styrene, isolated as the dibromide, m.p. 70.5–72.5°.[14] Further fractionation yielded 6.14 g. (60%) of recovered *t*-butyl 2-phenylpropanoate, b.p. 75–104° (10 mm.), and 3.78 g. (24%) of ester III (R′ = methyl; R″ = β-phenylethyl) (see Table II).

Treatment of Ethyl Phenylacetate with Excess Butyl Bromide and Sodamide.—To a stirred suspension of 0.225 mole of sodamide in 600 ml. of liquid ammonia was added a solution of 16.4 g. (0.1 mole) of ethyl phenylacetate and 30.8 g. (0.225 mole) of *n*-butyl bromide in 100 ml. of ether. After 4 hr., 12.0 g. (0.225 mole) of solid ammonium chloride was added, and the reaction was worked up as described above to give 10.39 g. (47%) of ethyl 2-phenylhexanoate (type II ester), b.p. 120–123° (4.5 mm.), and 7.13 g. (26%) of 5-carbethoxy-5-phenylnonane (type III ester), b.p. 144–145° (4.5 mm.). Each product showed a single v.p.c. peak (Apiezon L at 200°); their retention times were identical with those of authentic samples.

Alkylations by Means of Sodium Hydride.—To a stirred slurry of sodium hydride reagent[15] in 200 ml. of refluxing monoglyme, under dry nitrogen, was added a solution of the appropriate ester and alkyl halide in 100 ml. of monoglyme over a period of 20 min. Refluxing was continued for 3 hr., and most of the solvent was then removed under reduced pressure. The resulting paste was cooled in an ice bath, and 150 ml. of ether was added. After stirring the mixture, 100 ml. of water was added dropwise. The layers were separated, and the ethereal solution was extracted with two 100-ml. portions of water. The ethereal solution of the product was dried over anhydrous magnesium sulfate, and the solvent was removed. The residue was fractionally distilled *in vacuo* to give the mono- and dialkyl derivative; the pot residue was recrystallized to afford β-keto ester VIII. The mono- and dialkyl derivatives V and VI or VII, respectively, were indicated to be pure by v.p.c.; their retention times were identical with those of authentic samples. β-Keto ester VIII was identified by the mixture melting point method.

Hydrolysis of Alkylation Products II and III.—Esters of types II and III were hydrolyzed by appropriate methods to form carboxylic acids of types IX and X, respectively. The ethyl esters were refluxed for 24 hr. with ethanolic potassium hydroxide, and the *t*-butyl esters were refluxed with *p*-toluenesulfonic acid monohydrate in toluene until isobutylene ceased to be evolved. The resulting mixtures were worked up by common procedures (see ref. 2), and the carboxylic acids were distilled or recrystallized from appropriate solvents. The results are summarized in Tables V and VI.

Alkylations of Ethyl Diphenylacetate. A. With *n*-Butyl Bromide.—To a stirred suspension of 0.05 mole of sodamide in 250 ml. of liquid ammonia was added a solution of 12.02 g. (0.05 mole) of ethyl diphenylacetate[16] in 50 ml. of ether, followed after 15 min. by a solution of 6.85 g. (0.05 mole) of *n*-butyl bromide in 15 ml. of ether. After 2 hr. the reaction mixture was worked up as described above for the phenylacetic esters to give 11.17 g. (75%) of ethyl 2,2-diphenylhexanoate (XIa), b.p. 115–117° (0.1 mm.), which was indicated to be pure by v.p.c. using a 2-ft. silicone gum rubber column. A redistilled sample, b.p. 116–117° (0.07 mm.), was analyzed.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 81.00; H, 7.87.

This reaction was repeated employing a 10-hr. stirring period (Dry Ice condenser) to afford 11.46 g. (77%) of XIa, b.p. 122–125° (0.15 mm.).

A 1.48-g. sample of ester XIa was saponified with ethanolic potassium hydroxide (refluxed 24 hr.) to yield 1.24 g. (93%) of crude 2,2-diphenylhexanoic acid, m.p. 122–130°. Recrystallization from hexane afforded 1.09 g. (81%) of acid, m.p. 130–132°, lit[17] m.p. 130–132°.

B. With Benzyl Chloride.—This alkylation was effected as described above for *n*-butyl bromide to give, after recrystallization from aqueous alcohol, 11.72 g. (71%) of ethyl 2,2,3-triphenylpropanoate (XIb), m.p. 62–63°, lit.[10] b.p. 180–190° (1.1–1.2 mm.).

A 1.51-g. sample of XIb was saponified with ethanolic potassium hydroxide (refluxed 24 hr.) to yield 1.34 g. (97%) of 2,2,3-triphenylpropanoic acid, m.p. and m.m.p. 131.5–133°, lit.[18] m.p. 130–131.5°.

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(15) This reagent, obtained from Metal Hydrides, Inc., as an approximately 55% dispersion of sodium hydride in mineral oil, was used as received.

(16) R. S. Yost and C. R. Hauser, *J. Am. Chem. Soc.*, **69**, 2325 (1947).

(17) A. L. Mndzhoyan, G. T. Tatevosyan, S. G. Agbalyan, and R. Kh. Bostandzhyan, *Dokl. Akad. Nauk Arm. SSR*, **28**, No. 1, 11 (1959); *Chem. Abstr.*, **54**, 1412*e* (1960).

(18) C. R. Hauser and W. J. Chambers, *J. Am. Chem. Soc.*, **78**, 4942 (1956).

An Abnormal Dehydrogenation during the Preparation of 1,8-Diphenylnaphthalene[1]

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Received April 1, 1965

Dehydrogenation of 1,8-diphenyl-1-hydroxydecalin (**9**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone yielded a mixture of 1,8-diphenylnaphthalene (**1**) and 1,6-diphenylnaphthalene (**11**), the latter product arising from rearrangement. Several improvements in the previously reported synthesis of 1,8-diphenylnaphthalene (**1**) and a new synthesis of 1,6-diphenylnaphthalene (**11**) are described.

