Without further purification, this material (72.89 g.) was refluxed in diethylaniline (*ca.* 250 ml.) for 2 hr. and, on cooling, a solid separated. Refrigeration caused the separation of more solid, all of which was collected by filtration. A solution of the solid in ether was washed with two small portions of 5% hydrochloric acid followed by two portions of saturated aqueous sodium chloride. Evaporation of the ether left a colorless solid which crystallized from ethanol as colorless needles (52.30 g., 71% yield from 8-hydroxycoumarin), m.p. 158.5–159.5°.

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.27; H, 4.99. Found: C, 71.35; H, 5.31.

8-Acetoxy-7-allylcoumarin (Vd). Acetic anhydride (10 ml., 0.0935 mole) was added rapidly to a stirred solution of 7-allyl-8-hydroxycoumarin (10.0 g., 0.0495 mole) in pyridine (60 ml.). After 2 hr. of continued stirring, the solution was poured into a mixture of ice and water (*ca.* 600 ml.) and a colorless solid (10.55 g., 87%), m.p. 82–84°, was collected by filtration. Recrystallization from ethanol gave colorless needles, m.p. 84–85°.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 68.88; H, 5.11.

8-Acetoxy-7-(2′,3′-dibromopropyl)coumarin (Ve). A solution of bromine (6.84 g., 0.0430 mole) in chloroform was added to a stirred solution of 8-acetoxy-7-allylcoumarin (m.p. 82–84°, 10.50 g., 0.0430 mole) in chloroform at such a rate as to allow decolorization after each drop. Evaporation of the chloroform on a steam bath left a nearly colorless oil, which solidified on contact with 95% ethanol, and crystallized from the same solvent as colorless prisms (14.54 g., 84%), m.p. 141.5–143°.

Anal. Calcd. for $C_{14}H_{12}O_4Br_2$: C, 41.61; H, 3.00; Br, 39.55. Found: C, 41.48; H, 2.90; Br, 39.62.

2-Bromomethyl-2,3-dihydro-8H-furo[3,2-h][1]benzopyran-8-one (VI). 8-Acetoxy-7-(2′,3′-dibromopropyl)coumarin (11.90 g., 0.0295 mole) was added to a refluxing solution of sodium (3.38 g., 0.147 mole) in absolute ethanol (*ca.* 250 ml.) under an atmosphere of nitrogen. After 2 hr. the hot solution was poured into 2.5 l. of a mixture of ice, water, and concentrated hydrochloric acid (15 ml.). A chloroform extract of the aqueous suspension was washed thoroughly with 5% aqueous sodium hydroxide, 5% aqueous hydrochloric acid, and then water, and dried over anhydrous magnesium sulfate. Filtration through a pad of Celite, followed by evaporation of the chloroform left a residue, which was triturated with petroleum ether (b.p. 30–60°) and sublimed under vacuum. Washing the sublimate with 5% aqueous sodium hydroxide left a colorless solid, which crystallized from ethanol as ivory colored plates (1.80 g.), m.p. 169–171°. Three recrystallizations from ethanol gave colorless needles (0.65 g., 7.8%), m.p. 164–174°. The third recrystallization did not alter the m.p. Infrared and ultraviolet spectra were consistent with the proposed structure.

Anal. Calcd. for $C_{12}H_9O_3Br$: C, 51.29; H, 3.23; O, 17.01; Br, 28.43. Found: C, 50.91; H, 3.64; O, 17.45; Br, 28.09.

2-Methyl-8H-furo[3,2-h][1]benzopyran-8-one (VII). 2-Bromomethyl-2,3-dihydro-8*H*-furo[3,2-*h*][1]benzopyran-8-one (0.500 g., 0.00177 mole) was added to a refluxing solution of sodium (0.125 g., 0.00543 mole) in absolute ethanol (10 ml.) under an atmosphere of nitrogen. After 2 hr., the hot solution was poured into 150 ml. of a mixture of ice, water, and concentrated hydrochloric acid (3 ml.). The resultant precipitate (0.258 g.), m.p. 149–156°, was collected and recrystallized from 95% ethanol to give colorless needles (0.158 g., 44%), m.p. 158–159.5°. Both infrared and ultraviolet spectra were consistent with the proposed structure.

Anal. Calcd. for $C_{12}H_8O_3$: C, 72.00; H, 4.03; O, 23.97. Found: C, 72.22; H, 3.99; O, 24.00.

