crystallizing the potassium salt. These crystals were well formed cubes, very dark red in color.

The powder diffraction pattern, taken with copper Kα X-rays (λ = 1.5418 Å.) corresponds to a face-centered cubic lattice with a = 10.445 ± 0.005 Å. With four molecules to the unit cell, the density is calculated to be 4.34 g./cm.$^{-3}$. The intensities of most of the reflections were estimated visually from a rotation photograph taken about the (100) axis. Weissenberg photographs were used to obtain several reflections absent or not resolved in the rotation pattern. The magnitudes of 95 independent structure factors (all that are permitted by the space group up to (sin θ)/λ = 0.64) were calculated from these data after correction for Lorenz, polarization, and velocity factors. No correction was made for absorption other than to average the results for equivalent reflections. The crystal was a cube with edges about 0.1 mm. long.

Preliminary calculations showed these data to be consistent with the structure

Space group O_h^5—Fm3m; $Z = 4$
4 Re in 4(a): (000) + F.C.
8 K in 8(c): ± ($^1/_4$ $^1/_4$ $^1/_4$) + F.C.
24 Br in 24(e): ± (x00; 0x0; 00x) + F.C.

with the parameter x approximately 0.25. Signs of the structure factors were calculated on this basis; only seven were negative. An optical Fourier summation of the electron density made according to Huggins[6] for a section through a rhenium atom and four bromine atoms showed the series to be sufficiently convergent to give well-resolved peaks for the atoms. A numerical summation of the same series along the edge of the unit cell (Fig. 1) showed the bromine maximum at x = 0.2410. A series containing the same terms but using coefficients calculated for x = 0.242 gave a maximum at 0.2436. If a "back-shift" correction of −0.002 is applied, the experimental result is 0.239 ± 0.004.[7] The probable error was estimated from the rate of change of a few structure factors of large indices with change in x.

The calculated values of F are based on atomic form factors from the "Internationale Tabellen."[8] No temperature correction was made. It is possible that the absorption error in part compensates the temperature effect, allowing reasonably good agreement throughout the range of diffraction angles. The percentage discrepancy, 100 $(\Sigma\,||F_{\text{obsd.}}| - |F_{\text{calcd.}}||)/\Sigma\,|F_{\text{obsd.}}|$, is 25% for x = 0.242, which is as good as was expected because of the crude visual estimates and the neglect of absorption and temperature corrections. In view of the simplicity of the structure, further refinement of the observations was not deemed necessary.

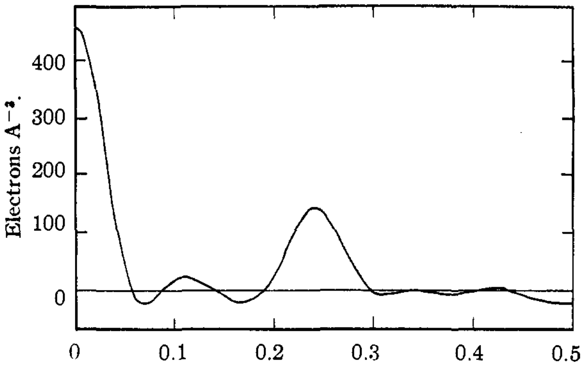

Fig. 1.—Electron density at (x00) in K_2ReBr_6. F_{000} is included in the calculation.

The bromine–rhenium distance in the bromorhenate ion is 2.50 ± 0.04 Å. If the covalent radius of bromine is taken[9] as 1.14 Å., the octahedral radius of rhenium is 1.36 Å., in good agreement with the value 1.38 Å. calculated in the same way from K_2ReCl_6.

We wish to thank Dr. Hugus for making available the crystals. This research was supported by the U. S. Atomic Energy Commission.

[6] M. L. Huggins, THIS JOURNAL, **63**, 66 (1941).

[7] We are indebted to Dr. V. Schomaker who independently derived the coefficients C_h from our tabulated values of F_{hkl}, and who computed the two series by a punched-card method. We checked his maxima by computing $d/dx\ \rho(x00) = -2\pi\Sigma hC_h \sin 2\pi hx$ for a few values of x near 0.24 for each series.