In continuing our study[2] of 1,8-diphenylnaphthalene (**1**)[3] and its derivatives, we wished to improve our previous synthesis in order to make derivatives with substituents in the phenyl rings more readily accessible. Several modifications (detailed in the Experimental and summarized in Scheme I) in our previous procedures have resulted in an improved yield of the intermediate ketone **3** and the characterization of the intermediate alcohol **7**; the stereochemistry assigned this alcohol **7** is based on the assumption that phenyllithium will attack the ketone **5** from the less hindered side. Difficulty was encountered in repeating the previously described[2b] dehydrohalogenation of the bromo ketone **4** with lithium chloride in dimethylformamide to form the rearranged[4] ketone **5**. In subsequent experiments with lithium chloride in dimethylformamide, mixtures of the rearranged product **5** and the unrearranged ketone **6** were produced. As was to be anticipated from other

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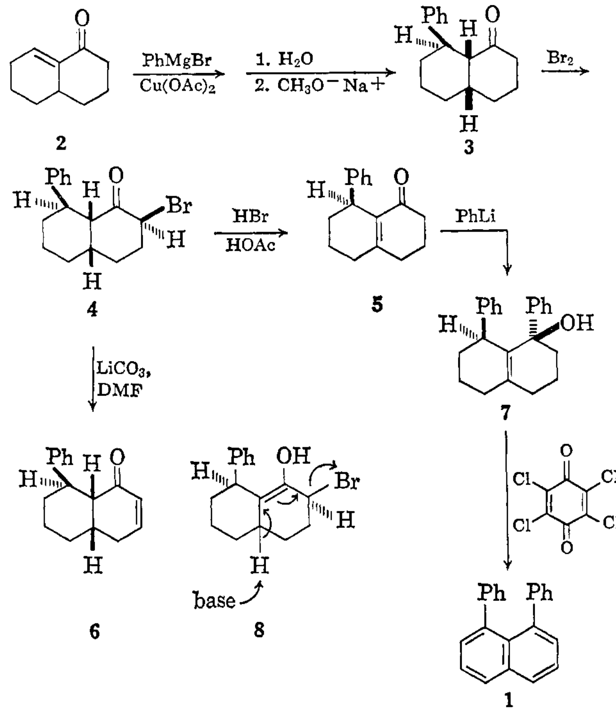
(1) This work has been supported by research grants from the National Science Foundation (Grant No. G-25214) and the National Institutes of Health (Grant No. GM-08761).

(2) (a) H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963); (b) H. O. House and H. W. Thompson, *ibid.*, **28**, 360 (1963); (c) *ibid.*, **26**, 3729 (1961).

(3) For a second synthesis of this hydrocarbon and discussion of its properties, 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).

(4) Analogous rearrangements during dehydrohalogenation of α-halo ketones with lithium chloride in dimethylformamide have been noted previously. For examples, see (a) W. G. Dauben, G. A. Boswell, and W. H. Templeton, *J. Am. Chem. Soc.*, **83**, 5006 (1961); (b) W. F. Johns, *J. Org. Chem.*, **28**, 1616 (1963).

SCHEME I



studies,[5] use of the more basic reagent lithium carbonate in dimethylformamide converted the bromo ketone **4** to the unrearranged product **6**, suggesting that the abnormal dehydrohalogenation **4** → **5** is in some way dependent on the presence of acid in the reaction medium. After considerable experimentation, dehydrohalogenation of the bromo ketone **4** with hydrogen bromide in refluxing acetic acid was selected as the most satisfactory procedure to prepare **5** uncontaminated with **6**. Although the less substituted olefin **6** was isomerized to **5** with hydrogen bromide in acetic acid, this isomerization was relatively slow, supporting the previously suggested[2b] conjugate-elimination (structure **8**) process for the formation of **5** from **4**. The enolization of the bromo ketone **4** to form **8** would, of course, be catalyzed by the presence of acid in the reaction medium.

With the aforementioned modifications the over-all yield of 1,8-diphenylnaphthalene (**1**) from the octalone **2**[2c] was approximately 6%. In this initial synthetic scheme, the second phenyl substituent was added (to form **7**) only after introduction of a carbon–carbon double bond (to form **5**) because of our concern that the final dehydrogenation step might be complicated by rearrangement. With a knowledge of the properties of the desired hydrocarbon **1**, we were encouraged to examine a more direct alternative synthesis in which phenyllithium was added to the saturated ketone **3**. The single alcohol **9** (Scheme II) isolated is assigned the indicated stereochemistry because of our expectation that the phenyllithium will have added from the less hindered side of the carbonyl function. The same alcohol **9** was formed from reaction of the ketone **3** with phenylmagnesium bromide; however, the yield of alcohol was definitely lower and a substantial amount of the starting ketone **3** was recovered, suggesting that enolization (to form **13** or its isomer) was a serious side reaction. Interestingly, the less stable diastereoisomeric ketone **12** reacted with phenylmagnesium bromide primarily by enolization (to form **13** or its isomer) rather than by addition. This observation indicates either that the side reaction leading to the enolate anion **13** is accelerated or that the addition to the carbonyl function is retarded by the nonbonded interactions (especially the axial phenyl group) present in ketone **12**.

Dehydrogenation of either the alcohol **9** or the corresponding olefin **10** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone,[6] under conditions similar to those which produced only 1,8-diphenylnaphthalene (**1**) from **7**, yielded both the desired hydrocarbon **1** and, in comparable amount, an isomeric hydrocarbon subsequently shown to be 1,6-diphenylnaphthalene (**11**). Consequently, our earlier concern about rearrangement had been well founded although the course of the rearrangement was unexpected. A probable path for the abnormal dehydrogenation is indicated in Scheme II, the novel step being the fragmentation (structure **14**) accompanying hydride ion abstraction[6] which produces a monocyclic intermediate such as structure **15**. While the sequence of subsequent steps leading to the 1,6 isomer **11** is obviously open to conjecture, there exists a very satisfying analogy[7] for the ring-closure steps **15** → **16** → **17**. It will also be noted that absence of rearrangement in the dehydration and dehydrogenation of the unsaturated alcohol **7** to **1** is in keeping with the absence of an intermediate in which a favorable fragmentation process (analogous to **14**) is possible.