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DEPARTMENT OF CHEMISTRY
KALAMAZOO COLLEGE
KALAMAZOO, MICH.

Peri-Substituted Naphthalene Compounds. V.[1,2] 1,8-Dilithionaphthalene

R. L. LETSINGER, J. A. GILPIN, AND W. J. VULLO

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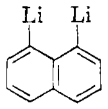
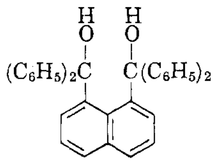
In connection with the synthesis of peri-substituted naphthalene compounds it was desirable to have available 1,8-dilithionaphthalene (I). We have found that this reagent may be obtained conveniently by the exchange reaction between 1,8-dibromonaphthalene and butyllithium. The dilithium product was characterized by conversion (a) to 1,8-naphthalic anhydride (85% yield based on dibromonaphthalene) by treatment with carbon dioxide and (b) to the diol, 1,8-bisdiphenylhydroxymethylnaphthalene (II) (58% yield) by reaction with benzophenone. The structure of the diol was deduced from the analysis, spectral data, mode of formation, and the facile dehydration to an ether (III). Analogous dehydration reactions have been reported with *o*-bisdiphenylhydroxymethylbenzene[3] and 1,8-bisphenylhydroxymethylnaphthalene.[4]


I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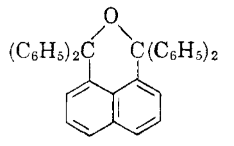
III

A practical route to 1,8-dibromonaphthalene was needed for this synthesis. Fieser and Seligman,[5] modifying an earlier procedure of Meldola and Streatfeild,[6] obtained 1,8-dibromonaphthalene in three steps from 1,8-diaminonaphthalene. When we prepared dibromonaphthalene in this way, however, the procedure was tedious and time consuming. Two shorter preparative methods have been reported. One involves direct tetrazotization of 1,8-

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(1) This work was supported by the National Science Foundation.

(2) For the previous paper in this series see R. L. Letsinger and W. J. Vullo, *J. Org. Chem.*, **25**, 1844 (1960).

(3) G. Wittig and F. Bickelhaupt, *Ber.*, **91**, 883 (1958).

(4) R. L. Letsinger and P. T. Lansbury, *J. Am. Chem. Soc.*, **81**, 935 (1959).

(5) L. F. Fieser and A. M. Seligman, *J. Am. Chem. Soc.*, **61**, 136 (1939).

(6) R. Meldola and F. W. Streatfeild, *J. Chem. Soc.*, **63**, 1054 (1893).

diaminonaphthalene[7] and the other, the action of bromine on silver naphthalate.[8] In our hands the former gave only very low yields of dibromonaphthalene and the latter afforded 1,4,5-tribromonaphthalene. It was then found that the Hunsdiecker reaction proceeded satisfactorily with 8-bromo-1-naphthoic acid. The following sequence therefore provided the most convenient route to 1,8-dibromonaphthalene: naphthalic anhydride → anhydro-8-hydroxymercuri-1-naphthoic acid → 8-bromo-1-naphthoic acid[9] → 1,8-dibromonaphthalene.

In view of the facile conversion of 1,8-dibromonaphthalene to a dilithium derivative, it was surprising to find that 5,6-dibromoacenaphthene exchanged only one bromine when treated with two equivalents of butyllithium in ether. Sterically, 5,6-dibromoacenaphthene should be more favorably constituted for di-exchange than 1,8-dibromonaphthalene.[10] The failure of the second bromine to exchange must therefore reflect the combined deactivating effects of the paramethylene groups and the neighboring carbon-lithium bond.

The reaction of 5,6-dichloroacenaphthene with excess magnesium in tetrahydrofuran afforded, after carbonation, 6-chloroacenaphthene-5-carboxylic acid. There was no indication that a di-Grignard reagent had formed.

EXPERIMENTAL

Infrared spectra were obtained with a Baird recording spectrometer with the sample in potassium bromide plates, unless otherwise noted. The ultraviolet spectra were obtained with a Beckman D. K. spectrometer. Carbon-hydrogen analyses were performed by Miss H. Beck, and the NMR spectra were obtained by C. J. Creswell.

All organometallic reactions were carried out in a nitrogen atmosphere with good stirring. Carbonation was effected by forcing the contents of the flask onto powdered Dry Ice by a positive nitrogen pressure. After the excess Dry Ice had evaporated, water was added and the layers separated. The ether layer was washed with aqueous alkali and the combined aqueous solutions then washed with ether. Neutral reaction products were obtained from the organic layers and the acid products were isolated after acidification of the aqueous layers.

