[CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE]

A New Synthesis of 3,4,5,6-Dibenzphenanthrene

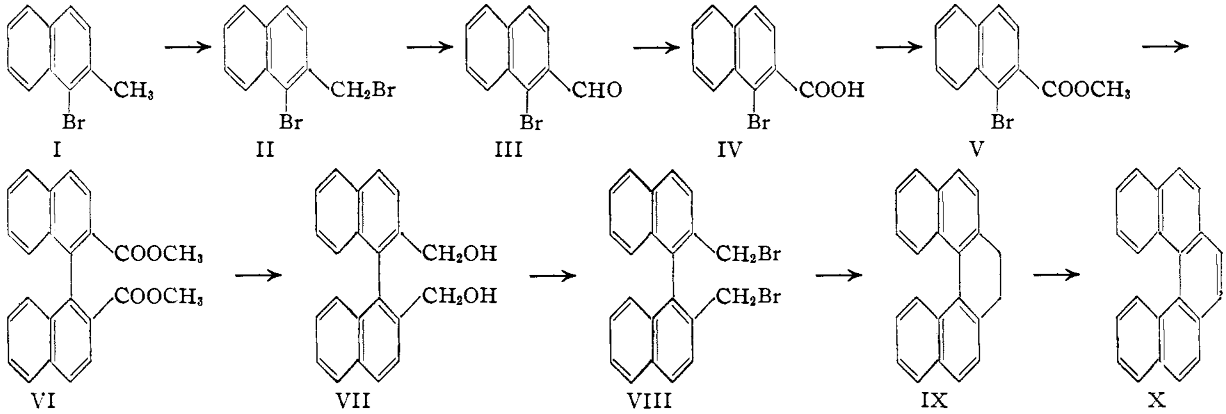
BY ERNST D. BERGMANN[1] AND JACOB SZMUSZKOVICZ

By reduction of dimethyl 1,1'-dinaphthyl-2,2'-dicarboxylate the corresponding dialcohol has been obtained. Treatment of the corresponding dibromide with lithium phenyl gave 9,10-dihydro-3,4,5,6-dibenzphenanthrene and dehydrogenation of the latter 3,4,5,6-dibenzphenanthrene. The ultraviolet spectra of the last two substances have been determined.

3,4,5,6-Dibenzphenanthrene (X) has been isolated by Cook[1a] from the mixture of 1,2,5,6-dibenzanthracene-4,8-dicarboxylic acid and 3,4,5,6-dibenzphenanthrene-1,8-dicarboxylic acid which results from the application of the Pschorr synthesis to the system phenylene-*p*-diacetic acid plus *o*-nitrobenzaldehyde.[2] A more rational synthesis has been devised by Weidlich[3]: 3,4,3',4'-tetrahydro-1,1'-dinaphthyl was condensed with maleic anhydride and the addition product first partially dehydrogenated with bromine and subsequently dehydrogenated and decarboxylated by heating at 400° in a nitrogen atmosphere in presence of anhydrous barium hydroxide, copper powder and stannous chloride. The last step of this process, which gives an over-all yield of 12% (based upon α-tetralone), did not prove satisfactory in our hands, especially in view of the easy further dehydrogenation of (X) to 1,12-benzperylene.

A reliable and not over-complicated method has been worked out which is represented by the following chart and is based essentially on the observation of Hall and Turner,[4] that 2,2'-di-(bromomethyl)-biphenyl is converted into 9,10-dihydrophenanthrene by treatment with lithium phenyl. The general applicability of this reaction is supported by the fact that substances of the benzyl bromide type are "dimerized" by lithium-aryl compounds (benzyl bromide to dibenzyl, diphenylbromomethane to tetraphenylethane, etc.).[5]