In a very recent publication[3a] the dehydrogenation of the saturated alcohol **19**, a stereoisomer of our alcohol **9**, to the naphthalene **1** was effected in 26% yield by the use of a palladium-on-carbon catalyst at 240–330°, no mention being made of the nature of the by-products. Application of this same procedure to our alcohol **9** afforded a rather complex mixture of hydrocarbons among which were compounds with gas chromatographic peaks coincident with the peaks of compounds **1** (*ca.* 28% of mixture), **10** (*ca.* 38% of mixture), and **11** (*ca.* 13% of mixture). In spite of the complexity of our mixture, it was possible to isolate 23% of the naphthalene **1** by crystallization, presumably because of its high melting point compared with those of other components of the mixture.

Although a synthesis for 1,6-diphenylnaphthalene (**11**) has been described earlier,[8] we elected to prepare an authentic sample of this hydrocarbon by the alternative route summarized in Scheme III. The ketone **22** was prepared following previous descriptions.[9] Reaction of the ketone **22** with phenyllithium followed by acidic hydrolysis provided both the desired intermediate **23** and the by-product **24**. This olefin **24**, which pre-

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[5] (a) B. Pelc, S. Hermanek, and J. Holubek, *Collection Czech. Chem Commun.*, **26**, 1852 (1961); (b) R. Joly, J. Warnant, G. Nomine, and D Bertin, *Bull. soc. chim. France*, 366 (1958); (c) G. F. H. Green and A. G. Long, *J. Chem. Soc.*, 2532 (1961); (d) C. Djerassi, D. H. Williams, and B. Berkoz, *J. Org. Chem.*, **27**, 2205 (1962); (e) F. J. Schmitz and W. S. Johnson, *Tetrahedron Letters*, **No. 15**, 647 (1962).

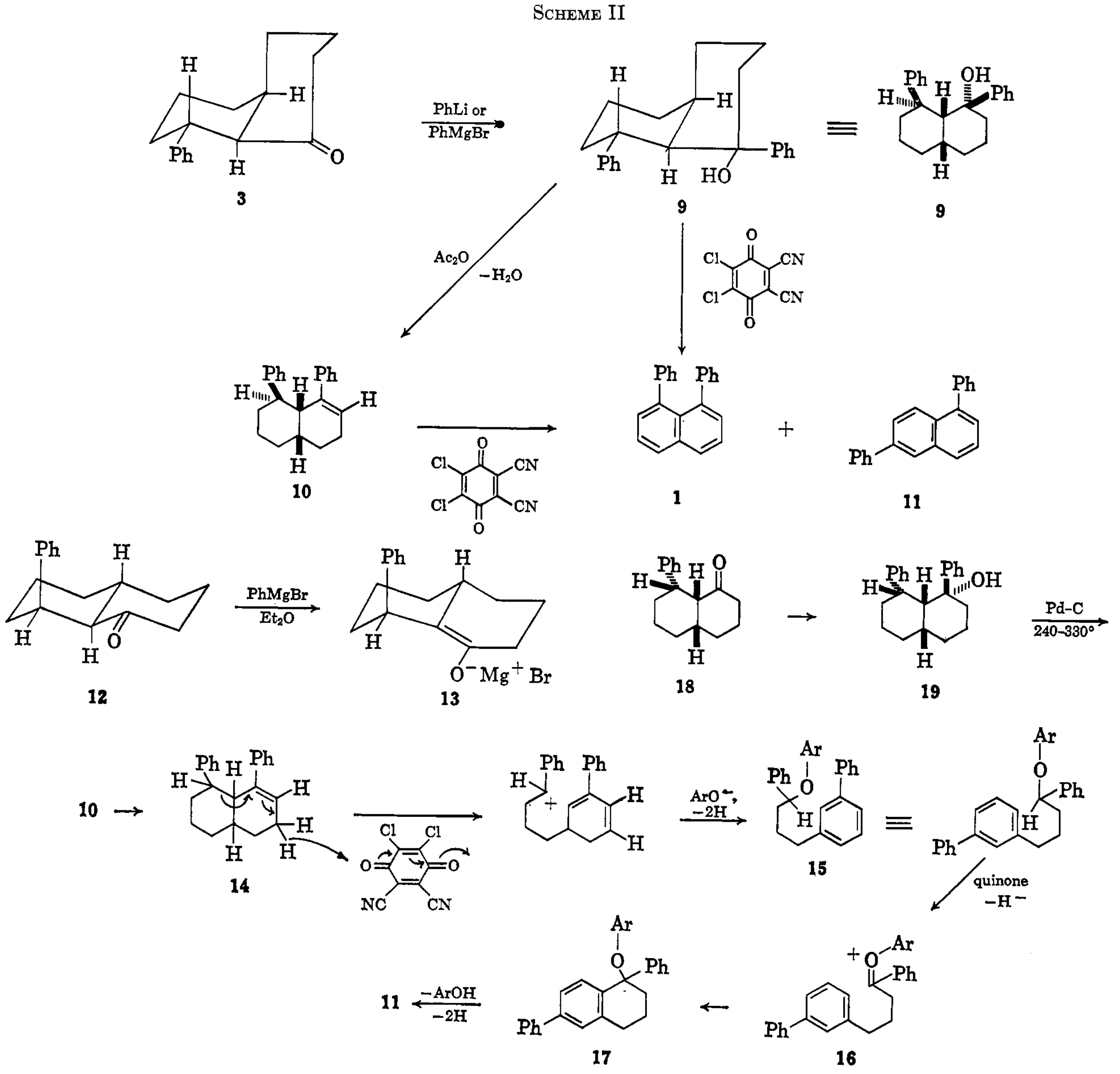
[6] For a review of dehydrogenation with this reagent, see L. M. Jackman, *Advan. Org. Chem.*, **2**, 329 (1960).

[7] A. M. Creighton and L. M. Jackman, *J. Chem. Soc.*, 3138 (1960).

