[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

The Synthesis of 1-Bromobenzo[c]phenanthrene[1]

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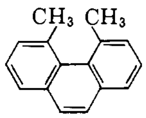
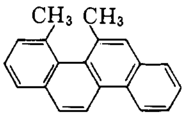
The synthesis of 1-bromobenzo[c]phenanthrene starting from *o*-bromobenzaldehyde is described.

For many years, work in this Laboratory has had as a goal the synthesis of highly strained polycyclic aromatic hydrocarbons. At first, the synthesis of a strained compound such as 4,5-dimethylphenanthrene (I) was of primary interest since difficulties met in attempts to prepare I led certain investigators[3] to doubt that such a compound could be made. However, the synthesis of 4,5-dimethylchrysene[4] (II) showed that such strained compounds are capable of existence and synthesis.

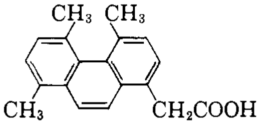


I

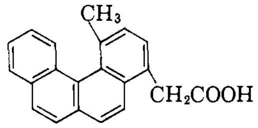


II

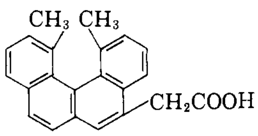
Theoretical interest in this type of hydrocarbon was stimulated by the discoveries that 1,4,5-trimethyl-8-phenanthrylacetic acid[5] (III) and 1-methyl-4-benzo[c]phenanthrylacetic acid[6] (IV) could be resolved. More stable (optically speaking) and more highly asymmetric examples of this type of optically active molecule[7] have been found in 1,12-dimethyl-5-benzo[c]phenanthrylacetic acid[8] (V) and hexahelicene[9]



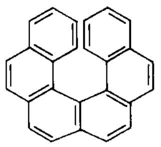
III, $[\alpha]_D$ 2.4°



IV, $[\alpha]_D$ 2.1°



V, $[\alpha]_D$ 348°



VI, $[\alpha]_D$ 3707°

There still remains much of interest to be done in this field and we are presently studying several aspects. The research herein reported illustrates two areas: first, the synthesis of highly strained polynuclear aromatic nuclei containing functional groups in various positions on these nuclei; and second, the study of the effect of strain on the chemical properties of the functions involved.

In this paper we report the synthesis of 1-bromobenzo[c]phenanthrene (XIV) by the sequence of reactions outlined in the chart. This is the first unambiguous synthesis of a highly strained polycyclic aromatic compound containing a functional group (bromine) on the nucleus.[10] The bromine occupies the most crowded position possible in this ring system. We hope to prepare other isomeric bromides and to compare their reactivities in reactions typical of aromatic bromo compounds. In the only reaction studied with XIV, the bromine atom was replaced readily by heating with cuprous cyanide in N-methyl-2-pyrrolidone to yield 1-cyanobenzo[c]phenanthrene in 71% yield.

Several points in connection with the synthesis are noteworthy. Initially, *o*-bromobenzaldehyde was condensed with diethyl malonate to yield diethyl *o*-bromobenzalmalonate in 88% yield. However, since conditions could not be found for the addition of phenylmagnesium bromide to this ester in high yield,[8] the route through the cyanoesters VII and VIII was tried and found excellent as in another case.[11] The product VIII obtained was a mixture of stereoisomers, which could be hydrolyzed to the malonic acid IX in good yield by long heating with 25% ethanolic potassium hydroxide. Attempts to hydrolyze VIII by heating with 10% sodium hydroxide in ethylene glycol at high temperatures (170–185°) were less successful in yielding IX as some decarboxylation occurred.

The steps outlined in the chart were accomplished without undue difficulty until the reduction of XII to XIII. Although the reduction of XII by either lithium aluminum hydride, or by the Meerwein–Ponndorf–Verley method, yielded quantitatively material in which no carbonyl group was detectable by infrared spectral analysis, it was not possible to isolate by direct crystallization material which gave acceptable carbon–hydrogen analyses.[12] Furthermore, the products all melted over wide ranges. Attempts to obtain a crystalline dihydrobromobenzo[c]phenanthrene by dehydration of the crude diol mixtures were unsuccessful. However, treatment of the crude diol XIII with iodine in xylene under reflux for very long periods of time (120 hours) afforded the aromatic bromo compound

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[1] The work herein reported was supported in part by a grant from the Office of Ordnance Research and Development under contract No. DA-33 019-ORD-1910, Project No. TB2-0001 (820).

