dissolved in a minimum volume of concd. ammonia and analyzed for cyanide.

"Pyrrole black" was prepared by refluxing for 4 hr. 50 ml. of a solution which contained 0.43 g. of silver nitrate and 1 ml. of pyrrole. The heavy black precipitate (0.36 g.) that began to appear after a few minutes was found to be free of silver cyanide and silver acetylide; it resembled the materials obtained by earlier authors through the action of certain oxidizing agents and/or metal ions on pyrrole.[13]

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[13] *Cf.*, *e.g.*, the chapter on "Pyrrolschwarzverbindungen" in H. Fischer and A. Stern, "Die Chemie des Pyrrols," Vol. II, Akademische Verlagsgesellschaft, Leipzig, 1940, pp. 437-440.

PASADENA, CALIFORNIA

[FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

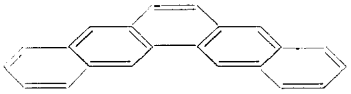
A Synthesis of 2,3,6,7-Dibenzophenanthrene

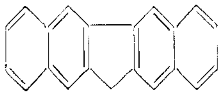
BY ERNST D. BERGMANN AND RAPHAEL IKAN

RECEIVED JULY 15, 1957

Starting from 2-methyl-3-decalone, 2,3,6,7-dibenzophenanthrene has been synthesized. The method is applicable to the synthesis of higher benzologs and of the analogous fluorene derivatives.

Among the dibenzophenanthrenes and -fluorenes, the 2,3,6,7-isomers are probably the least accessible.[1] 2,3,6,7-Dibenzophenanthrene (I) and 2,3,6,7-dibenzofluorene (II) are interrelated through 3,3′-dicarboxy-2,2′-binaphthyl (III, R = COOH) which can be cyclized *via* its lead salt to give 2,3,-6,7-dibenzofluorenone.[2] On the other hand, it should be possible in analogy with previous experience[3,4] to obtain I by reduction of III (R = COOH) to the dihydroxymethyl compound III (R = CH$_2$OH) from which the dibromo derivative III (R = CH$_2$Br) would be accessible by conventional means. Treatment of the latter with lithium phenyl, followed by dehydrogenation, should give I.


I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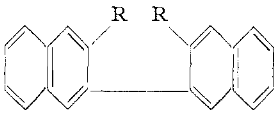
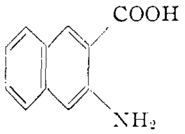


III



IV

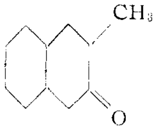
We have carried out this synthesis in an over-all yield of 21%, starting from 2-amino-3-naphthoic acid (IV) which was converted to III (R = COOH). However, this method suffers from the limitation that the preparation of IV is very cumbersome.[5] An alternative method has, therefore, been developed, which gives a lower over-all yield (10%) but has the advantage that the starting material is easily accessible.

As the above method has been described recently (after the completion of our experiments) by Badger and co-workers,[6] we refrain from a detailed discussion of this first part of our investigation.

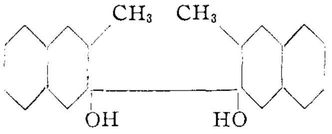
2-Methyl-3-decalone (V), available from cyclohexanone and methyl isopropenyl ketone with subsequent hydrogenation (over-all yield 82%),[7] was converted into the pinacol VI and the latter dehydrated (to VII) and dehydrogenated to 3,3′-dimethyl-2,2′-binaphthyl (III, R = CH$_3$). Upon treatment with NBS, this gave the same dibromo compound III (R = CH$_2$Br) obtained by the previous route.

By oxidation of III, R = CH$_3$, to III, R = COOH, the two alternative routes have been further linked to each other.

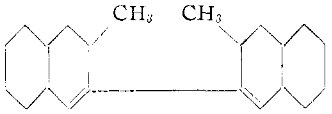
As analogs and homologs of V are easily available by similar Michael condensations,[7] this method appears applicable to the synthesis of even more highly condensed polycyclic systems.



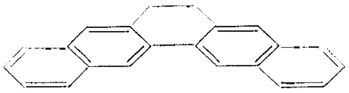
V



VI



VII


VIII

In studying the *spectra* of the compounds prepared in this investigation, some interesting observations have been made. The diene VII shows practically no selective absorption, most probably due to steric hindrance. The same effect will ex-

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[1] E. Clar and F. John, *Ber.*, **64**, 981 (1931); **62**, 3021 (1929); E. Clar, F. John and B. Hawran, *ibid.*, **62**, 940 (1929); E. Clar and D. G. Stewart, *J. Chem. Soc.*, 3215 (1951); R. H. Martin, *Helv. Chim. Acta*, **30**, 620 (1947); R. H. Martin and S. Vassart, *Bull. soc. chim. Belg.*, **61**, 234 (1952).