[8] (a) F. Bergmann, J. Szmuszkowicz, and G. Fawaz, *J. Am. Chem. Soc.*, **69**, 1773 (1947). (b) The ultraviolet spectrum of this hydrocarbon is reported by R. Hirshberg and R. N. Jones [*Can. J. Res.*, **27b**, 437 (1949)].

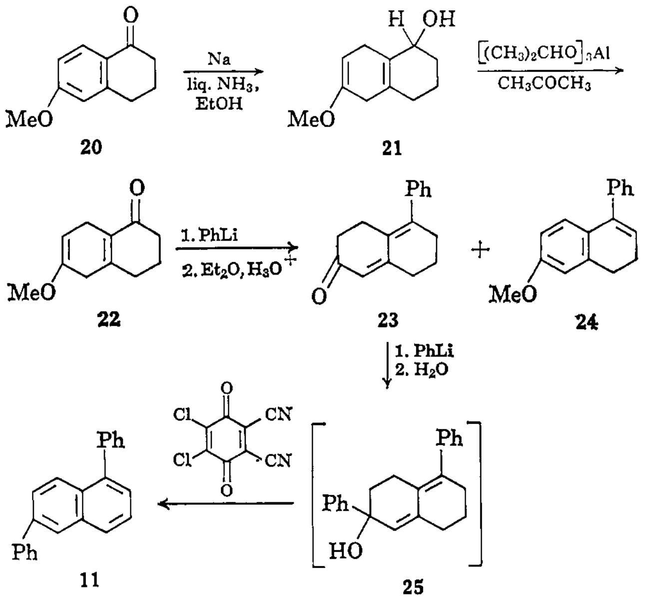
[9] (a) A. J. Birch, *Proc. Roy. Soc. N. S. Wales*, **83**, 245 (1949); (b) A. J. Birch, J. A. K. Quartey, and H. Smith, *J. Chem. Soc.*, 1768 (1952); (c) N. N. Gaidamovich and I. V. Torgov, *Bull., Acad. Sci. USSR, Div. Chem. Sci.*, 1682 (1961).

SCHEME II



sumably arose either from air oxidation or from acid-catalyzed disproportionation of the intermediate dihydro compound, was also prepared by reaction of the tetralone **20** with phenyllithium followed by dehydration.

SCHEME III



Experimental[10]

The 8-Phenyl-1-decalone (3).—A solution of 20.0 g. (132 mmoles) of the octalone **2** and 2.53 g. (14.0 mmoles) of anhydrous cupric acetate in 150 ml. of tetrahydrofuran was added to 100 ml. (169 mmoles) of 1.69 *M* ethereal phenylmagnesium bromide and the resulting mixture was stirred under a nitrogen atmosphere for 19 hr. at room temperature. After hydrolysis of the magnesium salts with an aqueous ammonia–ammonium chloride solution, the organic product was extracted with ether. A

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[10] 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 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 21-130, mass spectrometer. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory.

solution of the crude product from the ether extract in methanolic sodium methoxide (from 11.0 g. of sodium and 130 ml. of methanol) was refluxed for 10 hr. and then diluted with water and extracted with ether. After this ethereal extract had been dried and concentrated, crystallization of the residue from hexane afforded 18.508 g. (61%) of the ketone **3** as white needles, m.p. 98–99° (lit.[2b] m.p. 100–101°). An additional crop (1.2175 g. or 4%) of the ketone **3**, m.p. 95–96°, was obtained from the mother liquors. The remaining material from the mother liquors was chromatographed on 350 g. of Woelm alumina, activity grade II, to separate additional quantities of the crude ketone in fractions eluted with 7% ether in hexane. Recrystallization separated 2.6232 g. of the ketone **3**, m.p. 96–97°; thus the total yield of ketone **3** of sufficient purity for further use was 22.249 g. (73.5%).

A 203-mg. (0.90-mmole) sample of the ketone **3** was treated with 244.8 mg. (1.08 mmoles) of 2,4-dinitrophenylhydrazine in 10 ml. of refluxing ethanol containing several drops of concentrated hydrochloric acid. The **2,4-dinitrophenylhydrazone of ketone 3** separated as 334.7 mg. (93%) of orange needles, m.p. 166–170°. Recrystallization from ethanol afforded 278.7 mg. of the pure derivative, m.p. 167–169°.

Anal. Calcd. for $C_{22}H_{24}N_4O_4$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.45; H, 6.04; N, 13.52.

Reaction of the ketone **3** with bromine in acetic acid containing 1% of 48% aqueous hydrobromic acid as previously described[2b] produced the **bromo ketone 4**, m.p. 153–157° dec. (lit.[2b] m.p. 150–157° dec.). Both ketones **3** and **4** were identified with previously described[2b] samples by comparison of infrared and n.m.r. spectra.

Dehydrobromination of the Ketone 4. A. In Acetic Acid.—A solution of 9.9364 g. (32.5 mmoles) of the bromo ketone **4** and 120 ml. of 48% aqueous hydrobromic acid in 280 ml. of acetic acid was refluxed under a nitrogen atmosphere for 21.5 hr. and then diluted with water, neutralized with sodium carbonate, and extracted with ether. After the ether extract had been dried and concentrated, crystallization of the residue from hexane separated 4.0286 g. (54.9%) of the unsaturated ketone **5**, m.p. 73.5–75°. Sublimation (65–68° at 0.2 mm.) afforded the ketone **5** as white prisms, m.p. 74.5–76° (lit.[2b] m.p. 77–78°), identified with the previously described sample by comparison of infrared and n.m.r. spectra.