[8] "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Edwards Brothers, Ann Arbor, Michigan, 1944, II, pp. 572–573.

[9] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1942, p. 165.

DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
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4-Carboxyazelaic Acid

BY JOHN F. TINKER

The sodio derivative of 2-carbethoxycyclopentanone reacts with esters[1] of 4-bromobutyric acid in alcohol solution to yield esters of 4-carboxyazelaic acid.

4-Carboxyazelaic Acid (1,4,7-Tricarboxyheptane).—In a 500-cc. 3-necked flask, equipped with a Hershberg stirrer with a rubber seal, a reflux condenser with a drying tube, and a dropping funnel, was placed 8.0 g. (0.33 gram-atom) of metallic sodium; 80 cc. of anhydrous methanol was added dropwise, and the mixture stirred until the sodium had dissolved. Methyl 2-ketocyclopentanecarboxylate[2] (47.5 g. 0.33 mole) was added rapidly, the mixture stirred for a few minutes, and 60.5 g. (0.33 mole) of methyl 4-bromobutyrate[1] was added. The mixture was refluxed for 3 hours, and allowed to stand overnight. The mixture was poured onto 100 g. of ice in a 500-cc. separatory funnel, made basic with a little dilute alkali, and separated. The aqueous phase was extracted with three 100-cc. portions of chloroform, and the combined organic layers carefully fractionated. Nineteen grams of methyl adipate was obtained (b.p. 70–75° at 3 mm., refractive index 1.4277 at 24° sodium D line), and 56 g. (70% of theoretical) of trimethyl 4-carboxyazelate (b.p. 135–137° at 3 mm., n_D 1.4464 at 24°; d^{24}_4 1.088; molar refractivity calcd. 65.1, found 67.3). The triester has a single, sharp adsorption band in the carbonyl region of the infrared at 5.70 mμ, in dilute carbon tetrachloride solution. A sample redistilled for analysis through a short helix-packed column boiled at 121–123° (uncor.) at 0.3 mm. (bath temperature 170–175°).

Anal. Calcd. for $C_{13}H_{22}O_6$ (274.3): C, 56.92; H, 8.08. Found: C, 56.55; H, 7.69.

One gram of the triester was refluxed with 25 cc. of 2% hydrochloric acid until it had dissolved, the solution evap-

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[1] For the preparation of these esters see J. Tinker, *J. Org. Chem.*, in press.

[2] G. Komppa and A. Talvitie, *Ann. Acad. Sci. Finnicae*, Ser. A **57**, No. 15, 3 (1941); *C. A.*, **38**, 5496^8 (1944).

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
HARVARD UNIVERSITY
CAMBRIDGE 38, MASSACHUSETTS

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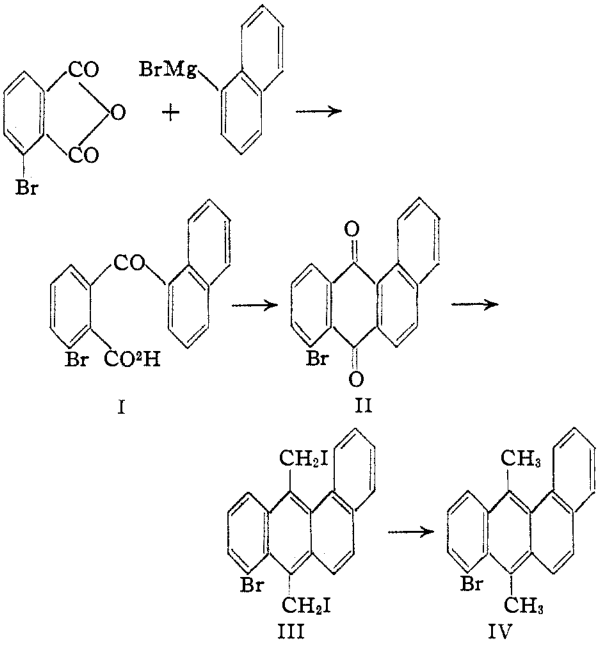
Derivatives of 9,10-Dimethyl-1,2-benzanthracene

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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(1) Fellow of Finney-Howell Research Foundation; present address, The University of Tennessee, Memphis, Tenn.

(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).