) than to the composition of the cyclic anhydride **17** (Calcd for $C_{24}H_{14}O_3$: C, 82.27; H, 4.03.). Repeated recrystallization of this crude material from acetic anhydride afforded several milligrams of fine, white crystals (mp 111–112°) with nmr absorption[14] comparable with that described for the crude sample. The mass spectrum of this recrystallized product exhibits a molecular ion peak at *m/e* 452 ($C_{28}H_{20}O_6$) with abundant fragment peaks at *m/e* 410 ($M^+ - CH_2CO$), 368 ($M^+ - 2CH_2CO$), and 43 (CH_3CO^+).

Nitration of 1-Phenylnaphthalene (20) and 1,8-Diphenylnaphthalene (**6**).—1-Phenylnaphthalene was synthesized from α-tetralone *via* the intermediate **1-phenyl-3,4-dihydronaphthalene**: bp 148–153° (1.8 mm) [lit.[27] bp 135–140° (2 mm)]; ultraviolet maximum[13] at 264 mμ (ε 3970) and shoulder 222 mμ (ε 11,600); nmr[12] δ 6.5–7.2 (9 H multiplet, aryl CH), 1.9–2.9 (4 H multiplet, aliphatic CH), 5.72 [1 H triplet (*J* = 4.5 cps), vinyl CH].

A mixture of 357.1 mg (1.78 mmoles) of 1-phenylnaphthalene (**20**), 0.70 ml (1.0 g, 11.1 mmoles) of concentrated HNO_3, and 1.0 ml of ethyl acetate was stirred at room temperature for 1.5 hr and then filtered to separate 329 mg (74%) of 1-phenyl-4-nitronaphthalene, mp 125–127°. Recrystallization from ethyl acetate afforded 307.4 mg (70.5%) of pure nitro derivative **22** as yellow needles: mp 128.5–129° (lit.[7] mp 132°); infrared[19] 1340 and 1515 cm^{-1} (NO_2); ultraviolet maximum[13] at 349 mμ (ε 6600), shoulder 251 mμ (ε 11,500), and intense end absorption. The nmr spectrum[14] of this product **22** differs from the spectrum of 1-phenylnaphthalene[2b] in having a low-field doublet (*J* = 7.5 cps) centered at δ 7.91 (1 H, C_3H) and a low-field doublet (*J* = 8 cps) of partially resolved multiplets centered at 8.30 (1 H, C_5H).

A mixture of 120 mg (0.43 mmole) of 1,8-diphenylnaphthalene, 0.17 ml (0.24 g, 2.7 mmoles) of concentrated HNO_3, and 2.0 ml of methylene chloride was stirred at room temperature for 1.1 hr and then poured into excess aqueous $NaHCO_3$. The crude product (160.1 mg mp 145–147°) was recrystallized from an ethanol–ethyl acetate mixture to separate 122.6 mg (86%) of mononitro compound **21**, mp 146–147°. Recrystallization gave pure mononitro compound **21** as yellow needles: mp 148–149°, infrared[19] 1350 and 1520 cm^{-1} (NO_2), ultraviolet maximum[13] at 237 mμ (ε 44,000) and shoulder 265 mμ (ε 12,900). The nmr spectrum[14] of this product, like 1-phenyl-4-nitronaphthalene (**22**), exhibits a low-field doublet (*J* = 8 cps) centered at δ 8.15 (1 H, C_3H) and a low-field doublet of doublets (*J* = 8 and 2 cps) centered at 8.55 (1 H, C_5H). The spectrum also exhibits a singlet at δ 6.98 (10 H, phenyl CH) and a multiplet in the region 6.9–7.8 (naphthyl CH).

Anal. Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.31; mol wt, 326. Found: C, 81.32; H, 4.65; N, 4.29; mol wt, 326 (mass spectrum).