1,8-Dibromonaphthalene. Naphthalic anhydride was converted to 8-bromo-1-naphthoic acid *via* anhydro-8-hydroxymercuri-1-naphthoic acid in 44% yield by the method of Rule and Pursell.[9] To an aqueous solution containing 5.0 g. of 8-bromo-1-naphthoic acid and 1.06 g. of sodium carbonate was added with stirring an aqueous solution containing 3.4 g. of silver nitrate. The resulting silver salt was collected by filtration and washed with water, methanol, and acetone, and then dried over phosphorus pentoxide at 75° (2 mm). The salt (6.5 g.) was suspended in dry carbon tetrachloride. To the mixture was added a solution of bromine (2.9 g.) (dried by distillation over phosphorus pentoxide) in dry carbon tetrachloride (19 ml.) at such a rate that the bromine color did not persist. After two additional hours of reflux the mixture was filtered and the filtrate extracted with four portions of aqueous sodium bicarbonate. Acidification afforded 0.8 g. (18%) of recovered 8-bromo-1-naphthoic acid. Evaporation of the carbon tetrachloride yielded 3.6 g. of semisolid product, which appeared on the basis of the infrared spectrum to be primarily 1,8-dibromonaphthalene. It was most readily purified by passage through a silica gel column (90:10 hexane-benzene solvent). After one subsequent recrystallization from ethanol the product (2.35 g., 45%) melted at 95–100°. Two additional recrystallizations yielded 1.57 g. of 1,8-dibromonaphthalene, m.p. 106–108°; lit. m.p. 109–110°[5]; λ^{KBr} 6.50, 7.40, 8.40, 8.74, 11.75, 12.33, 13.33 μ.

1,8-Dilithionaphthalene. (*a*) Reactions with carbon dioxide and with benzil. A solution of butyllithium in ether (85 ml., 0.385*M*) was added rapidly, dropwise, to 4.0 g. of 1,8-dibromonaphthalene in 60 ml. of ether at room temperature. The solution was allowed to stir for 45 minutes; then a 21 ml. aliquot was removed and poured onto Dry Ice. Acidification, extraction, and heat treatment afforded 0.34 g. (85%) of 1,8-naphthalic anhydride, m.p. 250–257°. A sample recrystallized from nitric acid melted at 270–271° (0.2 g.).

To the balance of the organolithium solution was added 2.5 g. of benzil in 30 ml. of ether. After 2.5 hours at room temperature and 0.5 hours at reflux, the mixture was hydrolyzed with an ammonium chloride solution. No crystalline products could be isolated from the reaction products.

(*b*) Reaction with benzophenone. To 1,8-dilithionaphthalene, prepared as previously described from 4.0 g. of dibromonaphthalene, was added a solution of benzophenone (5.2 g.) in 40 ml. of ether. The mixture was refluxed for 4 hours and hydrolyzed by addition of 35 ml. of saturated ammonium chloride. The ethereal layer was washed with water and dried over magnesium sulfate. Upon concentration, white crystals of 1,8-bisdiphenylhydroxymethylnaphthalene (II) separated; 3.5 g. (51%), m.p. 165–168°. Further concentration afforded 0.5 g. (7.3%) of a crystalline solid, m.p. 117–124°, which on heating above the melting point resolidified and remelted at 162–166°. This was the same compound (infrared spectrum) as that which melted at 165–168°. After recrystallization from chloroform-hexane it melted at 167–167.5°; λ^{KBr} 2.85, 3.20, 6.20, 6.68, 6.88, 9.60, 13.0, 14.27 μ; λ_{max}^{EtOH} 231.5 mμ (log E 4.90), 289 mμ (log E 3.96).

Anal. Calcd. for $C_{36}H_{28}O_2$: C, 87.8; H, 5.73. Found: C, 87.5; H, 5.49.

Diol II was only slightly soluble in ether, ethanol, and hexane, but it readily dissolved in acetone and in chloroform. Recrystallization from hexane-acetone afforded a crystalline product which melted at 118–120° and exhibited an infrared spectrum almost identical to that of II except for a strong absorption peak at 5.82 μ. This product was not changed on heating at 100° at 2 mm. for 3 hours; however, it was converted to II (m.p. 165–167°) by recrystallization from chloroform-hexane or by heating above its melting point. It therefore appears that the 118–120° product is an acetone inclusion compound derived from II (this substance is clearly different from the compound melting at 117–124° since the latter does not absorb in the carbonyl region).