B. With Lithium Carbonate in Dimethylformamide.—A solution of 1.753 g. (5.65 mmoles) of the bromo ketone **4** and 4.346 g. (58.8 mmoles) of lithium carbonate in 60 ml. of dimethylformamide was refluxed under a nitrogen atmosphere for 18.5 hr. and then cooled, diluted with water, and extracted with ether. After the ether extract had been dried and concentrated, the residual oil (1.304 g.) was chromatographed on 50 g. of Woelm alumina, activity grade II. The ketone **6**, 604.4 mg. (51%) of liquid eluted with 1% ether in hexane, was distilled in a short-path still (140–150° at 0.2 mm.) to separate 454.8 mg. (38%) of the pure **ketone 6** as a colorless liquid. The material has infrared absorption[11] at 1685 cm.$^{-1}$ (conjugated C═O) with an ultraviolet maximum[12] at 226 mμ (ϵ 9200) and an n.m.r. peak[11] at δ 7.18 (5H, aryl C–H), a pair of triplets (J = 11 and 3 c.p.s.) centered at δ 6.74 (1H, β-vinyl C–H), a doublet (J = 11 c.p.s., further splitting apparent but not resolved) centered at δ 5.78 (1H, α-vinyl C–H), and complex absorption in the region δ 1.2–3.3 (11H, aliphatic C–H).

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02; mol. wt., 226. Found: C, 84.83; H, 8.11; mol. wt., 226 (mass spectrum).

A solution of 160 mg. of the ketone **6** and 4.5 ml. of 48% aqueous hydrobromic acid in 10 ml. of acetic acid was refluxed for 19 hr. and then diluted with water, neutralized with sodium carbonate, and extracted with ether. After the ethereal extract had been dried and concentrated, distillation in a short-path still (140–150° at 0.3 mm.) separated 100 mg. of a mixture of ketones **5** and **6** as a colorless liquid. From the relative areas of the n.m.r.[11] peak at δ 3.92 (the benzylic C–H of ketone **5**)[2b] and the peaks in the region δ 5.7–5.9 (α-vinyl C–H of ketone **6**) the composition of this mixture was estimated to be 40% of **6** and 60% of **5**.

C. With Lithium Chloride in Dimethylformamide.—A solution of 103 mg. (0.34 mmole) of the bromo ketone **4** and 175.4 mg. (4.11 mmoles) of lithium chloride in 5 ml. of dimethylformamide was heated to 128° under a nitrogen atmosphere for 21 hr. After following the isolation procedure described in the above lithium carbonate–dimethylformamide reaction, the crude product was chromatographed on Woelm alumina, activity grade III. From the early fractions, eluted with 1% ether in hexane, the starting bromo ketone **4** was recovered; later chromatographic fractions afforded an oil which could not be induced to crystallize. Although the material showed a single spot on thin layer chromatography[13] and a single peak on gas chromatography,[14,15] its infrared[11] ($\tilde{\nu}_{max}$ 1675 with a shoulder at 1690 cm.$^{-1}$) and n.m.r.[11] absorption (peaks at δ 3.92 and in the region δ 5.7–5.9) indicated the presence of both unsaturated ketones **5** (*ca.* 35%) and **6** (*ca.* 65%).

1-Hydroxy-1,8-diphenyl-$\Delta^{9,10}$-octalin (7).—A solution of 4.613 g. (20.4 mmoles) of the ketone **5** in 50 ml. of ether was added to 60 ml. of an ethereal solution containing 42.1 mmoles of phenyllithium. After the solution had been refluxed under a nitrogen atmosphere for 12 hr., saturated aqueous ammonium chloride containing ammonia (pH ~8) was added and the ethereal solution of the organic products was separated, dried, and concentrated. The residual yellow oil (9.713 g.) was chromatographed on 450 g. of Woelm alumina, activity grade III, to separate 5.174 g. (84%) of the liquid alcohol **7** in fractions eluted with 2% ethe- in hexane. A sample of this alcohol was purified further by distilr lation in a short-path still (150–160° at 0.3 mm.). The sample has infrared absorption[11] at 3580 cm.$^{-1}$ (OH) with no absorption in the 6-μ region attributable to a carbonyl function; the n.m.r. spectrum[11] has complex multiplets in the regions δ 6.8–7.5 (10H, aryl C–H) and 1.2–2.4 (12H, aliphatic C–H) and a broad peak (half-band width 8 c.p.s.) at δ 3.18 (1H, benzylic C–H) as well as a sharp peak at δ 1.22 (1H, shifted by the addition of pyridine, O–H).

Anal. Calcd. for $C_{22}H_{24}O$: C, 86.80; H, 7.95. Found: C, 86.72; H, 7.91.

A solution of 4.442 g. (14.7 mmoles) of the alcohol **7** and 13.313 g. (59 mmoles) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 165 ml. of benzene was refluxed under a nitrogen atmosphere for 19.5 hr. and then subjected to the previously described[2a] isolation procedure. The 1,8-diphenylnaphthalene (**1**) crystallized from hexane as 2.098 g. (51%) of colorless needles, m.p. 150–150.5°, which was identified with the previous sample[2a] by a mixture melting point determination.

1-Hydroxy-1,8-diphenyldecalin (9).—A solution of 15.183 g. (0.067 mole) of the ketone **3** in 60 ml. of ether was added to 150 ml. of an ether solution containing 0.254 mole of phenylmagnesium bromide and the reaction mixture was stirred at room temperature for 21 hr. After the resulting mixture had been poured into cold (0°), 5% aqueous hydrochloric acid, the ether layer was separated, combined with the ether extract of the aqueous phase, washed with aqueous sodium bicarbonate, dried, and concentrated. The residual oil (23.511 g.) was chromatographed on 1175 g. of Alcoa alumina, No. F-20. Fractions eluted with hexane and 1% ether in hexane contained[16] biphenyl or mixtures of biphenyl and the alcohol **9**. The fractions (6.779 g. or 33.5% yield) eluted with 3% ether in hexane contained[16] the alcohol **9** which crystallized on standing, m.p. 65–68°. The fractions (9.506 g.) eluted with 14% ether in hexane contained mixtures of the alcohol **9** and the ketone **3**. Fractional crystallization of these latter fractions from hexane separated 1.4905 g. (9.8%) of the ketone **3**, m.p. 95–99°.