Carbonation of the Anion Radical Derived from 1-Phenylnaphthalene (**20**).—A mixture of 5.002 g (24.5 mmoles) of 1-phenylnaphthalene, 772 mg (33.5 mg-atoms) of sodium, and 25 ml of 1,2-dimethoxyethane[28] was stirred, at room temperature and under a nitrogen atmosphere, for 1.5 hr. The solution progressively turned a deep green and then dark brown in color and exhibited a complex esr signal[29] (peak width *ca.* 10 gauss) centered at 3406 gauss. The solution was cooled to −70° and CO_2 was passed through the resulting suspension for 1 hr at which time the color in the reaction mixture had been discharged. The resulting slurry was warmed to room temperature, stirred for 1.5 hr under a nitrogen atmosphere, and then filtered. The residual, white solid was partitioned between water and ether and the ether phase was combined with the original 1,2-dimethoxyethane filtrate. The residual oil (3.133 g or 62% recovery) from the organic phase was identified as 1-phenylnaphthalene by its infrared spectrum. The crude acidic product (2.713 g) from the aqueous phase was triturated with an ethyl acetate–hexane mixture. Residual, crude diacid **25a** amounted to 1.955 g (70%, based on the fact that 2 moles of radical anion will yield 1 mole of diacid and 1 mole of starting hydrocarbon): mp 180–186°; infrared[19] 1715 cm^{-1} (carboxyl C=O); nmr[14] δ 6.7–7.2 (multiplet, aryl CH), 5.87 [doublet (*J* = 4.5 cps), vinyl CH], 4.17 [doublet (*J* = 7.5 cps), C_4H], and 3.88 [pair of doublets (*J* = 4.5 and 7.5 cps), C_3H]. This nmr pattern corresponds closely to the pattern seen in the spectrum of subsequently described dimethyl ester **25b**. After 401 mg (1.35 mmoles) of crude acid **25a** had been esterified with excess ethereal diazomethane, the crude neutral product (467.5 mg of an oil) crystallized from an ethyl acetate–hexane mixture to separate 106 mg (24%) of pure dimethyl ester **25b** as white cubes: mp 100–101°; infrared[19] 1735 cm^{-1} (ester C=O); ultraviolet maximum[13] at 268 mμ (ε 7750), and shoulder 225 mμ (ε 21,500); nmr[14] δ 6.9–7.5 (9 H multiplet, aryl CH), 6.05 [1 H doublet (*J* = 4.5 cps), vinyl CH], 4.32 [1 H, doublet (*J* = 8.5 cps), C_4H], 4.03 [1 H, pair of doublets (*J* = 8.5 and 4.5 cps), C_3H], 3.78 (3 H, singlet, OCH_3), and 3.70 (3 H singlet, OCH_3).

Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63; mol wt, 322. Found: C, 74.62; H, 5.70; mol wt, 322 (mass spectrum).

Although our efforts to obtain more crystalline material from the mother liquors of diester **25b** were not successful, the infrared spectrum[19] of the residual oil corresponded very closely to the spectrum of crystalline ester **25b** suggesting that the remaining, noncrystalline material was a mixture of *cis* and *trans* isomers of structure **25b**.

Carbonation of the Anion Radical Derived from 1,8-Diphenylnaphthalene (**6**).—A mixture of 697.1 mg (2.48 mmoles) of naphthalene **6**, 94.7 mg (4.10 mg-atoms) of sodium, and 30 ml of 1,2-dimethoxyethane[28] was stirred at room temperature under a nitrogen atmosphere for 2.75 hr. The resulting solution which

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[24] H. O. House, R. A. Latham, and G. M. Whitesides, *J. Org. Chem.*, in press.

[25] Determined as a suspension in a potassium bromide pellet.

[26] The esterification procedure of F. H. Stodola, *ibid.*, **29**, 2490 (1964).

[27] R. Weiss, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 729.

[28] This solvent was distilled from lithium aluminum hydride immediately before use.

[29] We are indebted to Professor Kerry Bowers for determining this spectrum. The oscillator frequency used was 9.5425 kMc.

was pink at very low concentrations and green-brown to dark brown when more concentrated exhibited a complex esr signal (peak width *ca.* 25 gauss)[29] centered at 3406 gauss. The resulting solution was subjected to the previously described carbonation and isolation procedures. 1,8-Diphenylnaphthalene (**6**, 319.6 mg, 46% recovery, mp 150–150.5°) was recovered from the ether phase. The crude acidic product (523.5 mg) was esterified with excess ethereal diazomethane and the resulting mixture[18] of methyl esters was chromatographed on silicic acid employing a benzene–chloroform–methanol mixture as an eluent. From the early fractions, 128.8 mg of diester **26b** (mp 138–139°) was isolated. Recrystallization from hexane gave pure diester **26b** as white plates: mp 139–140°; infrared[19] 1735 cm^{-1} (ester C=O); ultraviolet maximum[13] at 233 mμ (ε 67,500) and shoulder 260 mμ (ε 13,500); nmr[14] δ 6.8–7.6 (13 H multiplet, aryl CH), 4.0–4.4 (2 H multiplet, C_4H and C_3H), 6.15 [1 H doublet (J = 5 cps), vinyl CH], and 3.72 and 3.77 (two 3 H singlets, OCH_3).

Anal. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57; mol wt, 398. Found: C, 78.13; H, 5.44; mol wt, 398 (mass spectrum).