[2] This work is described in more detail in the Ph.D. Thesis of Donald K. Phillips, The Ohio State University, 1958.

[3] See ref. 14 and 15 in ref. 4 following.

[4] M. S. Newman, THIS JOURNAL, **62**, 2295 (1940); see also ref. 16–19 in this paper.

[5] M. S. Newman and A. S. Hussey, *ibid.*, **69**, 978, 3023 (1947).

[6] M. S. Newman and W. B. Wheatley, *ibid.*, **70**, 1913 (1948).

[7] This type of optical activity is termed "optical activity due to intramolecular overcrowding"; see F. Bell and D. H. Waring, *J. Chem. Soc.*, 2689 (1949).

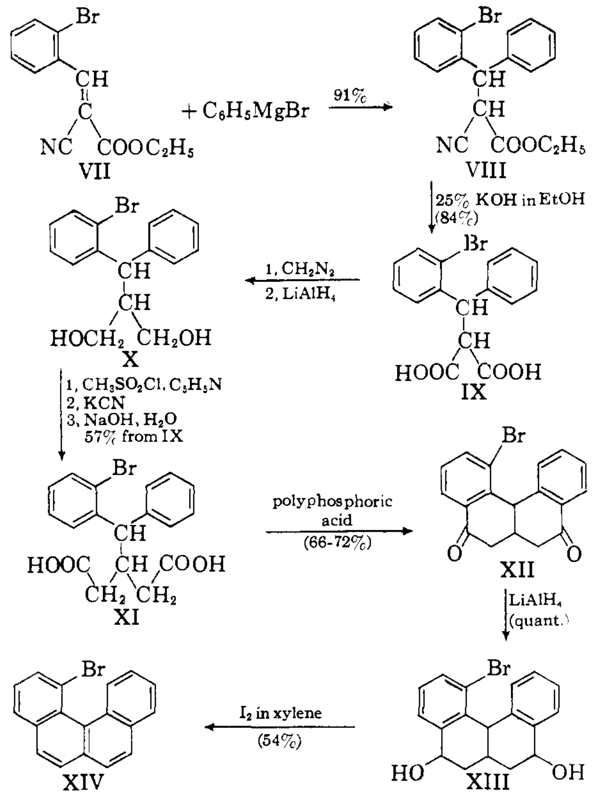
[8] (a) M. S. Newman and R. M. Wise, *ibid.*, **78**, 450 (1956); (b) M. S. Newman and M. Wolf, *ibid.*, **74**, 3225 (1952).

[9] M. S. Newman and D. Lednicer ,THIS JOURNAL, **78**, 4765 (1956).

[10] (a) D. E. Adelson and M. T. Bogert, *ibid.*, **59**, 1776 (1937), claimed to have synthesized 1,2-dicarboxy-5-isopropyl-9-methylbenzo[c]phenanthrene, but this structure for their compound has been shown to be incorrect by L. V. Thoi and A. Belloc, *Compt. rend.*, **239**, 500 (1954). (b) The synthesis of 1-acetoxy-4-methylbenzo[c]phenanthrene has been reported by C. Djerassi and T. T. Grossnickle, THIS JOURNAL, **76**, 1741 (1954), but its structure has not been proved.

[11] M. S. Newman and H. R. Flanagan, *J. Org. Chem.*, **23**, 796 (1958).

[12] A pure sample was obtained by formation of the crystalline dicarbethoxy derivative and subsequent hydrolysis.



XIV directly in 54% yield.[13] This process is puzzling since treatment of the non-crystalline residues from which XIV was obtained with dehydrogenating agents has not afforded further appreciable amounts of XIV. The yield of XIV from diol was sensitive to the amount of iodine used as well as the concentration of reactants and time of heating. The iodine cannot be the oxidizing agent as the optimal concentration was far too low.