Dehydration of 1,8-bisdiphenylhydroxymethylnaphthalene. When a solution containing 0.4047 g. of II in 10 ml. of acetic acid was refluxed for 20 hours and then cooled, white crystals of the ether (III) separated; m.p. 243–245°; weight, 0.3380 g. (87%); λ^{KBr} 3.21, 6.2, 6.67, 6.88, 7.42, 8.4, 9.7, 10.5, 12.16, 12.85, 13.3, 14.3 μ, λ_{max}^{EtOH} 236.5 mμ (log E 4.08), 295 mμ (log E 3.32). The spectrum exhibited a small O—H band when taken in KBr; however, no absorption was found in the hydroxyl region when the sample was well dried and dissolved in chloroform.

Anal. Calcd. for $C_{36}H_{26}O$: C, 91.1; H, 5.52. Found: C, 89.6; H, 5.43.

Compound II was likewise transformed to III (m.p. 243–245°, 91%) by heating in formic acid 5.5 hours on a steam

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(7) H. H. Hodgson and J. S. Whitehurst, *J. Chem. Soc.*, 80 (1947).

(8) S. S. M. Nur Nawaz Lodi and Mofiz-ud-Din Ahmad, *Pakistan J. Sci. Research*, 6, 92 (1954); *Chem. Abstr.*, **49**, 8218^a (1955).

(9) H. Rule and W. Pursell, *J. Chem. Soc.*, 168 (1934).

(10) See, for example, the molecular dimensions of acenaphthene: A. I. Kitaigorodskii, *Zhur. Fiz. Khim.*, **23**, 1036 (1949); *Chem. Abstr.*, **44**, 897^i (1950).

bath. The same conversion was also effected by dissolving II in concd. sulfuric acid and then pouring the solution onto ice.

5,6-Dibromoacenaphthene. The following modification of the bromination procedure described by Dashevskii and Karishin[11] was more satisfactory in our hands than the originally reported method.

Bromine (15.5 ml.) was slowly swept by a stream of nitrogen into a solution of 20 g. of acenaphthene in 120 ml. of 95% ethanol at reflux temperature. The mixture was refluxed an additional two hours; then the solvent was distilled and the residue chromatographed on a large silica gel column (solvent: 96 parts hexane, 4 parts benzene). Eight crystalline fractions (total, 8.4 g.) with similar infrared spectra were recombined and recrystallized several times from ethanol, yielding 4.0 g. (10%) of 5,6-dibromoacenaphthene; m.p. 138–140°; lit. m.p.[11] 140°; λ^{KBr} 6.33, 7.40, 9.12, 11.6, 12.90 μ. From subsequent chromatographic fractions was obtained a mixture (7.6 g.) of higher brominated products which was not further characterized. The NMR spectrum of 5,6-dibromoacenaphthene contained a single sharp peak at 97 c.p.s. (relative to tetramethylsilane) and a group of four peaks between 218 and 236 c.p.s. the total area of which was approximately equal to that of the 97 c.p.s. peak. This spectrum is consistent with the assignment of the two bromine atoms to the 5 and 6 positions in acenaphthene.

Anal. Calcd. for $C_{12}H_8Br_2$: C, 46.2; H, 2.58. Found: C, 45.6; H, 2.56.

Reaction of 5,6-dibromoacenaphthene with butyllithium. To 2.0 g. of 5,6-dibromoacenaphthene in 50 ml. of ether at 0° was added 40 ml. of 0.60*M* butyllithium. After the mixture had warmed to room temperature, it was stirred for 45 minutes and then carbonated. The spectrum of the crude 6-bromo-5-acenaphthenecarboxylic acid (1.08 g., 61%), which was isolated did not show any absorption in the 5.5–5.8 μ range either before or after sublimation, indicating the absence of the peri-dicarboxylic acid.[12] A sample recrystallized from ethanol melted at 285–290° (dec.); λ^{KBr} 5.92, 7.78, 7.88, 8.98 μ. It gave a positive halogen test (sodium fusion; Beilstein).

Anal. Calcd. for $C_{13}H_9BrO_2$: C, 56.3; H, 3.3; neut. equiv. 277. Found: C, 56.2; H, 3.2; neut. equiv. 279, 273.

