orated to 1 cc., treated with darco, and cooled. Filtering the mixture yielded 0.7 g., 83%, of white crystals of 4-carboxyazelaic acid. Several recrystallizations from water gave a sample of melting point[3] 114–115°, resolidifying and remelting at 122–124°. It contained a persistent trace of alkali, as judged by the alkaline residue it left when ignited. A sample, dissolved in water, passed through Amberlite IR-100 (hydrogen form),[4] and recrystallized several times, yielded an analytical sample, m.p. 114–115°, but without resolidifying.

Anal. Calcd. for $C_{10}H_{16}O_6$ (232.2): C, 51.68; H, 6.95. Found: C, 51.39; H, 6.88.

A sample of the acid was converted[5] into **tris-*p*-bromophenacyl 4-carboxyazelate,** which was recrystallized several times from dioxane or dioxane–ethanol mixtures, and melted[3] at 124.5–125.5°. Two different samples were analyzed.

Anal. Calcd. for $C_{34}H_{31}Br_3O_9$ (823.41): C, 49.60; H, 3.80. Found: C, 49.83, 49.57; H, 3.73, 3.77.

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(3) The melting points were determined with Anschütz thermometers in a Hershberg melting-point apparatus.

(4) Supplied by the Resinous Products and Chemical Co., Washington Square, Philadelphia.

(5) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 157.

CONVERSE LABORATORY
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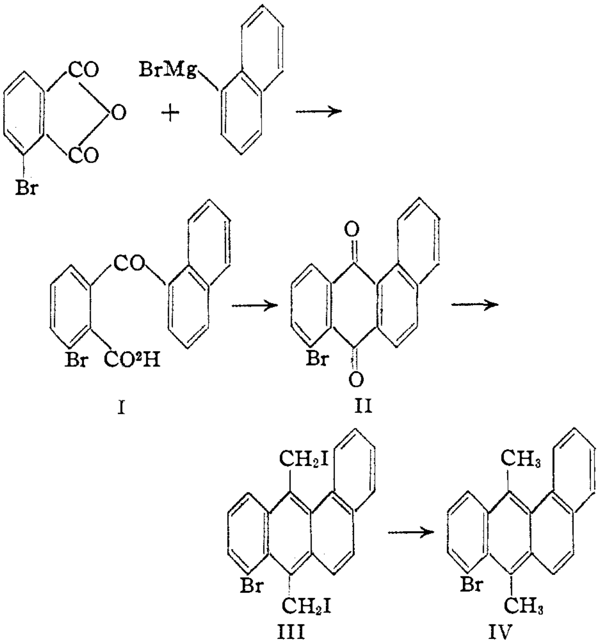
Derivatives of 9,10-Dimethyl-1,2-benzanthracene

BY JOHN L. WOOD[1] AND LOUIS F. FIESER

Tests for carcinogenicity of 5-bromo- and 5-cyano-9,10-dimethyl-1,2-benzanthracene have been reported[2] but the synthesis of the compounds ash remained undescribed. Condensation of α-naphthylmagnesium bromide with 3-bromophthalic anhydride[3] gave a mixture from which we isolated 60% of 2-(α-naphthoyl)-6-bromobenzoic acid (I) and 15% of 2-(α-naphthoyl)-3-bromobenzoic acid. The structure of I was established by decarboxylation to a ketone identical with that synthesized from *m*-bromobenzoyl chloride and α-naphthylmagnesium bromide. Ring closure of I by the method of Badger and Cook[4] gave 5-bromo-1,2-benzanthraquinone (II), as evidenced by conversion of II to 1,2-benzanthracene by reduction with stannous chloride and then with zinc, alkali and toluene. The quinone II was converted into 5-bromo-9,10-dimethyl-1,2-benzanthracene (IV) through III by the method of Sandin and Fieser[5]; IV afforded the 5-cyano derivative on reaction with cuprous cyanide in pyridine.