CHART



1-Bromo-2-methylnaphthalene (I)[6] is brominated to (II) by N-bromosuccinimide with a yield of 87%, therefore, greatly superior to that obtained with elementary bromine.[6] The conversion of (II) to (III) by the Sommelet method (yield, 39%) has already been described by Hewett,[7] but for the oxidation of the aldehyde (III) to 1-bromo-2-naphthoic acid (IV) a more satisfactory method than the known one[6] has been worked out, which uses potassium permanganate in aqueous acetone and gives a yield of 78%. The methyl ester (V) of (IV), which is obtainable in quantitative yield, was subjected to the Ullmann synthesis according to Martin[8] (93% yield, taking into account that 21% of (V) are recovered) and the dimethyl 1,1'-dinaphthyl-2,2'-dicarboxylate (VI) reduced by means of lithium aluminum hydride in boiling ether (yield, quantitative). The diol (VII) was then converted into the corresponding dibromide (VIII) by means of phosphorus tribromide and (VIII) treated with lithium phenyl; the yields in these two steps were 83 and 90%, respectively. Thus, 9,10-dihydro-3,4,5,6-dibenzphenanthrene (IX) was obtained; its absorption spectrum (Fig. 1) resembles in type that of 1,1'-dinaphthyl,[9] but differs from it considerably in the location of the group of bands of longer wave length (3200, log E_m 4.04; 3360, log E_m 4.12; 3480, log E_m 4.12). This shift toward the visible by 300–500 Å. can perhaps be ascribed to the fact that in 1,1'-dinaphthyl the two naphthalene systems are twisted against each other and, therefore, do not form one resonating system,[9c] whilst in (IX) they are forced largely into a monoplanar position so that resonance becomes possible.

The dehydrogenation to (X) proceeded with quantitative yield, when palladium–charcoal was applied in boiling cymene as solvent; sulfur gave an inferior yield. An interesting and probably generally applicable method of dehydrogenation con-

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(1a) Cook, *J. Chem. Soc.*, 1592 (1933).

(2) Weitzenboeck and Klingler, *Monatsh.*, **39**, 315 (1918).

(3) Weidlich, *Ber.*, **71**, 1203 (1938).

(4) Hall and Turner, *Nature*, **163**, 537 (1949).

(5) Wittig and Witt, *Ber.*, **74**, 1474 (1941).

(6) Mayer and Sieglitz, *ibid.*, **55**, 1835 (1922).

(7) Hewett, *J. Chem. Soc.* unpublished.

(8) Martin, *ibid.*, 679 (1941).

(9) (a) Pestemer and Cecelsky, *Monatsh.*, **59**, 119 (1932); (b) Brass and Patzelt, *Ber.*, **70**, 1349 (1937); (c) Friedel, Orchin and Reggel, THIS JOURNAL, **70**, 199 (1948); (d) Frampton, Edwards and Henze, *ibid.*, **70**, 2284 (1948).

sists in the successive treatment of the dihydrophenanthrene derivative (IX) with N-bromosuccinimide and with anhydrous potassium acetate in glacial acetic acid. This method will be preferable in cases in which the usual means of dehydrogenation are apt to lead to undesirable secondary reactions at the high temperatures required.[10]

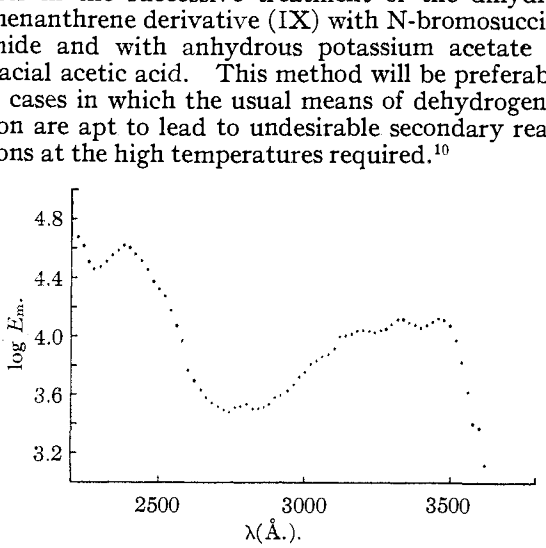

Fig. 1.—9,10-Dihydro-3,4,5,6-dibenzphenanthrene (IX) in dioxane.

(X), which is known[1] to give no crystalline picrate, is characterized by a trinitrobenzene complex.

The over-all yield of the synthesis of (X) from 1-bromo-2-methylnaphthalene is 21%.

The ultraviolet spectrum of 3,4,5,6-dibenzphenanthrene (Fig. 2) shows 6 bands: 232 mμ (log E_m 4.89); 270 (4.54); 304 (4.48); 330 (4.15); 376 (2.56); 396 (2.30).

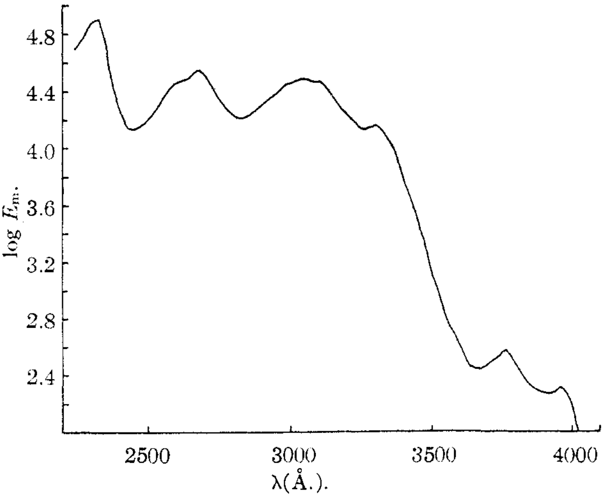

Fig. 2.—3,4,5,6-Dibenzphenanthrene (X) in dioxane.