That the compound XIV was in reality the fully aromatic compound was established by analyses of XIV and of its 2,4,5,7-tetranitrofluorenone complex,[14] by comparison of its ultraviolet absorption spectrum with those of benzo[c]phenanthrene[15] and 1-methylbenzo[c]phenanthrene,[15] and by n.-m.r. spectroscopy.[16]

By heating a solution of XIV and an excess of dry cuprous cyanide in N-methyl-2-pyrrolidone[17] at reflux (202°) for one hour a 71% yield of 1-cyanobenzo[c]phenanthrene was obtained. The use of N-methyl-2-pyrrolidone as a solvent in the Rosenmund–von Braun nitrile synthesis is to be looked into further in view of previous observations about this nitrile synthesis.[18] We hope to be able to determine the relative reactivity of the isomeric bromobenzo[c]phenanthrenes, as well as bromo derivatives of other strained polynuclear hydrocarbons, in this nitrile synthesis since cuprous cyanide is soluble in hot N-methyl-2-pyrrolidone.

Experimental[19]

o-Bromobenzaldehyde was prepared essentially as described for *p*-bromobenzaldehyde.[20] Purification by means of the sodium bisulfite addition compound afforded *o*-bromobenzaldehyde, b.p. 100–104° (8–9 mm.), in 58% over-all yield.

Diethyl *o*-Bromobenzalmalonate.—After a solution of 180 g. of *o*-bromobenzaldehyde, 160 g. of diethyl malonate, 6 g. of benzoic acid, 7 ml. of piperidine and 500 ml. of benzene had been distilled into a column topped with a phase-separating head for 19 hours (2 ml. of piperidine added after 11 hours), 17.5 ml. of water layer (97%) had accumulated. After an acid wash, the reaction mixture was treated in the usual manner. Distillation afforded 280 g. (88%) of diethyl *o*-bromobenzalmalonate, b.p. 178–181° at 1 mm. On triturating a small amount with Skellysolve F and recrystallizing from the same solvent, this bromoester was obtained as colorless crystals, m.p. 42.6–43.5° cor.; infrared absorption; 5.79(s) C=O, 6.10(s) C=C (KBr wafer).

Anal. Calcd. for $C_{14}H_{15}O_4Br$: C, 51.4; H, 4.6; Br, 24.4. Found: C, 51.0; H, 4.7; Br, 24.1.

Ethyl *o*-Bromobenzalcyanoacetate (VII).—A reaction similar to the above involving 168 g. of *o*-bromobenzaldehyde, 105 g. of ethyl cyanoacetate, 600 ml. of benzene, 1 g. of benzoic acid and 5 ml. of piperidine yielded 94% of the theoretical water after 7 hours. After the usual treatment 232 g. (91%) of VII, b.p. 148–150° (0.5 mm.), was obtained as a yellow oil which soon solidified. Recrystallization from Skellysolve C yielded colorless needles of VII, m.p. 68.9–69.3°, cor., infrared absorption, 4.53(w) CN, 5.75(s) C=O, 6.20(s) C=C (KBr wafer).

Anal. Calcd. for $C_{12}H_{10}O_2NBr$: C, 51.4; H, 3.6; N, 5.0; Br, 28.5. Found: C, 51.2; H, 3.7; N, 4.9; Br, 28.1.

***o*-Bromobenzalmalononitrile.**—As above, refluxing of a solution of 20 g. of *o*-bromobenzaldehyde, 7.1 g. of malononitrile, 0.5 ml. of piperidine, 0.15 g. of benzoic acid and 300 ml. of benzene for 7 hours yielded 93% of the theoretical water. After the usual treatment the undistilled product was crystallized from ethanol-water to yield 71% of dinitrile,[21] m.p. 89–91°; infrared absorption, 4.50(m) CN, 6.30–6.35(m-s) C=C (KBr wafer).[22] This dinitrile is a sternutator and skin irritant.[23]