Experimental

2-(α-Naphthoyl)-6-bromobenzoic Acid (I).—The Grignard reagent from 24.2 g. of α-bromonaphthalene diluted with 200 cc. of dry benzene was added to 26 g. of *m*-bromophthalic anhydride[3] in 350 cc. of benzene. After refluxing for one hour and processing in the usual way, crystallization of the reaction product from benzene–hexane gave 39 g. of a mixture, m.p. 124–155°. Fractionation from benzene gave 24.2 g. (60%) of 2-(α-naphthoyl)-6-bromobenzoic acid (I), m.p. 160–162°; nine further crystallizations from benzene–hexane gave slightly yellowish rhombs, m.p. 160.8–161.1°.

Anal. Calcd. for $C_{18}H_{11}O_3Br$: C, 60.85; H, 3.12. Found: C, 61.31; H, 3.19.

Decarboxylation was accomplished by heating 0.5 g. of the keto acid with a small amount of its copper salt at 270° for 15 minutes and subliming the mixture at 5 mm. pressure and at temperatures up to 310°; crystallization of the sublimate from methanol gave colorless crystals of **α-(*m*-bromobenzoyl)-naphthalene,** m.p. 91–92°. This material did not depress the m.p. of a sample synthesized from 5 g. of *m*-bromobenzoic acid (treated with thionyl chloride) and the Grignard reagent from 4 g. of α-bromonaphthalene. The once crystallized product (2 g., 33%) melted at 87–90°; five crystallizations from methanol gave material of the constant m.p. 91.7–92.1°.

Anal. Calcd. for $C_{17}H_{11}OBr$: C, 65.61; H, 3.56. Found: C, 65.87; H, 3.98.

2-(α-Naphthoyl)-3-bromobenzoic acid was isolated as a companion of I in 15% yield (m.p. 223–224°). Four crystallizations from toluene gave yellowish rhombs, m.p. 222.9–223.9°.

Anal. Calcd. for $C_{18}H_{11}O_3Br$: C, 60.86; H, 3.12. Found: C, 60.48; H, 3.47.

5-Bromo-1,2-benzanthraquinone (II).—In accordance with the procedure of Badger and Cook,[4] 5 g. of I (m.p. 161°) was heated with 5 cc. of benzoyl chloride to 130° and 0.1 cc. of 95% sulfuric acid was added; gas was evolved at once and the solution became deep blue. After one hour at 130° the mixture was poured into a large excess of 3 *N* sodium hydroxide and a little ethanol was added to react with the excess benzoyl chloride. The resulting yellow precipitate on crystallization from ethyl acetate (Norit) afforded long, golden needles, m.p. 193° (2 g., 42%). Five crystallizations from ethyl acetate raised the m.p. to 194.4–194.6°.

Anal. Calcd. for $C_{18}H_9O_2Br$: C, 64.12; H, 2.69. Found: C, 63.90; H, 3.18.

Ring closure of the isomeric 2-(α-naphthoyl)-3-bromobenzoic acid by the same procedure also afforded II (m.p. 192–193°, 51% yield).

A mixture of 0.5 g. of II, 3 g. of stannous chloride, 2 cc. of 36% hydrochloric acid and 5 cc. of acetic acid was refluxed for one hour and the product was precipitated with water and refluxed with 1.2 g. of zinc dust, 20 cc. of 2 *N* sodium hydroxide and 5 cc. of toluene for 36 hours. The reaction mixture was diluted with water, extracted with benzene, and the extract passed through a tower of alumina and diluted with methanol. The colorless crystals that separated, m.p. 160–161° (30 mg.), did not depress the m.p. of authentic 1,2-benzanthracene.

5-Bromo-1,2-benzanthracene (IV).—A solution of 1 g. of pure II in 30 cc. of warm benzene was dropped into a stirred solution prepared by treating 1 g. of magnesium with excess

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(2) C. E. Dunlap and S. Warren, *Cancer Research*, **6**, 454 (1946).

(3) H. N. Stephens, THIS JOURNAL, **43**, 1950 (1921).