Acknowledgment.—The ultraviolet spectra have been measured by Dr. Y. Hirshberg and the methods for the preparation of (II) and (IV) worked out by Dr. D. Lavie, both of this Institute.

Experimental[11]

1-Bromo-2-bromomethylnaphthalene (II).—A mixture of 88.4 g. (0.4 mole) of 1-bromo-2-methylnaphthalene,[6,12] 79 g. (0.4 mole) of NBS and 0.2 g. of benzoyl peroxide was refluxed in 500 cc. of carbon tetrachloride for four hours. The hot solution was filtered and deposited, upon cooling, a first crop of the desired product. The remainder was isolated by evaporation of the solvent. Recrystallization from petroleum ether gave a product of m.p. 107–108° (Mayer and Sieglitz[6] report the same m.p.); yield 104 g. (87%).

1-Bromo-2-naphthoic Acid (IV).—1-Bromo-2-naphthaldehyde (III)[7] (15 g.) was dissolved in acetone (200 cc.), and a solution of potassium permanganate (15 g.) in a mixture of water (75 cc.) and acetone (500 cc.) was added with stirring at room temperature. After three hours, the solution was filtered and the acetone removed with steam. The residue was acidified and recrystallized from acetic acid; needles of m.p. 186°, yield 78%.

Methyl 1-Bromo-2-naphthoate (V).—The chloride of the acid (IV) was prepared from the acid (30.5 g.) and thionyl chloride (60 cc.) in benzene (50 cc.) and refluxed with 300 cc. of methanol for five hours.[13] Vacuum distillation (b.p. 135–138° (0.4 mm.)) gave the ester in quantitative yield, m.p. 58–59° (Boyes, Grieve and Rule[14] give m.p. 60°).

Dimethyl 1,1′-Dinaphthyl-2,2′-dicarboxylate (VI).—The Ullmann reaction of (V) (39 g.) was carried out according to Martin[8]; 21% (8 g.) of the starting material was recovered. The ester (VI) (19.6 g., 72%) boiled at 215–218° (0.4 mm.) and was purified by recrystallization from methanol; m.p. 156–157°.

2,2′-Di-(hydroxymethyl)-1,1′-dinaphthyl (VII).—A solution of 0.733 g. of the dimethyl ester (VI) in 100 cc. of ether was added to a solution of lithium aluminum hydride (1 g.) in 100 cc. of the same solvent. The reaction mixture was refluxed for one hour and decomposed carefully, first with water, then with dilute sulfuric acid. It was extracted twice with ether and the solution washed with water and dried. On evaporation, a quantitative yield of white crystalline material was obtained, m.p. 184–188°. Recrystallization from 95% ethanol gave hexagonal plates, m.p. 189.5–190.5°.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.1; H, 5.8. Found: C, 84.1; H, 5.8.

2,2′-Di-(bromomethyl)-1,1′-dinaphthyl (VIII).—The dialcohol (VII) (9.4 g.) was dissolved in 1025 cc. of boiling benzene, and the solution cooled to 50°. Two drops of pyridine and then, dropwise, 17.9 g. of phosphorus tribromide were added. The solution was kept at 50° for two hours. Ice was added and the benzene layer washed with water, sodium bicarbonate and water, and dried. On evaporation, an oil was obtained which solidified on trituration with petroleum ether. Crystallization from benzene–petroleum ether afforded prisms, m.p. 147–149°; yield 11 g. (83.6%). Another recrystallization raised the melting point to 148–149.5°.

Anal. Calcd. for $C_{22}H_{16}Br_2$: Br, 36.4. Found: Br, 36.4.