Reaction of 5,6-dichloroacenaphthene with magnesium. 5,6-Dichloroacenaphthene, m.p. 168–170° was obtained in 40% yield by chlorination of acenaphthene with sulfuryl chloride by the procedure of Dashevskii and Petrenko.[13] Small portions of this dichloride (4.5 g. total) and *n*-butyl chloride (4.2 ml. total) in tetrahydrofuran were added alternately over a 90 minute period to 1.9 g. of magnesium turnings in tetrahydrofuran (20 ml. total at the end of the reaction) at the reflux temperature. After an additional nine hours of stirring the mixture was jetted onto Dry Ice. Hydrolysis and acidification afforded 2.8 g. (60%) of crude 6-chloro-5-acenaphthenecarboxylic acid; m.p. 185–195°; after three recrystallizations from ethanol it melted at 200–203°; neut. equiv. 225, 229. A pure sample, m.p. 222–224°, was obtained by chromatographing the crude material on silica gel (eluant, 95:5 benzene-ether).

Anal. Calcd. for $C_{13}H_9O_2Cl$: C, 67.1; H, 3.9. Found: C, 67.2; H, 3.7.

In another experiment, with 30% excess magnesium over that needed to react with dichloroacenaphthene (2 mole equivalents of magnesium) and butyl chloride, comparable results were obtained.

Department of Chemistry
Northwestern University
Evanston, Ill.

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[11] M. M. Dashevskii and A. P. Karishin, *Org. Chem. Ind.* (*U.S.S.R.*), **4**, 406 (1937).

[12] Like 1,8-naphthalic acid, 5,6-acenaphthenedicarboxylic acid dehydrates to the anhydride on heating [M. Freund and K. Fleischer, *Ann.*, **399**, 222 (1913)]. Acid anhydrides may be identified by the characteristic doublet in the 5.5–5.8 μ region in the spectrum; L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Wiley, New York, 1954, p. 109.

[13] M. M. Dashevskii and G. P. Petrenko, *Ukrain. Khim. Zhur.*, **21**, 370 (1955).

A Novel Reaction Leading to (1,2-Diphenylethyl)diphenylphosphine

A. M. Aguiar,[1] J. Giacin, and A. Mills

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A convenient method of preparation of lithium diphenylphosphide lies in the cleavage of readily available and easily handled triphenylphosphine by lithium metal in tetrahydrofuran.[2] The usefulness of this preparation depends upon the extent and nature of side reactions of the phenyllithium concurrently produced in the cleavage.

When an excess of benzyl chloride was added at reflux to a reaction solution of triphenylphosphine and lithium metal in tetrahydrofuran and the solution thus obtained treated with water and 3% hydrogen peroxide, a white solid shown to contain (1,2-diphenylethyl)diphenylphosphine oxide (I) in 55.0% yield and benzyldiphenylphosphine oxide[3] (II) in 25% yield was obtained.

Support for the structure assigned to compound I was obtained by fusion with sodium hydroxide to obtain diphenylphosphinic acid and a mixture of *trans*-stilbene and bibenzyl. The formation of bibenzyl can be explained in terms of the mechanism presented by Horner *et al.*[4] for the degradation of II. Stilbene production can be explained in terms of a beta elimination, while the *trans* nature of the product may be due to an "eclipsing effect" in the transition state if the elimination is assumed to proceed through an E_2 mechanism.

An alternate synthesis of I was accomplished by the reaction of phenyllithium and II to obtain ylid III which was then treated with benzyl bromide.[5] The product thus obtained was found to be identical to I in infrared spectrum of its chloroform solution and melting point. Mixed melting point determinations were undepressed.

$$(C_6H_5)_2P(O)(\underline{C}HC_6H_5) \qquad \text{(III)}$$

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[1] To whom inquiries regarding this article should be sent.

[2] D. Wittenberg and H. Gilman, *J. Org. Chem.*, **23**, 1063 (1958).

[3] A. E. Arbuzov and K. V. Nikonorov, *Zhur. Obshchei. Khim.*, **18**, 2008 (1948).

[4] L. Horner, H. Hoffmann, and H. G. Wippel, *Chem. Ber.*, **91**, 64 (1958).

[5] L. Horner, H. Hoffmann, H. G. Wippel, and G. Klahre, *Chem. Ber.*, **92**, 2499 (1959). L. Horner and P. Beck, *Chem. Ber.*, **93**, 1371 (1960).