Later fractions from the chromatograph contained 42.6 mg of a mixture[18] of esters **26b** and **27b** and then 101.8 mg of crude diester **27b**, mp 183–185°. Recrystallization from ethyl acetate afforded diester **27b** as white cubes: mp 186–187°; infrared[19] 1740 cm^{-1} (ester C=O); ultraviolet maximum[13] at 263 mμ (ε 8150), shoulder 229 (24,000), and shoulder 300 (1078); nmr[14] δ 6.7–7.4 (13 H multiplet, aryl CH), 6.53 [1 H, doublet of doublets (J = 3 and 9.5 cps), vinyl CH], 5.90 [1 H, doublet of doublets (J = 3 and 9.5 cps), vinyl CH], 4.46 [1 H triplet (J = 3 cps), C_2H], 3.55 (3 H singlet, OCH_3), and 3.18 (3 H singlet, OCH_3).

Anal. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57; mol wt, 398. Found: C, 78.50; H, 5.51; mol wt, 398 (mass spectrum).

In a subsequent experiment, the anion radical solution derived from 1.501 g (5.37 mmoles) of 1,8-diphenylnaphthalene **6** was carbonated and subjected to the previously described isolation procedure. The crude, acidic product (1.042 g) was chromatographed on 60 g of silicic acid. The early fractions eluted with ether–hexane mixtures contained[30] first crude diacid **27a** (396 mg) and subsequently mixtures (271 mg) of diacids **26a** and **27a**. Portions of these fractions were subjected to fractional recrystallizations from methylene chloride to separate a 98-mg portion of relatively pure diacid **27a** (mp 200–201° dec), which could be esterified with ethereal diazomethane to yield dimethyl ester **27b**, mp 184–185°.

A mixture of 40.2 mg (0.108 mmole) of diacid **27a** and 2.5 ml of acetic anhydride was heated under reflux for 55 min and the resulting solution was concentrated under reduced pressure. A solution of the residue in a benzene–hexane mixture was decolorized with charcoal and cooled to separate 25 mg (62%) of **anhydride 31** as white plates, mp 146–147°. An additional recrystallization raised the melting point to 147–148°; infrared[19] 1785 and 1870 cm^{-1} (C=O of five-membered cyclic anhydride); nmr[14] δ 6.4–7.5 (14 H multiplet, vinyl and aryl CH), 5.84 [1 H, pair of doublets (J = 3.5 and 10 cps), vinyl CH], and 4.06 [1 H, pair of doublets (J = 2.5 and 3.5 cps), allylic CH].

Anal. Calcd for $C_{24}H_{16}O_3$: C, 81.80; H, 4.58; mol wt, 352. Found: C, 81.72; H, 4.61; mol wt, 352 (mass spectrum).

A mixture of the 51.6 mg of diester **26b**, 49 mg of a 5% Pd–C catalyst, and 5.0 ml of cumene was refluxed, under a nitrogen atmosphere and with stirring, for 23 hr and then filtered and concentrated. The residual solid (48.7 mg, mp 136–145°) was recrystallized from an ethyl acetate–hexane mixture to separate 28.8 mg (56%) of **diester 28** as flat, white prisms: mp 158–159°; infrared[19] 1730 cm^{-1} (conjugated ester C=O); ultraviolet maxima[13] at 248 mμ (ε 44,900) and 307 mμ (ε 9160); nmr[14] δ 6.7–8.0 (14 H multiplet, aryl CH), and 4.04 and 3,85 (two 3 H singlets, OCH_3).

Anal. Calcd for $C_{26}H_{20}O_4$: C, 78.77; H, 5.09; mol wt, 396. Found: C, 78.55; H, 5.06; mol wt, 396 (mass spectrum).

Registry No.—**2c**, 7731-41-1; **2a**, 7731-42-2; **7**, 7731-43-3; **2d**, 7775-63-5; iv, 7731-44-4; **4**, 7731-45-5; **29**, 7731-46-6; **5**, 7731-47-7; **10**, 7731-48-8; **11**, 7731-49-9; **12**, 7775-64-6; **13**, 7784-68-1; 1-(3-chlorophenyl)-8-(3-cyanophenyl)naphthalene, 7775-65-7; **14**, 7775-66-8; **15**, 7775-67-9; **16**, 7775-68-0; **18**, 7775-70-4; **21**, 7775-69-1; **25a**, 7775-71-5; **25b**, 7775-72-6; **26b**, 7775-73-7; **27b**, 7775-74-8; **27a**, 7775-75-9; **31**, 7775-76-0; **28**, 7775-77-1; **3**, 7731-39-7; 2,4-dinitrophenylhydrazone of **3**, 7731-40-0; **9**, 4061-25-0.

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[30] A thin layer chromatography plate coated with silicic acid and eluted with a chloroform–formic acid mixture was employed for this analysis.