[2] R. H. Martin, *J. Chem. Soc.*, 679 (1941).

[3] See, also for previous literature, E. D. Bergmann and Z. Pelchowicz, *J. Org. Chem.*, **19**, 1383, 1387 (1954); G. Wittig and H. Zimmerman, *Ber.*, **86**, 629 (1953); D. M. Hall, E. E. Turner and K. E. Hamlett, *J. Chem. Soc.*, 1242 (1955).

[4] Interesting variations of this method are the preparation, from 2,2′-dibromomethylbiphenyl, of phenanthrene with sodamide in liquid ammonia (I. A. Kaye, THIS JOURNAL, **73**, 5467 (1951)) and that of 9,10-dihydrophenanthrene with sodium in the presence of catalytic quantities of tetraphenylethylene (E. Mueller and G. Roescheisen, *Ber.*, **90**, 543 (1957)).

[5] The original method of Moehlau (*Ber.*, **28**, 3096 (1895)) could not be duplicated by H. A. Harrison and F. A. Royle (*J. Chem. Soc.*, 84 (1926)). The present methods are based on the prolonged reaction of 2-hydroxy-3-naphthoic acid with ammonia and zinc chloride or ferrous sulfate at high temperature and pressure; *Org. Syntheses*, **22**, 19 (1942); German Patent 488,946 ("Beilstein," 2nd Suppl., Vol. 14, p. 323).

[6] G. M. Badger, P. R. Jefferies and R. W. L. Kimber, *J. Chem. Soc.*, 1837 (1957).

[7] E. D. Bergmann, R. Ikan and H. Weiler-Feilchenfeld, *Bull. soc. chim. France*, 290 (1957).

plain the absence of much fine structure in the compounds III, as compared to 2,2'-binaphthyl[8]: All of them show an intense absorption at about 240 mμ (log ε 5.00) and after some inflections a much lower second maximum (log ε 2.78 to 3.00) at approximately 320 mμ. Compound I has a very pronounced fine structure; its spectrum consists of two absorption regions: six high-intensity bands between 290 and 350 mμ and five low-intensity bands between 390 and 430 mμ.

Experimental

3,3'-Dihydroxymethyl-2,2'-binaphthyl (III, R = CH_2OH), prepared from 3,3'-dicarbomethoxy-2,2'-binaphthyl (III, R = $COOCH_3$) and lithium aluminum hydride in 96% yield, crystallized from isopropyl alcohol in colorless needles of m.p. 230° (literature[6] 228–229°); ultraviolet spectrum (in alcohol): 234 mμ (log ε 5.16); inflections at 280 mμ (4.19) and 293 mμ (3.76); 320 mμ (2.75).

Pinacol (VI) of 3-Methyl-2-decalone (V).—The mixture of 198 g. of 3-methyl-2-decalone (V),[7] 21 g. of aluminum turnings, 8.5 g. of mercuric chloride and 180 ml. of dry benzene was refluxed for 1 hr. with stirring. At room temperature 60 ml. of water and 180 ml. of benzene were added gradually, and the content of the flask was refluxed for 1 hr. more. The product was filtered while still hot, and the solid phase washed with 200 ml. of hot benzene. Evaporation of the benzene *in vacuo* gave 130 g. (65%) of a viscous oil, which was used directly for the next step.

3,3'-Dimethyl-2,2'-di-3,4,5,6,7,8,9,10-octahydronaphthyl (**VII**).—The mixture of 100 g. of VI and 20 g. of dehydrated alum was heated at 160–170° for 4 hr. and extracted with hot benzene. The solution was dried and distilled, b.p. 170–175° (0.2 mm.), yield 60 g. (67%); ultraviolet spectrum (in alcohol): inflection at 250 mμ (log ε 3.46).

Anal. Calcd. for $C_{22}H_{34}$: C, 88.5; H, 11.5. .Found: C, 87.8; H, 11.3.

3,3'-Dimethyl-2,2'-binaphthyl (III, R = CH_3).—In an atmosphere of nitrogen, 10 g. of VII was heated at 300–330° with 7 g. of 10% palladium–charcoal for 12 hr. The product was extracted with a mixture of benzene and ether and the residue of the solution triturated with petroleum ether and recrystallized from butyl alcohol; prisms of m.p. 144°, yield 6.5 g. (68%); ultraviolet spectrum (in alcohol): 233 mμ (log ε 5.10); 290 mμ (4.13); 321 mμ (2.98).

Anal. Calcd. for $C_{22}H_{18}$: C, 93.6; H, 6.4. Found: C, 93.9; H, 6.6.

The compound gave an addition product with 2 moles of **1,3,5-trinitrobenzene**; from isopropyl alcohol, yellow needles of m.p. 140°.