The fractions containing the alcohol **9** were recrystallized from hexane at Dry Ice temperatures to separate the pure alcohol **9** as white prisms, m.p. 70–70.5°. The product has infrared absorption[11] at 3580 cm.$^{-1}$ (O–H) with a series of low-intensity (ϵ 277 to 444) ultraviolet peaks[12] in the region 248–270 mμ and n.m.r. multiplets[11] in the regions δ 6.7–7.6 (10H, aryl C–H) and 1.0–3.0 (15H, aliphatic C–H) as well as a sharp peak at δ 1.17 (1H, OH) which disappeared when the solution was shaken with deuterium oxide.

Anal. Calcd. for $C_{22}H_{26}O$: C, 86.23; H, 8.55. Found: C, 85.94; H, 8.54.

The following reactions were performed to compare the behavior of stereoisomeric ketones **3** and **12** with phenylmagnesium

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[11] Determined as a solution in carbon tetrachloride.

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

[13] The plate was coated with silica gel and eluted with a hexane–ether mixture.

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

[15] A gas chromatography column packed with Versamid 900 suspended on Chromosorb P was employed for this analysis.

[16] A thin layer chromatographic plate coated with silica gel and eluted with a 1:2 ether–petroleum ether (b.p. 60–70°) mixture was employed.

bromide. A solution of 111.4 mg. (0.485 mmole) of ketone **12** in 5 ml. of ether was added to 5 ml. of an ethereal solution containing 8.45 mmoles of phenylmagnesium bromide. After the solution had been stirred under nitrogen at room temperature for 12 hr., it was poured into saturated aqueous ammonium chloride containing ammonia (pH ~8) and the organic products were extracted with ether. The extract was dried and concentrated to leave 162.3 mg. of crude product as a brown oil which was mixed with 55.3 mg. of *o*-terphenyl (as an internal standard) and analyzed by gas chromatography[17] using a column previously calibrated with known mixtures. The only volatile product detected was the ketone **3** (or **12**; either these two ketones are not resolved or **12** is converted to **3** on the column used), the calculated yield being 52%. Similarly, reaction of 102.5 mg. (0.450 mmole) of the ketone **3** with 8.45 mmoles of phenylmagnesium bromide in 10 ml. of ether yielded 173.8 mg. of crude product after a reaction period of 15 hr. at room temperature. Following the addition of 85.0 mg. of *o*-terphenyl, analysis[17] indicated the presence of both the ketone **3** (and/or **12**) (eluted first) and the alcohol **9** (eluted second), the calculated yields being 30% of **3** and 38% of **9**. From a comparable reaction of 2.542 g. (11 mmoles) of the ketone **12** with 23.5 mmoles of phenylmagnesium bromide overnight at room temperature in 63 ml. of ether, the crude product isolated (1.973 g. or 78%) was identified from its infrared spectrum as the crude starting ketone **12**. Chromatography of the crude product on alumina (which epimerizes[2b] ketone **12** to ketone **3**) followed by recrystallization from hexane separated 661.8 mg. (26%) of the ketone **3**, m.p. 97–98°.

A solution of 244.8 mg. (1.08 mmoles) of the ketone **3** and 1.54 mmoles of phenyllithium in 10.2 ml. of ether was refluxed for 5 hr. and then treated with 5 ml. of cold (0°), 5% aqueous hydrochloric acid. The ethereal extract of the mixture was washed with aqueous sodium bicarbonate, dried, and concentrated to leave 350.4 mg. of the crude product as a yellow oil. Chromatography of a 103.3-mg. portion of this crude product on alumina followed by recrystallization of appropriate fractions from hexane separated 30 mg. (31%) of the alcohol **9**, m.p. 69–70° (identified by a mixture melting point determination), and 4.1 mg. (6%) of the ketone **3**, m.p. 93–99°. From a comparable experiment with 184 mg. (0.81 mmole) of the ketone **3** and 1.54 mmoles of phenyllithium in 9.2 ml. of ether, an aliquot of the crude product (279.5 mg.) was mixed with a known quantity of *o*-terphenyl and analyzed.[16] The calculated yields were 87% of the alcohol **9** and 9% of the ketone **3** (and/or **12**).

1,8-Diphenyl-$\Delta^{1,2}$-octalin (10).—A solution of 555.4 mg. of the alcohol **9** in 25 ml. of acetic anhydride was refluxed for 25.5 hr. under a nitrogen atmosphere at which time the reaction mixture contained[16] the olefin **10** but no significant amount of alcohol **9**. The reaction mixture was concentrated under reduced pressure and then neutralized with aqueous sodium hydroxide and extracted with ether. The ether layer was washed with water, dried, and concentrated to leave 483.7 mg. (94%) of the crude olefin **10**, m.p. 99–105°. Recrystallization from hexane afforded 360.6 mg. (72%) of the pure olefin **10** as white needles, m.p. 107–108.5°. The product has no infrared absorption[11] in the 3- or 6-μ region attributable to hydroxyl or carbonyl functions and has an ultraviolet maximum[12] at 245 mμ (ϵ 6450) with a shoulder at 215 mμ (ϵ 13,800). The n.m.r. spectrum[11] has multiplets in the regions δ 6.3–7.1 (10H, aryl C–H) and 1.2–3.2 (13H, aliphatic C–H) with a triplet (J = 3 c.p.s.) at δ 5.50 (1H, vinyl C–H in the environment $>C{=}CH{-}CH_2{-}$).

Anal. Calcd. for $C_{22}H_{24}$: C, 91.61; H, 8.39; mol. wt., 288. Found: C, 91.36; H, 8.46; mol. wt., 288 (mass spectrum).

After a mixture of 116.8 mg. of the alcohol **9** and 5 ml. of 85% phosphoric acid had been heated to 100° for 4.5 hr., the mixture was neutralized with aqueous sodium bicarbonate and extracted with ether. After the ether extract had been dried and concentrated, crystallization of the crude product (98.0 mg.) from hexane gave 42.1 mg. (39%) of the olefin **10**, m.p. 104–108°. Recrystallization sharpened the melting point of the product to 107–108°. This product was identified with the previous sample by a mixture melting point determination and comparison of infrared spectra.

