NOTES

A New Synthesis of Acenaphthene

By Ernst D. Bergmann and Jacob Szmuszkovicz

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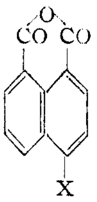
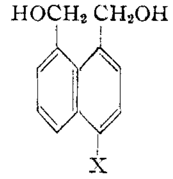
Reaction of bis-(2,2′-bromomethyl)-biphenyl with lithium phenyl gives 9,10-dihydrophenanthrene.[1] It seemed interesting to investigate whether, analogously, a five-membered ring could be fused to the naphthalene system by the reaction of 1,8-bis-(bromomethyl)-naphthalene (III, X = H) with lithium phenyl. This paper describes the synthesis of acenaphthene (IV, X = H) and 5-bromoacenaphthene (IV, X = Br) by this method.



I



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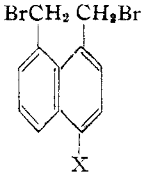
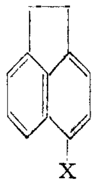


III



IV

Dimethyl naphthalate, prepared from naphthalic anhydride (I, X = H), was reduced to (II, X = H) by means of lithium aluminum hydride (yield, 98%) and the dialcohol (II, X = H) converted into the corresponding dibromide (III, X = H). Reaction with lithium phenyl gave acenaphthene (IV, X = H) in an over-all yield of 53% (calculated on dimethyl naphthalate). The hydrocarbon was identified by mixed m.p. and by its picrate. The dialcohol has recently[2] been obtained analogously from naphthalic anhydride, but only in 61% yield.

The same sequence of reactions was applied to 4-bromonaphthalic anhydride (I, X = Br), which is obtained by bromination of I (X = H).[3] The over-all yield of (IV, X = Br) was 41% (calculated on dimethyl 4-bromonaphthalate).

This synthesis of the acenaphthene system from an 1,8-disubstituted naphthalene recalls the preparation of the hydrocarbon from 1,8-malonylnaphthalene by successive treatment with alkaline permanganate and phosphorus and hydriodic acid[4] and from naphthalene with the phenylimidochloride of oxalic acid in the presence of aluminum chloride.[5]

Experimental

Dimethyl Naphthalate.—Naphthalic anhydride was dissolved in hot alkali, the solution filtered and acidified. The resulting acid was dried in air and esterified with diazomethane. The dimethyl ester was purified by recrystallization from methanol, m.p. 100°.[6]

1,8-Bis-(hydroxymethyl)-naphthalene (II, X = H).—The above dimethyl ester (2.6 g.) dissolved in a mixture of 100 ml. of ether and 50 ml. of benzene was added to a solution of 2 g. of lithium aluminum hydride in 200 ml. of ether. The mixture was refluxed for 1.5 hours, then decomposed with ice and dilute sulfuric acid. Part of the product crystallized spontaneously; the balance was obtained by evaporation of the organic solvent. Recrystallization from water afforded elongated needles, m.p. 153.5–155.5° (lit.[2] 158°), yield 1.9 g. (95%).

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.6; H, 6.4. Found: C, 76.8; H, 6.6.

1,8-Bis-(bromomethyl)-naphthalene (III, X = H).—The dialcohol (1.6 g.) was dissolved in 300 ml. of boiling benzene, which contained a few drops of pyridine. The solution was cooled to about 70°, treated dropwise with 4.8 g. of phosphorus tribromide, and then kept at 55° for 2 hours. After cooling, it was washed with water, bicarbonate solution and water and dried over anhydrous sodium sulfate. Evaporation of the solvent and recrystallization of the residue from benzene–petroleum ether afforded prisms, m.p. 129–131° (2.2 g., 81.4%). Further recrystallization from the same solvent mixture raised the m.p. to 130–131.5°.

Anal. Calcd. for $C_{12}H_{10}Br_2$: Br, 51.0. Found: Br, 50.8, 51.2.

Acenaphthene (IV, X = H).—Eleven ml. of a solution of lithium phenyl prepared as described previously[1e] was added dropwise during ten minutes in an atmosphere of nitrogen and at room temperature to a solution of 1.9 g. of (III, X = H) in 25 ml. of benzene. The product was stirred for one-half hour at room temperature, refluxed for one hour, and worked up as usual. The residue, upon recrystallization from a small amount of benzene, formed elongated needles, m.p. 92–93°. The benzene filtrate was diluted with petroleum ether, filtered from some amorphous impurity and evaporated, and the residue recrystallized from ethanol, m.p. 92–93°; total yield 0.65 g. (69%), mixed m.p. with pure acenaphthene (m.p. 93.4°) 92–94°. **The picrate** of the above product melted at 160–161.5°; its mixed m.p. with an authentic sample of acenaphthene picrate (m.p. 161–162.5°) showed no depression.