Ethyl *o*-Bromobenzhydrylcyanoacetate (VIII).—To a well stirred solution of 257 g. of VII in 550 ml. of benzene was added dropwise 980 ml. of 1.04 *N* phenylmagnesium bromide in ether with cooling to keep the reaction mixture at 20–25°. After adding 100 ml. of benzene, solvent was distilled until the internal temperature was 60° (2 hr.). The homogeneous orange-red reaction mixture was held at 60° (2 hr.), and then poured with stirring into 750 ml. of cold *N* hydrochloric acid. After the usual treatment, distillation and redistillation yielded 298 g. (91%) of VIII (197 g., b.p. 196–199° (0.5 mm.), and 102 g., b.p. 188–189° at 0.2–0.3 mm.; infrared spectra of the two fractions of the distillate were nearly identical so both fractions were combined). On standing the mixture of stereoisomers of VIII crystallized. Several recrystallizations of a portion from

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[13] Dr. M. Okawara (at O.S.U.) noted a similar formation of 5,8-dimethylbenzo[c]phenanthrene on iodine-catalyzed dehydration of 5,8 - dimethyl - 5,8 - dihydroxy - 5,6,6a,7,8,12b - hexahydrobenzo[c] phenanthrene, although in smaller yield.

[14] M. S. Newman and W. B. Lutz, THIS JOURNAL, **78**, 2469 (1956).

[15] G. M. Badger and I. S. Walker, *J. Chem. Soc.*, 3238 (1954).

[16] We thank Dr. George M. Slomp of the Upjohn Co., Kalamazoo, Mich., for this determination and analysis of the results.

[17] We thank the Antara Chemicals Co. for a sample of N-methyl-2-pyrrolidone.

[18] C. F. Koelsch and A. G. Whitney, *J. Org. Chem.*, **6**, 795 (1941).

[19] All melting points are uncorrected unless otherwise stated. All microanalyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn. The term "treated in the usual manner" means that an ether-benzene solution of the products was washed with a saturated solution of sodium chloride and then filtered through a layer of anhydrous magnesium sulfate. The solvents then were removed by distillation under reduced pressure. Skellysolve F, b.p. 35–55°, Skellysolve B, b.p. 65–69°, and Skellysolve C, b.p. 90–97°, are aliphatic hydrocarbon solvents. All infrared absorption values are in μ; (s) = strong, (m) = medium, (w) = weak.

[20] G. H. Coleman and G. E. Honeywell, "Org. Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 89.

[21] H. G. Sturz and C. R. Noller, THIS JOURNAL, **71**, 2949 (1949), give a m.p. of 90.0–90.5°.

[22] Note that replacement of carbethoxy by cyano in the three analogous *o*-bromobenzal derivatives causes a shift toward longer wave length of the C=C absorption; compare with a similar series in D. G. I. Felton and S. F. D. Orr, *J. Chem. Soc.*, 2170 (1955).

[23] Compare B. B. Corson and R. W. Stoughton, THIS JOURNAL, **50**, 2825 (1928).

Skellysolve C yielded colorless VIII, m.p. 87.0–88.8° cor.; infrared absorption, 4.48(vw) CN, 5.73(s) C=O (Nujol mull).

Anal. Calcd. for $C_{18}H_{16}O_2NBr$: C, 60.4; H, 4.5; Br, 22.3. Found: C, 60.3; H, 4.5; Br, 22.2.

_o_-Bromobenzhydrylmalononitrile.—To a well-stirred ice cold solution of 9.08 g. of *o*-bromobenzalmalononitrile in 190 ml. of 1:1 ether–benzene was added dropwise 49 ml. of 1.19 *N* phenylmagnesium bromide in ether. After addition of 125 ml. of benzene solvent was distilled until the inside temperature was 65°. Heating and stirring of the non-homogeneous mixture was continued for 5 hours. After hydrolysis with cold hydrochloric acid and distillation there was obtained 9.2 g. of oil from which 7.2 g. (59%) of colorless *o*-bromobenzhydrylmalononitrile, m.p. 109–111°, was isolated by crystallization from chloroform–Skellysolve C. The analytical sample melted at 110.2–111.0° cor., infrared absorption at 4.45(w-m) CN (KBr wafer).

Anal. Calcd. for $C_{16}H_{11}N_2Br$: C, 61.8; H, 3.6; Br, 25.7. Found: C, 62.0; H, 3.6; Br, 25.5.