9,10-Dihydro-3,4,5,6-dibenzphenanthrene (IX).—Lithium phenyl was prepared from 1.07 g. of lithium and 11 g. of bromobenzene in 40 cc. of ether, and diluted to 100 cc. with ether. Seventeen cc. of this solution was added, drop by drop and with stirring, in a nitrogen atmosphere to the solution of 4.4 g. of the dibromide (VIII) in 20 cc. of benzene, during 15 minutes. The suspension was stirred at room temperature for one further hour, 20 cc. of benzene was added and the mixture refluxed for one hour. Water was added and the mixture acidified with dilute hydrochloric acid. The aqueous layer was extracted once with benzene, and the combined organic layers were washed with water. The residue obtained, on evaporation of the solvent, was dissolved in boiling benzene, filtered from a small amount of insoluble material and allowed to crystallize. 2.2 g. (80%) of a product melting at 211–213° was thus obtained. Recrystallization from benzene gave colorless rods, m.p. 212–213°.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.3; H, 5.7. Found: C, 94.4; H, 5.7.

The mother liquor gave 0.3 g. of additional material, m.p. 209–212°.

3,4,5,6-Dibenzphenanthrene (X) (a).—In 20 cc. of cymene, 0.3 g. of (IX) and 0.2 g. of 10% palladium–charcoal were refluxed for four hours. The solution was filtered,

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(10) Dibenzyl has been analogously dehydrogenated to stilbene, tetrahydronaphthalene to naphthalene and acenaphthene to acenaphthylene: Barnes, This Journal, **70**, 145 (1948).

(11) All melting points uncorrected.

(12) It was found advantageous to purify the crude product by treatment with steam which removed the dissolved hydrogen bromide.

(13) Compare Hirshberg, Lavie and E. Bergmann, *J. Chem. Soc.*, 1030 (1951).

(14) Boyes, Grieve and Rule, *ibid.*, 1833 (1938).

the catalyst washed with benzene and the combined filtrates were evaporated *in vacuo* at 100°. The residue crystallized spontaneously; yield 0.29 g.; m.p. 172–176°. Recrystallization from acetic acid and then from alcohol gave colorless, elongated rods of the correct m.p. 177–178°.

The trinitrobenzene complex crystallized in yellow leaflets, m.p. 136–137°.

Anal. Calcd. for $C_{28}H_{17}N_3O_6$: C, 68.5; H, 3.5. Found: C, 68.9; H, 3.4.

(b) A mixture of 280 mg. of (IX) and 70 mg. of sulfur was heated for 20 minutes at 250–280°. Sublimation at 170° (0.1 mm.) gave pale yellow crystals of m.p. 176–177°; yield 150 mg. Recrystallization from acetic acid gave pure material of m.p. 177–178°.

Anal. Calcd. for $C_{22}H_{14}$: C, 95.0; H, 5.0. Found: C, 94.8; H, 4.9.

(c) The dihydro-compound (IX) (280 mg.), N-bromosuccinimide (200 mg.), benzoyl peroxide (10 mg.) and carbon tetrachloride (15 cc.) were refluxed for 45 minutes. Hydrogen bromide was evolved throughout the reaction. The reaction mixture was cooled to room temperature, filtered and evaporated *in vacuo*. The residue (m.p. 130–140°) was dissolved in 10 cc. of glacial acetic acid. One gram of anhydrous potassium acetate was added and the whole refluxed for one hour. The solvent was evaporated *in vacuo*, water added and the precipitate filtered and washed with water; m.p. 140–145°. After three crystallizations from acetic acid the material melted at 176–177° (50 mg.), and the trinitrobenzene complex at 136–137°. Both products showed no depression in melting point in mixture with the materials obtained by methods (a) and (b).

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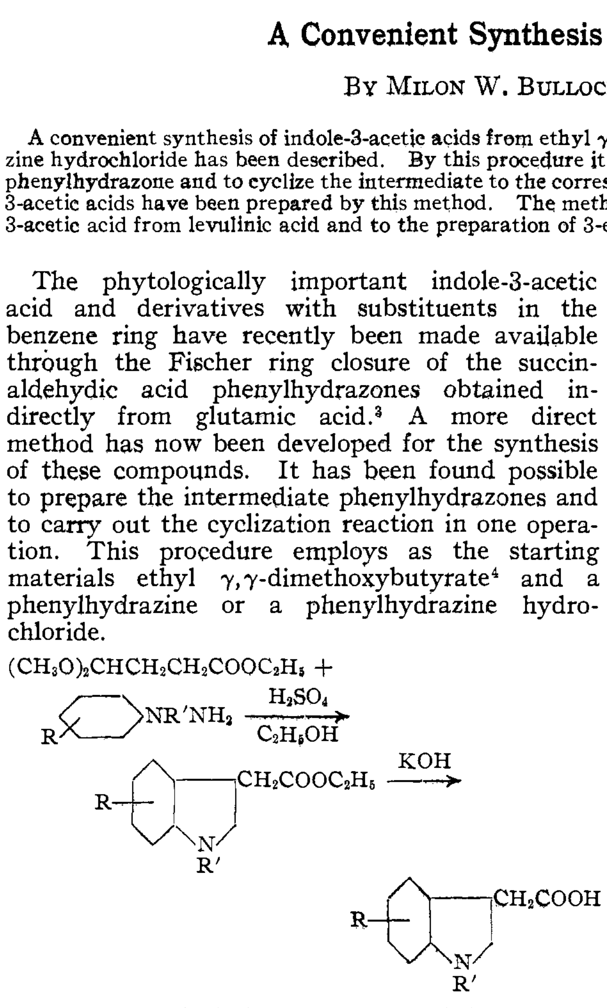
A Convenient Synthesis of Indole-3-acetic Acids[1]