(4) G. M. Badger and J. W. Cook, *J. Chem. Soc.*, 802 (1939).

(5) R. O. Sandin and L. F. Fieser, THIS JOURNAL, **62**, 3098 (1940).

methyl iodide in ether–benzene and displacing the ether with benzene to a volume of 50 cc. After six hours, the solution was chilled and poured into an ice-cold mixture of 60 cc. of acetic acid and 12 cc. of hydriodic acid (sp. gr. 1.7) with stirring and ice cooling. Evaporation of the benzene in vacuum in a bath kept below 40° resulted in separation of yellow crystals of the iodo compound III, which were collected, after the mixture had stood overnight in the refrigerator, and washed with cold 90% acetic acid. A solution of the product (m.p. about 110° with liberation of iodine) in 25 cc. of pure dioxane was added to a warm mixture of 20 cc. of dioxane, 12 cc. of 36% hydrochloric acid and 2 g. of stannous chloride. The brown solution soon became light yellow; after being refluxed for 15 minutes it was poured into 250 cc. of hot water and the dioxane was removed by distillation. A crystalline precipitate (700 mg., m.p. 145°) resulted and on crystallization from benzene–methanol afforded 460 mg. (46%) of IV, m.p. 164.5–165.5°. After four more crystallizations the substance was obtained as greenish-yellow plates, m.p. 165.2–166°.

Anal. Calcd. for $C_{20}H_{15}Br$: C, 71.65; H, 4.51. Found: C, 71.79; H, 4.88.

5-Cyano-9,10-dimethyl-1,2-benzanthracene was obtained by heating IV (150 mg.) under reflux for six hours with a solution prepared by adding pyridine dropwise to a suspension of 150 mg. of cuprous cyanide in 4 cc. of nitrobenzene until the solid dissolved. The solution was poured into hot hydrochloric acid and the mixture was extracted exhaustively with benzene and the extract steam distilled. The residue was extracted with benzene and the very red solution passed through a column of alumina; the eluate was light yellow and on dilution with methanol gave 50 mg. (40%) of yellow, hair-like filaments, m.p. 158–158.5° (fluorescent in ultraviolet light).

Anal. Calcd. for $C_{21}H_{15}N$: C, 89.65; H, 5.37. Found: C, 89.68; H, 5.50.

CONVERSE MEMORIAL LABORATORY
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RECEIVED MAY 10, 1951

NEW COMPOUNDS

3-Isothiocyanocyclohexene and Derivative

3-Bromocyclohexene was prepared in 60% yield from cyclohexene and N-bromosuccinimide in purified carbon tetrachloride. The product was collected at 54–63° (10 mm.); n^{25}D 1.5300.

In a 200-ml. flask fitted with a stirrer and dropping funnel was placed a solution of 25.1 g. (0.309 mole) of dry, C.P. sodium thiocyanate in 85 ml. of absolute methanol. To this stirred solution 49.8 g. (0.309 mole) of 3-bromocyclohexene was added dropwise over a period of two hours. Little heat was evolved during the course of the reaction. The reaction mixture was stirred at room temperature for an additional two hours. The sodium bromide which separated was filtered from the reaction mixture, and the methanol removed from the filtrate by vacuum distillation. At this point more sodium bromide had separated. This was removed by filtration, and the solid washed with petroleum ether. The combined filtrate and washings were vacuum distilled. 3-Isothiocyanocyclohexene (32.8 g., 76%) was collected at 70–76° (3 mm.); n^{25}D 1.5565; d^{25} 1.068. When first distilled the material was colorless, but on standing it became a faint yellow color. Analysis of the product for isothiocyanate[1] showed it to be 98% isothiocyanate.

Anal. Calcd. for C_7H_9NS: C, 60.4; H, 6.5; N, 10.1; S, 23.0. Found[2]: C, 60.2; H, 6.6; N, 10.0; S, 23.0.

Upon reaction of the isothiocyanate with concentrated aqueous ammonia a thiourea, m.p. 133–134°, was readily obtained.