_o_-Bromobenzhydrylmalonic Acid (IX).—A solution of 101 g. of potassium hydroxide, 328 ml. of absolute ethanol and 55.0 g. of VIII was refluxed under nitrogen, the ammonia evolved being trapped in standard sulfuric acid. After 21.5 hours 91% (by titration) of the theoretical amount of ammonia had been evolved. The tan dipotassium salt that crystallized on cooling overnight was isolated by filtration and dissolved in 150 ml. of water. The solution was treated twice with activated charcoal and added dropwise with stirring to 130 ml. of 6 *N* hydrochloric acid maintained at −5 to 0° with an ice-salt-bath. The viscous semi-solid solidified after several hours in the cold and was filtered, washed several times with water and dried under vacuum to yield 45.2 g. (84%) of cream-colored IX, m.p. 167° dec. Several recrystallizations from acetone–benzene afforded colorless crystals, m.p. 168–170° dec., infrared absorption at 5.75–5.80(triplet, s) C=O (KBr wafer).

Anal. Calcd. for $C_{16}H_{13}O_4Br$: C, 55.0; H, 3.8; Br, 22.9; neut. equiv., 175. Found: C, 55.4; H, 3.8; Br, 22.6; neut. equiv., 173, 174.

Dimethyl _o_-Bromobenzhydrylmalonate.—An ice-cold solution of diazomethane[24] (from 46.0 g. of N-methyl-N-nitrosourea) in ether was added slowly to an ice-cold solution of 34.9 g. of IX in 100 ml. of methanol. After the usual workup and one recrystallization from methanol–water 33.2 g. (88%) of colorless needles, m.p. 87–90°, and 1.73 g. of a tan oil were obtained. Several additional recrystallizations from methanol–water afforded colorless needles, m.p. 91.7–92.6° (cor.); infrared absorption at 5.68(s) C=O, 5.74(shoulder, s) C=O (KBr wafer).

Anal. Calcd. for $C_{18}H_{17}O_4Br$: C, 57.3; H, 4.5; Br, 21.2. Found: C, 57.3; H, 4.5; Br, 21.0.

2-(_o_-Bromobenzhydryl)-1,3-propanediol (X).—The dimethyl ester of IX (31.0 g.) was treated with 8.0 g. of lithium aluminum hydride in 425 ml. of ether at reflux for 13 hours. After the usual workup, 24.2 g. (92%) of a very viscous oil, b.p. 221–236° (1.5 mm.), infrared absorption at 2.9–3.0(s) OH, ($CHCl_3$), was obtained. All attempts to crystallize the diol were unsuccessful, but this material was suitable for use in the next step.

3-(_o_-Bromobenzhydryl)-glutaric Acid (XI).—The above glycol X (23.7 g.) was converted essentially as described[8a] into 35.1 g. (theory, 35.2 g.) of viscous light yellow oily **2-(_o_-bromobenzhydryl)-1,3-propanediol bis-(methanesulfonate)**. The infrared spectrum of the oil showed no OH peak. A small portion of the oil after long cooling yielded light tan crystals, m.p. 110–114°, infrared absorption at 7.35(s) and 8.5(s) $ROSO_2OR$ (KBr wafer).[25] The analytical sample, recrystallized several times from chloroform–Skellysolve B, melted at 111.4–114.0° (cor.).

Anal. Calcd. for $C_{18}H_{21}O_6BrS_2$: C, 45.3; H, 4.4. Found: C, 45.2; H, 4.5.

The bis-methanesulfonate (34.9 g.) was converted into crude bis-nitrile (24.5 g.) as described before.[8a] The crude red-brown oil had infrared absorption at 2.9(w) NH, and 5.9(s) C=O, which indicated that some hydrolysis of the dinitrile had occurred.

Hydrolysis of 23.9 g. of the above oil as before[8a] yielded solid sodium salts, which, on solution in water and acidification, afforded 12.8 g. of cream-colored diacid, m.p. 182–184°.

The red-brown glycol filtrate from the solid sodium salts was poured into 500 ml. of water and the solution was filtered and washed with 1:1 ether–benzene. Addition of the solution to 200 ml. of cold 6 *N* hydrochloric acid yielded 8.4 g. of tan-colored solid, m.p. 170.5–177.0°. Recrystallization from chloroform–Skellysolve B yielded 6.2 g. of white crystals, m.p. 182.5–185.0°. A total of 19.0 g. (70% from X) of XI, m.p. 182–185°, was obtained. The analytical sample, recrystallized several times from chloroform–Skellysolve B, melted at 187.8–188.6° (cor.), infrared absorption at 5.84(s) C=O (Nujol mull).