BY MILON W. BULLOCK AND SIDNEY W. FOX[2]

A convenient synthesis of indole-3-acetic acids from ethyl γ,γ-dimethoxybutyrate and a phenylhydrazine or phenylhydrazine hydrochloride has been described. By this procedure it is possible to prepare the intermediate ethyl succinaldehydate phenylhydrazone and to cyclize the intermediate to the corresponding indole-3-acetic acid in one operation. Several indole-3-acetic acids have been prepared by this method. The method has also been applied to the preparation of 2-methylindole-3-acetic acid from levulinic acid and to the preparation of 3-ethylindole from butyraldehyde.

The phytologically important indole-3-acetic acid and derivatives with substituents in the benzene ring have recently been made available through the Fischer ring closure of the succinaldehydic acid phenylhydrazones obtained indirectly from glutamic acid.[3] A more direct method has now been developed for the synthesis of these compounds. It has been found possible to prepare the intermediate phenylhydrazones and to carry out the cyclization reaction in one operation. This procedure employs as the starting materials ethyl γ,γ-dimethoxybutyrate[4] and a phenylhydrazine or a phenylhydrazine hydrochloride.



To prepare the indole-3-acetic acid it is necessary only to reflux a solution of the acetal and a phenylhydrazine in a solution containing a suitable catalyst, similarly to the direct ring closure of cyclohexanone phenylhydrazone.[5] In the indole-3-acetic acid series a solution of sulfuric acid in ethanol is employed to catalyze the phenylhydrazone formation and to effect the cyclization. The yields obtained by this method parallel those in which the succinaldehydic acid phenylhydrazones were used as starting material,[3] a fact which suggests that the limiting factor is the cyclization reaction and that the formation of the phenylhydrazone from the acetal occurs in good yield.

The method has been applied to the synthesis of 5-fluoroindole-3-acetic acid, 5,7-dichloroindole-3-acetic acid and 1-methylindole-3-acetic acid as well as to indole-3-acetic acid itself. The products were in most experiments obtained from the saponification reaction in a nearly pure state. The 5,7-dichloro derivative was an exception. An unidentified by-product was formed in large amounts and was separated from the desired product with some difficulty.

In order to determine whether carbonyl compounds could be substituted for acetals, experiments were conducted with levulinic acid and butyraldehyde. A 79% yield of 2-methylindole-3-acetic acid was obtained by refluxing equimolar quantities of levulinic acid and phenylhydrazine hydrochloride in ethanolic sulfuric acid. Only traces of impure 3-ethylindole were obtained from butyraldehyde and phenylhydrazine in ethanolic sulfuric acid; however, a 15% yield of 3-ethylindole was obtained with boron trifluoride in benzene.[6] It is not surprising that no 3-ethylindole was obtained from the sulfuric acid solution, as Korczynski and co-workers[7] have reported that the

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[1] Journal Paper No. J-1925 of the Iowa Agricultural Experiment Station, Project 1110, Preparation of Chemicals for Agricultural Utility.

[2] Author to whom inquiries should be addressed.

[3] S. W. Fox and M. W. Bullock, THIS JOURNAL, **73**, 2756 (1951).

[4] Ethyl γ,γ-dimethoxybutyrate apparently has not been described in the literature; however, the closely related ethyl γ-oxobutyrate and ethyl γ,γ-diethoxybutyrate have been described and are readily available through the hydroformylation of ethyl acrylate; *cf.*, H. Adkins and G. Krsek, *ibid.*, **71**, 3051 (1949).

[5] C. U. Rogers and B. B. Corson, *ibid.*, **69**, 2910 (1947).

[6] H. R. Snyder and C. W. Smith, *ibid.*, **65**, 2452 (1943).

[7] A. Korczynski, W. Brydowna and L. Kierzek, *Gazz. chim. ital.*, **56**, 903 (1926).