Anal. Calcd. for $C_7H_{12}N_2S$: C, 53.8; H, 7.7; N, 17.9. Found[2]: C, 53.8; H, 7.7; N, 17.8.

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[1] S. Siggia and J. G. Hanna, *Anal. Chem.*, **20**, 1084 (1948).

[2] Analysis by Dr. Carol K. Fitz, Melrose, Mass.

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RECEIVED APRIL 19, 1951

Some Fluorinated Propanes

1,2-Dibromo-1,1,2-trichloro-3,3,3-trifluoropropane.—A solution of 759 g. (4.75 moles) of bromine and 946.5 g. (4.75 moles) of 1,1,2-trichloro-3,3,3-trifluoropropene[1] was placed in a three-necked flask equipped with an internal water cooled coil, sealed stirrer and thermometer. The flask was illuminated for 96 hours with a G.E. AH-4 lamp, with the reactants maintained below 25°. Most of the unreacted starting material was pumped off at 60 mm. The pressure was then slowly reduced to 5 mm., yielding 855.4 (2.38 moles, 50% yield) of the saturated dibromide. It was recrystallized from ethanol–water, m.p. 151–152° (sealed tube). A carbon tetrachloride solution of the dibromide liberated bromine on exposure to ultraviolet light, indicating that the bromination is reversible at room temperature.

Anal. Calcd. for $C_3Br_2Cl_3F_3$: C, 10.03; Ag equiv.[2] (Br and Cl), 71.85. Found: C, 10.3; Ag equiv., 72.1.

2-Bromo-1,2-dichloro-1,1,3,3,3-pentafluoropropane and 2-Bromo-1,1,2-trichloro-1,3,3,3-tetrafluoropropane.—A mixture of 71.0 g. (0.198 mole) of 1,2-dibromo-1,1,2-trichloro-3,3,3-trifluoropropane, 0.198 mole of antimony trifluorodichloride[3] and 10 ml. of 1,1,2-trichloro-1,2,2-trifluoroethane (as solvent) was shaken in a steel bomb at room temperature for six hours, and at 120–130° for six hours. The reaction product was washed with dilute hydrochloric acid, water and dried over calcium chloride. On fractional distillation there was obtained 35.9 g. (64% yield) of 2-bromo-1,2-dichloro-1,1,3,3,3-pentafluoropropane, b.p. 90.1–91.8°, m.p. 23.5–24.5° (cooling curve), n^{26}D 1.3795 and 1.9 g. (3% yield) of 2-bromo-1,1,2-trichloro-1,3,3,3-tetrafluoropropane, b.p. 131–133°. The tetrafluoride was recrystallized from ethanol–water, 68–69° (sealed tube). The position of the entering fluorine atoms was deduced from the presence of bromine in each of the above compounds, coupled with the previous observations of perhalogenated propanes[4,5] that the chlorine atoms of the trichloromethyl group are replaced more readily by fluorine than the halogen atoms of the dichloromethylene group.

Anal. Calcd. for $C_3BrCl_2F_5$: C, 12.78; Ag equiv. (Cl and Br), 93.95. Found: C, 12.7; Ag equiv., 93.9. Calcd. for $C_3BrCl_3F_4$: C, 12.08; Ag equiv. (Cl and Br), 74.57. Found: C, 12.5; Ag equiv., 74.9.

RESEARCH LABORATORY
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SCHENECTADY, NEW YORK
MAURICE PROBER

RECEIVED FEBRUARY 17, 1951

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[1] Obtained from Halogen Chemicals, Inc., 616 King St., Columbia, S. C.

[2] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **13**, 882 (1948).

[3] "Organic Reactions," Vol. II, R. Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 61.

[4] A. L. Henne and Mary W. Renoll, THIS JOURNAL, **61**, 2489 (1939).

[5] A. L. Henne, A. M. Whaley and J. K. Stevenson, *ibid.*, **63**, 3478 (1941).