Anal. Calcd. for $C_{18}H_{17}O_4Br$: C, 57.3; H, 4.5; Br, 21.2; neut. equiv., 189. Found: C, 57.1, 57.2; H, 4.5, 4.6; Br, 21.3, 21.3; neut. equiv., 187, 186.

1-Bromo-5,8-diketo-5,6,6a,7,8,12b-hexahydrobenzo[c]-phenanthrene (XII).—A mixture of 20.00 g. of finely ground XI, m.p. 184–186°, and 400 g. of polyphosphoric acid[26] was vigorously stirred at 130–135° for 90 minutes. During this time the color of the mixture changed from colorless to deep red to brown. The hot mixture was poured on 1500 g. of ice and water. The crude ketone was collected, dissolved in 1:1 ether–benzene, and the deep red solution was washed twice with water. On adding 10% potassium carbonate solution and shaking a tan solid separated mainly confined in the aqueous layer. The lower layer was separated and the organic layer was washed two additional times with carbonate solution, which removed all of the solid from the organic layer. The organic layer was treated in the usual manner. The resulting orange-red oil crystallized readily from ethanol to yield 12.91 g. of tan needles, m.p. 174.5–178.0°, and 2.77 g. of yellow-brown crystals, m.p. 150–176°. One recrystallization of the first crop from ethanol afforded 12.33 g. (68%) of light tan XII, m.p. 177.0–178.5°, infrared absorption at 5.90(s) C=O (Nujol mull). The analytical sample, colorless prisms, m.p. 179.3–179.8° cor., was obtained by several recrystallizations from ethanol.

Anal. Calcd. for $C_{18}H_{13}O_2Br$: C, 63.4; H, 3.8; Br, 23.4. Found: C, 63.3; H, 4.1; Br, 23.3.

The second crop of crystals, m.p. 150–176°, was not readily purified. Several activated charcoal treatments and recrystallizations afforded 2.56 g. of light yellow crystals, m.p. 149–170°, infrared absorption at 5.90(s) C=O (Nujol mull).

When 2.50 g. of XI was treated with 50 g. of polyphosphoric acid at 115–120° for 35 minutes, a yield of 27% of sharp-melting diketone XII was obtained, along with 1.19 g. of cream-colored solid that precipitated upon addition of potassium carbonate solution to the crude reaction product dissolved in 1:1 ether–benzene. The solid was dissolved in water and added to cold 6 *N* hydrochloric acid to yield 0.99 g. of pale tan solid, m.p. 151–154°. Several recrystallizations from chloroform–Skellysolve B afforded colorless crystals, m.p. 152.9–154.0° (cor.). The infrared spectrum (KBr wafer) showed bands at 5.81(s) C=O. 5.86(s) PhCO, 12.2(w) 1,2,3-trisubst. phenyl,[27] 13.2(s) *o*-subst. phenyl,[27] 13.5(w), 14.1(w.m) monosubst.- and or 1,2,3-trisubst.-phenyl[27] indicating that the solid was mainly, **1,2,3,4-tetrahydro-1-_o_-bromophenyl-4-keto-2-naphthaleneacetic acid.**

Anal. Calcd. for $C_{18}H_{15}O_3Br$: C, 60.2; H, 4.2; Br, 22.3; neut. equiv., 359. Found: C, 59.8; H, 4.5; Br, 22.3; neut. equiv., 355.

1-Bromo-5,8-dihydroxy-5,6,6a,7,8,12b-hexahydrobenzo-[c]phenanthrene (XIII).—A solution of 97.6 g. of distilled aluminum isopropoxide[28] in 500 ml. of dry isopropyl alcohol and 61.1 g. of XII was refluxed for 0.5 hr., and then slowly distilled through a 20-cm. packed column (glass helices). After 13 hours, 300 ml. of solvent had distilled and the distillate gave a negative test with 2,4-dinitrophenylhydrazine reagent.[26] The solution was refluxed overnight, 100 ml. of

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[24] F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

[25] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954, p. 300.