Reaction of the Alcohol 9 wtih Dehydrogenating Agents.—A solution of 1.145 g. (3.75 mmoles) of the alcohol **9** and 4.510 g. (20 mmoles) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 25 ml. of chlorobenzene was refluxed for 40 hr. under a nitrogen atmosphere. After the mixture had been filtered (to remove hydroquinone), it was concentrated and the residue was extracted with several portions of boiling hexane. After filtering the hexane extract through alumina, concentration left 535.5 mg. of yellow solid containing[18] both diphenylnaphthalenes **1** and **11**. Repeated recrystallization from hexane separated 109.2 mg. of the crude 1,8 isomer **1**, m.p. 143–145°, identified by its infrared absorption. The material recovered from the mother liquors was chromatographed on 10.96 g. of Merck silica gel employing hexane as the eluent. The early fractions (148.7 mg.) contained[18] primarily the 1,8 isomer **1**, while subsequent fractions (57.2 mg.) were mixtures[18] of **1** and **11**, and the final fractions (95 mg.) contained[14,18] the 1,6 isomer **11**. Recrystallization of these latter fractions from a hexane–ethanol mixture gave the pure **1,6-diphenylnaphthalene (11)** as white plates, m.p. 84–84.5° (lit.[8a] m.p. 86–87°). This sample has no infrared absorption[11] in the 3- or 6-μ region attributable to hydroxyl or carbonyl functions and exhibits a complex n.m.r. multiplet[11] in the region δ 7.0–8.0 (aryl C–H) with ultraviolet maxima[12] at 238 mμ (ϵ (ϵ 26,200), 258 (46,600), and *ca.* 290 (10,300).

Anal. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75; mol. wt., 280. Found: C, 93.95; H, 5.84; mol. wt., 280 (mass spectrum).

From a comparable experiment employing 97.3 mg. of the olefin **10**, the crude product (74.4 mg.) was recrystallized repeatedly to separate 20.2 mg. (22%) of the 1,8 isomer **1** melting in the range 146–148°. An additional recrystallization gave 8 mg. of the naphthalene derivative **1**, m.p. 150–151°, identified by a mixture melting point determination and comparison of infrared spectra. Analysis[14] of the crude hexane-soluble product from a comparable quinone dehydrogenation indicated the presence of 54% of the 1,8 isomer **1** and 46% of the 1,6 isomer **11**. Similarly, a solution of 54.2 mg. (0.19 mmole) of the olefin **10** and 220.2 mg. (0.97 mmole) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 7 ml. of chlorobenzene was refluxed under nitrogen for 12 hr. and then the hexane-soluble products were separated as in previous cases. The crude product (31.2 mg.) contained[14] the 1,8 isomer **1** (56%) and the 1,6 isomer **11** (44%).

A mixture of 448.6 mg. (1.48 mmoles) of the alcohol **9** and 82.7 mg. of a 30% palladium-on-carbon catalyst was heated under a stream of hydrogen gas for 30 min. at each of the temperatures, 240, 300, and 340° (*cf.* ref. 3a). The resulting mixture was extracted with chloroform and the extract was filtered and concentrated to leave 509 mg. of an oily solid which contained[14] at least six components, three of which corresponded in retention times to the olefin **10** (eluted first, *ca.* 38% of the mixture), the 1,8 isomer **1** (eluted second, *ca.* 28% of the mixture), and the 1,6 isomer **11** (eluted third, *ca.* 13% of the mixture). Repeated recrystallization from hexane–ethanol mixtures separated 94.3 mg. (23%) of the 1,8 isomer **1**, m.p. 144–147°. Further recrystallizations gave the pure 1,8 isomer, m.p. 149–150°, which was identified with the previously described material by comparison of infrared spectra. Our efforts to isolate other pure materials from the mixture were unsuccessful.

1-Keto-6-methoxy-1,2,3,4,5,8-hexahydronaphthalene (22).—6-Methoxy-1-tetralone (**20**, 30.04 g.)[19] was reduced with sodium and ethanol in liquid ammonia as previously described[9] to yield 13.308 g. (44.5%) of the **methoxy alcohol 21** as white prisms, m.p. 72–74° (lit.[9c] m.p. 71–73°), from a hexane–ether mixture. Oxidation of this alcohol **21** (13.308 g.) with acetone, aluminum isopropoxide, and toluene as previously described[9] gave 9.691 g. (68%) of the ketone **22** as white needles, m.p. 49–50° (lit.[9c] m.p. 45–47°). This product lacks infrared bands[11] in the 3-μ region attributable to a hydroxyl function and has bands at 1690, 1685 (shoulder), and 1670 cm.$^{-1}$ (conjugated C=O and enol ether; the hydroxy enol ether **21** has bands[11] at 1695 and 1670 cm.$^{-1}$) as well as a weak band at 1640 cm.$^{-1}$ (conjugated C=C); the material has an ultraviolet maximum[12] at 238 mμ (ϵ 9600). The ketone has a molecular ion peak in the mass spectrum at m/e 178 and n.m.r. peaks[11] at δ 4.62 (1H, partially resolved multiplet, vinyl C–H), 3.47 (3H, O–CH_3), and 2.78 (4H, half-band width 3 c.p.s., allylic CH_2) as well as a multiplet in the region δ 1.7–2.6 (6H, aliphatic C–H).

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(17) A gas chromatography column packed with silicone fluid, no. 710, suspended on Chromosorb P was employed for this analysis.

(18) A thin layer chromatographic plate coated with silica gel and eluted with pentane was employed for this analysis.

(19) We are indebted to Dr. Erich Marcus of the Union Carbide Chemicals Co. for providing us with a generous sample of this ketone.