Dimethyl 4-Bromonaphthalate.—Naphthalic anhydride was brominated according to Rule and Thompson.[3] The 4-bromo derivative (I, X = Br) melted at 214–216° after recrystallization from nitrobenzene, acetic anhydride and again nitrobenzene; it was dissolved in dilute alkali, filtered, precipitated with acid in the cold and dried in air. Esterification of the methanolic suspension of the acid thus obtained with an excess of ethereal diazomethane afforded the dimethyl ester, which was recrystallized twice from methanol (charcoal) and melted at 109.5–110.5°.

Anal. Calcd. for $C_{14}H_{11}O_4Br$: C, 52.0; H, 3.4. Found: C, 52.0; H, 3.4.

4-Bromo-1,8-bis-(hydroxymethyl)-naphthalene (II, X = Br).—A solution of 2.43 g. of the dimethyl ester in a mixture of 25 cc. of benzene and 25 cc. of ether was added to 2 g. of lithium aluminum hydride dissolved in 120 cc. of ether. The product was refluxed for one hour, kept overnight at room temperature and decomposed with 100 cc. of 25% sulfuric acid. Part of the dialcohol separated spontaneously, the remainder was obtained by evaporation of the organic layer. Recrystallization from dilute methyl alcohol gave material melting at 145–150°. One further recrystallization raised the melting point to 162–163.5° which remained unchanged on further treatment.

Anal. Calcd. for $C_{12}H_{11}O_2Br$: C, 54.0; H, 4.2. Found: C, 53.9; H, 4.4.

4-Bromo-1,8-bis-(bromomethyl)-naphthalene (III, X = Br).—The dialcohol (2 g.) was dissolved in 200 ml. of boiling benzene, and the solution treated at about 70° dropwise with 4.5 g. of phosphorus tribromide. The solution was heated at 55° for two hours, cooled to room temperature, washed with water, bicarbonate solution and water, and evaporated. The residue (m.p. 113–115.5°) was recrys-

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[1] (a) D. M. Hall and E. E. Turner, *Nature*, **163**, 537 (1949); (b) D. M. Hall, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 711 (1950); (c) D. M. Hall and E. E. Turner, *ibid.*, 3072 (1951); *cf.* (d) E. D. Bergmann and Z. Pelchovitz, This Journal, **75**, 2663 (1953); (e) E. D. Bergmann and J. Szmuszkovicz, *ibid.*, **73**, 5153 (1951).

[2] R. E. Beyler and L. H. Sarett, *ibid.*, **74**, 1406 (1952).

[3] H. G. Rule and S. B. Thompson, *J. Chem. Soc.*, 1764 (1937).

[4] G. Errera and A. Cuffaro, *Gazz. chim. ital.*, **41**, II, 807 (1911); G. Errera and G. Ajon, *ibid.*, **44**, II, 92 (1914).

[5] H. Staudinger, H. Goldstein and E. Schlenker, *Helv. Chim. Acta*, **4**, 342 (1921).

[6] *Cf.* F. A. Mason, *J. Chem. Soc.*, **125**, 2116 (1924).

tallized twice from benzene–petroleum ether, and once from petroleum ether alone, m.p. 117.5–119° (yield 75%).

Anal. Calcd. for $C_{12}H_9Br_3$: Br, 61.1. Found: Br, 60.1.

5-Bromoacenaphthene (IV, X = Br).—The cyclization of the dibromide (III, X = Br) was carried out as before, and the crude product dissolved in a mixture of methanol and ethanol. On scratching, a small amount of material, m.p. 90–102°, was obtained which was not investigated any further. The filtrate, upon concentration, left an oil which gave a very soluble picrate,[7] but afforded a very well-crystallized **trinitrobenzene complex**, m.p. 141–144° and after recrystallization from alcohol (elongated yellow rods) 144–146° (yield 55%).

Anal. Calcd. for $C_{18}H_{12}N_3O_6Br$: N, 9.4. Found: N, 9.3.

The TNB complex was decomposed by adsorption of its benzene solution on alumina and elution with ethanol. Evaporation and recrystallization from methanol gave **5-bromoacenaphthene** in plates, m.p. 53–54° (literature[8] 52–53°).

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(7) The picrate, m.p. 114°, has been described by H. Crompton and M. Walker, *J. Chem. Soc.*, **101**, 958 (1912).

(8) M. Blumenthal, *Ber.*, **7**, 1092 (1874).

SCIENTIFIC DEPARTMENT
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Highly Polarizable C=C Double Bonds (Fulvenes and Thermochromic Ethylenes. Part 28)[1]