[26] A sample of polyphosphoric acid was generously supplied by the Victor Chemical Co., Chicago, Ill.

[27] Ref. 25, p. 65–67.

[28] A. L. Wilds, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 198.

solvent was distilled, and the warm solution was poured into 2000 g. of ice and water containing 100 ml. of concentrated sulfuric acid. Filtration yielded 61.9 g. (expected, 61.8 g.) of white solid, m.p. 110–184°, infrared absorption (Nujol mull) at 2.90–3.05(s) OH but no band near 5.9. Crystallization of 6.08 g. of the diol from chloroform yielded 3.56 g. of fluffy white needles, m.p. 178–215°, 1.82 g. of light tan solid, m.p. 110–128°, 0.35 g. of light tan solid, m.p. 128–196°, and 0.34 g. of tan oil.[29] Repeated recrystallization of the diol raised the melting point considerably, but no satisfactory carbon–hydrogen analyses were obtained.

The dicarbethoxy derivative[30] of XIII was prepared: to a solution of 1.00 g. of the diol, m.p. 178–215°, in 20 ml. of dry pyridine cooled in an ice-bath was added dropwise with swirling 3 ml. of ethyl chloroformate (distilled Eastman Kodak Co. white label). During the addition the mixture turned from colorless to pink to deep red and a white solid formed. The mixture was allowed to stand at room temperature for five hours and then refluxed gently for one hour. The cooled mixture was poured onto 100 g. of ice and water and stirred well. After having been cooled in the refrigerator overnight, filtered, and dried, the white solid was crystallized from ethanol to yield 1.14 g. (80%) of small colorless plates, m.p. 156–159°. One recrystallization of the first crop from ethanol yielded 1.03 g. (72.5%) of the diester, m.p. 159–160°, infrared absorption (Nujol mull) at 5.72(s) C=O in $ROCO_2R$. The analytical sample, recrystallized several times from ethanol, melted at 159.8–161.3° (cor.).

Anal. Calcd. for $C_{24}H_{25}O_6Br$: C, 58.9; H, 5.1; Br, 16.3. Found: C, 58.8, 58.7; H, 5.1, 5.2; Br, 16.1, 16.2.

Alkaline hydrolysis of 0.150 g. of the diester yielded 0.100 g. of white solid, m.p. 206–222°. Three recrystallizations from warm N-methyl-2-pyrrolidone–water afforded 0.07 g. of XIII as short colorless fibers, m.p. 220–223°.

Anal. Calcd. for $C_{16}H_{17}O_2Br$: C, 62.6; H, 5.0; Br, 23.2. Found: C, 62.5; H, 5.0; Br, 23.3.

1-Bromobenzo[c]phenanthrene (XIV).—A mixture of 1.997 g. of XIII, m.p. 120–193°, 5 ml. of xylene (distilled Mallinckrodt analytical reagent) and 8 mg. of iodine was heated to the reflux temperature. Within a minute after refluxing started, the iodine color disappeared and water began to collect on the sides of the condenser. After 15 minutes all of the diol had dissolved leaving a light yellow solution. After the mixture had refluxed for 24 hours, an additional 4 mg. of iodine was added to the yellow solution. The iodine color again rapidly disappeared. After having been refluxed for a total of 120 hours, the deep red-brown solution was diluted with 1:1 ether benzene, washed with sodium bisulfite solution and treated in the usual manner. The resulting yellow-brown oil was purified by chromatography over alumina using first chloroform and then Skellysolve B. The desired product was contained in the first fractions to be eluted and was characterized by a dark gray-violet fluorescent band on the column when illuminated with ultraviolet light. Crystallization from chloroform–Skellysolve B yielded 1.08 g. of yellow crystals, m.p. 139.0–143.5°, and a yellow oil. Several recrystallizations of the crystals from chloroform–Skellysolve B afforded 0.96 g. (54%) of yellow XIV, m.p. 144–146°. A sample of XIV, purified for analysis by several recrystallizations from chloroform–Skellysolve B and then vacuum sublimation, formed pale yellow crystals, m.p. 146.8–147.3° (cor.); λ_{max}^{EtOH} 225 mμ (log *E* 4.66), 289 (4.76), 323 (3.96), 363 (2.61); λ_{min} 243 (4.00), 318 (3.94), 356 (2.56); points of inflection, 249 (4.03), 259 (4.18), 269 (4.39), 282 (4.66), 338 (3.62), 376 (2.34) and 382 (2.27).