1-Phenyl-6-keto-2,3,4,6,7,8-hexahydronaphthalene (23).—A solution of 8.824 g. (49.5 mmoles) of the ketone **22** in 40 ml. of ether was added to 55 ml. of an ether solution containing 67.5 mmoles of phenyllithium and the resulting solution was stirred, at room temperature and under a nitrogen atmosphere, for 3 hr. Then 75 ml. of 3% aqueous hydrochloric acid was added and the stirring, under a nitrogen atmosphere and at room temperature, was continued for an additional 4.25 hr. The ether layer was separated, combined with the ether extract of the aqueous phase, washed with aqueous sodium bicarbonate, dried, and concentrated. The residual yellow oil (14.406 g.), which contained[13] the ketone **23** and the olefin **24**, was chromatographed on 179 g. of Woelm alumina, activity grade II. The early fractions (2.774 g. of oil), eluted with hexane, deposited 260.4 mg. of the crystalline olefin **24**, m.p. 68.5–70°. Recrystallization from hexane separated the pure **olefin 24** as colorless plates, m.p. 71–72°. This product was identified with the subsequently described sample by a mixture melting point determination and by comparison of infrared spectra. The later fractions (11.246 g.) from the chromatogram, eluted with 1–7% ether in hexane, were washed with hexane to leave 4.525 g. of the crude crystalline ketone **23**, m.p. 60–64°. Recrystallization of the appropriate chromatographic fractions from hexane–ether mixtures separated fractions of the ketone **23**, m.p. 78–79° (2.904 g.) and m.p. 73–75° (1.581 g.), for a total yield of 4.485 g. (40%). An additional recrystallization from hexane afforded the pure ketone **23** as white prisms, m.p. 78.5–79°. This product has infrared absorption[20] at 1660 (conjugated C=O) and 1615 cm.$^{-1}$ (conjugated C=C) with ultraviolet maxima[12] at 232 mμ (ϵ 8800) and 307 mμ (ϵ 18,500) and n.m.r. multiplets[21] in the regions δ 7.0–7.5 (5H, aryl C–H) and 1.6–2.9 (10H, aliphatic C–H) as well as a partially resolved multiplet (half-band width 3 c.p.s.) at δ 5.81 (1H, vinyl C–H).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19; mol. wt., 224. Found: C, 85.98; H, 7.32; mol. wt., 224 (mass spectrum).

To obtain an authentic sample of the olefin **24**, a solution of 528.8 mg. (3.0 mmoles) of the ketone **20** in 10 ml. of ether was added, with stirring under a nitrogen atmosphere, to 3.0 ml. of an ether solution containing 3.7 mmoles of phenyllithium. After the mixture had been refluxed with stirring for 40 min. and then allowed to stand overnight at room temperature, 25 ml. of 12% aqueous hydrochloric acid was added, and stirring at room temperature was continued for 4.5 hr. The organic layer was separated, combined with the ether extract of the aqueous phase, washed with aqueous sodium bicarbonate, dried, and concentrated. A solution of the residual oil (860 mg.) in hexane deposited 75.4 mg. (10.6%) of the **olefin 24** as colorless plates, m.p. 71–71.5° (lit.[8a] m.p. 65°). The product, with no infrared absorption[11] in the 3- or 6-μ regions attributable to hydroxyl or carbonyl functions, has an ultraviolet maximum[12] at 273 mμ (ϵ 11,700) with an n.m.r. triplet[11] (J = 5 c.p.s.) at δ 5.87 (1H, vinyl C–H), a singlet at δ 3.71 (3H, OCH_3), and multiplets in the regions δ 6.3–7.4 (8H, aryl C–H) and 2.0–3.0 (4H, aliphatic C–H).

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83; mol. wt., 236. Found: C, 86.37; H, 6.93; mol. wt., 236 (mass spectrum).

1,6-Diphenylnaphthalene (11).—To a solution of 2.743 g. (12.2 mmoles) of the ketone **23** in 25 ml. of ether was added, with stirring and under a nitrogen atmosphere, 13 ml. of an ethereal solution containing 13.4 mmoles of phenyllithium. The mixture was refluxed, with stirring, for 2.5 hr. and then poured into aqueous ammonium chloride containing ammonia (pH 7–8). The ether layer was separated, combined with the ether extract of the aqueous phase, washed with water, dried, and concentrated. The residual viscous liquid (3.501 g.) contained[13] one major component believed to be the **alcohol 25** as well as a minor component, possibly the corresponding olefin resulting from partial dehydration. This crude product had infrared absorption[20] at 3590 and 3440 (broad) cm.$^{-1}$ (O–H) but lacked absorption in the 6-μ region attributable to a carbonyl function; the material had an ultraviolet maximum at 261 mμ (ϵ *ca.* 18,600) with n.m.r. multiplets[11] in the regions δ 7.0–7.6 (10H, aryl C–H) and 1.5–2.8 (11H, OH and aliphatic C–H) as well as a partially resolved multiplet (half-band width 3 c.p.s.) at δ 5.48 (1H, vinyl C–H). Our efforts to obtain a pure sample of the alcohol **25** were not successful.

A solution of 3.275 g. (10.5 mmoles) of the crude alcohol **25** and 9.040 g. (39.6 mmoles) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 270 ml. of benzene was refluxed for 7.5 hr. and then filtered and concentrated. The residual solid was extracted with several portions of boiling hexane; after the hexane solution had been filtered through alumina, it was concentrated and the residue (1.12 g.) was crystallized from hexane to separate 860.5 mg. (29%) of crude 1,6-diphenylnaphthalene (11), m.p. 71–80°. A 280.7-mg. aliquot of this crude product was recrystallized repeatedly from hexane and from hexane–ethanol mixtures to separate 140 mg. of the 1,6 isomer **11**, m.p. 83.5–84°. The remainder of the crude product was chromatographed on 55 g. of Woelm alumina, activity grade I; the early crystalline fractions (520 mg., eluted with hexane) afforded, after recrystallization from hexane, 358.8 mg. of the 1,6 isomer **11**, m.p. 84–85°. Thus, the total yield of pure 1,6-diphenylnaphthalene (11) was 498.8 mg. (16.5%). This product was identified with the previous sample of the 1,6 isomer **11** by a mixture melting point determination and by comparison of infrared spectra.

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[20] Determined as a solution in chloroform.

[21] Determined as a solution in deuteriochloroform.