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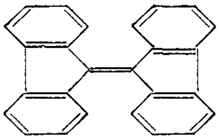
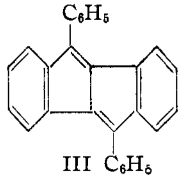
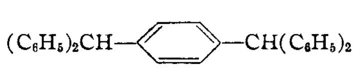
Whilst the addition reactions of fulvenes with reagents typical for polar double bonds (metal-organic compounds,[2,3] lithium aluminum hydride,[4] donors in the Michael reaction,[5] can be explained by the polar character of the semicyclic double bond,[6,7] the analogous behavior of so symmetrical a substance as dibiphenylenethylene (I),[7,8] is very surprising. Bergmann, Fischer and Jaffe[9] and Lavie and Bergmann[1] have suggested that the "polar reactions" of I are due to the high *polarizability* of the central double bond. Indeed, the molecular refraction of I, which is a measure of the polarizability of the molecule, is unusually large, even in the infrared.[10,11] If this hypothesis is correct, other hydrocarbons which show the same phenomenon of an abnormally large molecular refraction, should be capable of reactions similar to I. This has been found to be true for tetraphenyl-*p*-quinodimethane (II) (*MR*, calcd., 138; *MR* found, 182 ± 4[12]), and diphenyldiphensuccindadiene (III) (for the corresponding dimethyl compound: *MR*, calcd., 75.5; *MR*, found, 86.5 ± 0.8[9,13]). *Both hydrocarbons add lithium aluminum hydride.* With this reagent, II gives in N-methylmorpholine as solvent a colored addition product, which, by hydrolysis, is converted into *p*-dibenzhydrylbenzene (IV). Analogously, III is transformed into diphenylsuccindene (V).


I

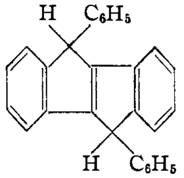

II

$(C_6H_5)_2C=C_6H_4=C(C_6H_5)_2$


III


IV

$(C_6H_5)_2CH-C_6H_4-CH(C_6H_5)_2$


V

The spectrum of V (Fig. 1) shows a maximum (3225 Å., log ε 4.20) similar to that of the unsubstituted diphensuccindene (3100 Å., log ε 4.56[14]); a second maximum lies at 2400 Å. (log ε 4.25).

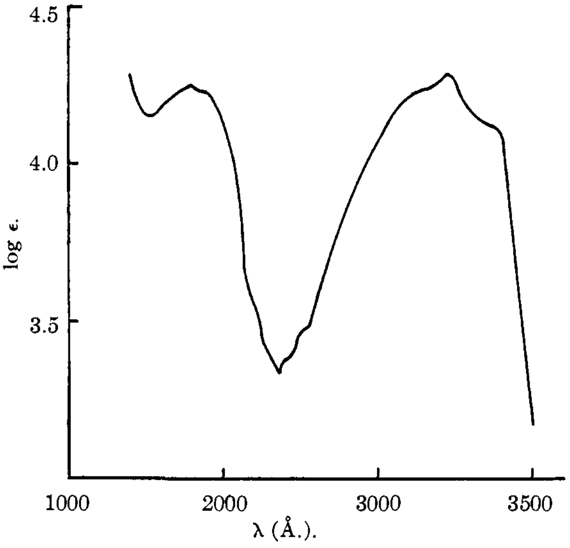


Fig. 1.—Diphenylsuccindene (V) in alcohol.

Experimental

Tetraphenyl-*p*-quinodimethane (II) was prepared according to Staudinger[15] (from xylene, m.p. 268°), **diphenyldiphensuccindadiene** (III) according to Brand[16] (from amyl alcohol, m.p. 260°).

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(1) Part 27, D. Lavie and E. Bergmann, *J. Org. Chem.*, **18**, in press (1953).

(2) K. Ziegler and W. Schaefer, *Ann.*, **511**, 101 (1934).

(3) R. C. Fuson and H. D. Porter, THIS JOURNAL, **70**, 895 (1948).

(4) D. Lavie and E. Bergmann, *Bull. soc. chim. France*, **18**, 250 (1951).

(5) L. A. Pinck and G. E. Hilbert, THIS JOURNAL, **68**, 2014, 2739 (1946).

(6) A. Pullman, G. Berthier and B. Pullman, *Bull. soc. chim. France*, **17**, 1097 (1950).

(7) B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson et Cie, Paris, 1952, p. 333 ff.

(8) E. Bergmann, G. Berthier, A. Pullman and B. Pullman, *Bull. soc. chim. France*, **17**, 1079 (1950).

(9) E. Bergmann, E. Fischer and J. Jaffe, THIS JOURNAL, **75**, in press (1953).

(10) E. Bergmann and E. Fischer, *Bull. Israeli Research Council*, **1**, No. 4, 84 (1952).

(11) E. Bergmann and E. Fischer, *Bull. soc. chim. France*, **19**, 712 (1952).

(12) B. Pullman, A. Pullman, E. Bergmann, G. Berthier, E. Fischer, D. Ginsburg and Y. Hirshberg, *ibid.*, **18**, 707 (1951).

(13) B. Pullman, A. Pullman, E. Bergmann, G. Berthier, E. Fischer, Y. Hirshberg and J. Pontis, *J. chim. phys.*, **49**, 24 (1952).

(14) L. F. Fieser and M. U. Pechet, THIS JOURNAL, **68**, 2577 (1946).

(15) H. Staudinger, *Ber.*, **41**, 1355 (1908); H. Staudinger and S. Bereza, *Ann.*, **380**, 276 (1911).

(16) K. Brand, *Ber.*, **45**, 3071 (1912).