Anal. Calcd. for $C_{18}H_{11}Br$: C, 70.4; H, 3.6; Br, 26.0. Found: C, 70.4, 70.2; H, 3.7, 3.6; Br, 26.2, 26.3.

The 2,4,5,7-tetranitrofluorenone complex[14] of XIV was prepared by mixing a hot solution of 100 mg. of XIV in acetic acid with a hot solution of 130 mg. of the nitro compound in acetic acid, concentrating the solution and cooling. The dark wine-red needles that crystallized were recrystallized several times from acetic acid to a constant m.p. of 192.3–193.5° (cor.). The nuclear magnetic resonance spectrum[16] of XIV showed no non-aromatic hydrogens.

Anal. Calcd. for $C_{31}H_{15}O_9N_4Br$: C, 55.8; H, 2.3; N, 8.4; Br, 12.0. Found: C, 56.1; H, 2.6; N, 8.6; Br, 12.0.

Various other methods of dehydration of XIII were tried. Thermal dehydration, thermal dehydration in the presence of an iodine crystal or thermal dehydration in the presence of potassium bisulfate all led to non-hydroxylic but high melting substances, which could not be converted by standard methods to XIV. Treatment of XIII with phenyl isocyanate, thionyl chloride in pyridine or pyrolysis of the dicarbethoxy derivative gave some non-crystalline dehydrated material but the results did not appear promising.

1-Cyanobenzo[c]phenanthrene.—A mixture of 0.500 g. of XIV, 0.258 g. of dry cuprous cyanide and 2.5 ml. of distilled N-methyl-2-pyrrolidone[17] was refluxed (b.p. 202°) for one hour. During this time the dark red-brown solution became dark brown in color and a brown precipitate formed. The cooled mixture was processed in a standard way to yield an oil which was chromatographed on alumina using benzene as eluent. The first 600 ml. contained the nitrile which had a brilliant violet fluorescence under ultraviolet light. Concentration of the solution and crystallization from benzene–ethanol yielded 0.310 g. of flat cream-colored crystals, m.p. 167–169°. Several recrystallizations from benzene–ethanol afforded 0.292 g. (71%) of flat cream-colored crystals, m.p. 169–171°. The analytical sample, recrystallized several times from benzene–ethanol, melted at 171.2–172.0° (cor.), infrared absorption 4.52-(w-m) CN (KBr wafer).

Anal. Calcd. for $C_{19}H_{11}N$: C, 90.1; H, 4.4; N, 5.5. Found: C, 90.4; H, 4.3; N, 5.5.

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(29) Lithium aluminum hydride reduction of the diketone resulted in the same kind of mixtures.

(30) L. F. Fieser, J. E. Herz, M. W. Kloko, M. A. Romero and T. Utne, THIS JOURNAL, **74**, 3309 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE]

Synthetic Studies on Resin Acids. III.[1] Synthesis of a Stereoisomer of Desisopropyldehydroabietic Acid

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The synthesis of an isomer of 1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylic acid is described and the stereochemistry of this substance is discussed.

For the synthesis of the tricarbocyclic resin acids represented by abietic acid and its congeners, the tricyclic ketone I appears to be a potentially useful intermediate. This ketone was first synthesized by Stork, *et al.*,[3] by the cyclization of 2-(β-phenethyl)-3-methyl-Δ^2-cyclohexenone with phosphoric acid.

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(1) (a) N. N. Saha, B. K. Ganguly and P. C. Dutta, *Chemistry & Industry*, 412 (1956). Presented at a symposium at the Forest Research Institute, Dehradun, India, October 6, 1955. (b) Part II, U. Ghatak, N. N. Saha and P. C. Dutta, THIS JOURNAL, **79**, 4487 (1957).

(2) Communications regarding this paper should be sent to this author.

(3) G. Stork and A. Burgstahler, THIS JOURNAL, **73**, 3544 (1951).