3,3'-Dibromomethyl-2,2'-binaphthyl (III, R = CH_2Br).—(a) A solution of 5 g. of III (R = CH_2OH) in 600 ml. of benzene was prepared at 50°; after addition of 2 drops of pyridine, 10 g. of phosphorus tribromide was added with stirring and the mixture kept at 50° for 2 hr. Cold water was added and the benzene layer washed with sodium bicarbonate solution and water, dried and concentrated; from benzene–petroleum ether colorless needles of m.p. 172° (lit.[6] 165–166°), yield 6.1 g. (87%); ultraviolet spectrum (in ethanol): 238 mμ (5.01); inflection at 300 mμ (3.76); 331 mμ (2.98).

Anal. Calcd. for $C_{22}H_{16}Br_2$: C, 60.0; H, 3.7. Found: C, 60.3; H, 4.0.

(b) The solution of 2.8 g. of 3,3'-dimethyl-2,2'-dinaphthyl (III, R = CH_3) in 100 ml. of carbon tetrachloride was refluxed for 6 hr. with 3.6 g. of NBS and a trace of benzoyl peroxide. The product was filtered and the solution concentrated; from benzene–petroleum ether, m.p. 172°, yield 3.5 g. (75%).

9,10-Dihydro-2,3,6,7-dibenzophenanthrene (**VIII**).—The reaction between lithium phenyl and the dibromo compound III (R = CH_2Br) was carried out in the same manner as described by Badger, *et al.*[6] VIII was obtained in 37% yield from benzene, m.p. 137–138° (lit.[6] 140–141°); ultraviolet spectrum (in alcohol): 231 mμ (4.63); 264 (4.68); 276 (4.48); 279 (4.49); 319 (3.82).

Anal. Calcd. for $C_{22}H_{16}$: C, 94.7; H, 5.3. Found: C, 94.3; H, 6.0.

2,3,6,7-Dibenzophenanthrene (I).—In an atmosphere of nitrogen, 0.5 g. of VIII and 0.5 g. of palladium–charcoal (10%) were heated at 350° for 4 hr. The product was extracted with hot benzene and the residue of the solution recrystallized from the same solvent; yellow needles of m.p. 257°, yield 0.45 g. (90%); ultraviolet spectrum (in alcohol): 260 mμ (4.83); 305 (4.70); 318 (4.90); 333 (4.57); 343 (4.34); 349 (4.42); 360 (4.28); 380 (2.70); 392 (2.57); 403 (2.78); 415 (2.45); 427 (2.76).

Anal. Calcd. for $C_{22}H_{14}$: C, 95.0; H, 5.0. Found: C, 94.8; H, 5.4.

The dipicrate, prepared in benzene solution and recrystallized from benzene, formed orange-red needles of m.p. 184°, as indicated in the literature.[9]

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(8) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," No. 309, John Wiley and Sons, New York, N. Y., 1951. The main absorption bands of 2,2'-binaphthyl are 254 mμ (log ε 4.95) and 305 mμ (4.25).

(9) E. Clar and F. John, ref. 1.

JERUSALEM, ISRAEL

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

cis-Hydroxylation of a Synthetic Steroid Intermediate with Iodine, Silver Acetate and Wet Acetic Acid

BY R. B. WOODWARD AND F. V. BRUTCHER, JR.[1]

RECEIVED AUGUST 23, 1957

Iodine, silver acetate and wet acetic acid oxidize the 6,7-double bond of *dl-anti-trans*-4,4a,4b,5,8,8a-hexahydro-1,8a-dimethyl-2(3H)phenanthrone (I) to give, after hydrolysis, a β-*cis*-glycol IVc in 71% yield and an α-*cis*-glycol in 2.5% yield. This reagent offers a method for producing in quantity the opposite *cis*-glycol stereoisomer compared with that derived from osmium tetroxide hydroxylation.

During recent steroid total synthesis work,[2] osmium tetroxide was used with success in *cis*-hydroxylating *dl-anti-trans*-4,4a,4b,5,8,8a-hexahydro-1,8a-dimethyl-2(3H)phenanthrone (I). Since this reagent possesses certain undesirable characteristics, we later developed a new *cis*-hydroxylation technique which has the unique feature of producing the opposite *cis*-glycol stereoisomer compared with that derived from osmium tetroxide. This paper describes our reagent and discusses its mechanism of hydroxylation.

We have found that when I is treated in acetic acid with iodine (1.05 equivalents), silver acetate (2.25 equivalents) and water (1.0 equivalent) and finally heated at 90–95° for three hours, oxidation

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(1) Dept. of Chemistry, University of Pennsylvania, Phila. 4, Pa.

(2) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, THIS JOURNAL, **74**, 4223 (1952).