Thus 7-chlorothiophanthraquinone (XV) freshly crystallized from a high boiling gasoline fraction melted at 189–190°. After two months it melted at 190°, resolidified and remained solid up to 240°. Samples from ethanol melted at 190°, resolidified and remelted at 240°.

The 6-chlorothiophanthraquinone (XIV) crystallized from a high boiling gasoline fraction melted at 211°, two months later it melted at 214°, then resolidified and melted over 250°. Freshly crystallized from ethanol it melted at 205–206°.

An aminothiophanthraquinone prepared by ring-closure of 5-nitro-2-(2-thenoyl)-benzoic acid (made from 4-nitrophthalic anhydride and thiophene by the Friedel–Crafts reaction) with sulfuric acid followed by reduction gave a chlorothiophanthraquinone melting at 195°, and after crystallization 197–199°. Since it gave no mixed melting point depression with 7-chlorothiophanthraquinone (XV), m.p. 190°, and some depression with 6-chlorothiophanthraquinone (XIV), m.p. 214°, this ring-closure involved a rearrangement to produce 7-chlorothiophanthraquinone contaminated with some 6-chlorothiophanthraquinone.

An aminothiophanthraquinone prepared by an aluminum chloride ring-closure of 4-nitro-2-(2-thenoyl)-benzoic acid (made from 4-nitrophthalic anhydride by the Grignard reaction on 2-bromothiophene) followed by reduction gave a chlorothiophanthraquinone melting at 197–198°. It too was 7-chlorothiophanthraquinone contaminated with some 6-chlorothiophanthraquinone.

An aminothiophanthraquinone prepared by ring-closing 5-amino-2-(2-thenoyl)-benzoic acid with sulfuric acid yielded a chlorothiophanthraquinone, m.p. 203–205°, after vatting and crystallizing from alcohol. This was apparently almost pure 6-chlorothiophanthraquinone (mixed m.p.). The ring-closure of 5-amino-2-(2-thenoyl)-benzoic acid proceeds therefore without rearrangement.

An aminothiophanthraquinone prepared by a sulfuric acid ring-closure of 5-nitro-2-(2-thenoyl)-benzoic acid (made from 4-nitrophthalic anhydride by the Grignard reaction with 2-bromothiophene) followed by reduction afforded pure 7-chlorothiophanthraquinone, m.p. 190°. Ring-closure had therefore taken place by rearrangement.

Rearrangement of 3-Nitro-2-(2-thenoyl)-benzoic Acid. 3-Nitro-2-(3-thenoyl)-benzoic Acid.—A solution of 3-nitro-2-(2-thenoyl)-benzoic acid (10 g.), m.p. 215°, in 100% sulfuric acid (100 g.) was heated to 70–72° and tested periodically by withdrawal of 5-cc. aliquots containing theoretically 0.55 g. of the starting material. The following table illustrates the results.

Time/min. at 70°	Wt. of acid	M.p., °C.	Mixed m.p. with starting materials
30	0.20	188-190	160-165
60	0.155	189-190	160-165
120	0.035	188-190	160-165
240	Trace	.....	

Only one-third of the acid expected was present after 30 minutes of heating to 70° indicating a considerable loss during heating. To check this point 1 g. of 3-nitro-2-(2-thenoyl)-benzoic acid was dissolved in 10 g. of 100% sulfuric acid at 20°, raised to 70° in ten minutes and drowned on ice. Only 0.65 g. of acid m.p. 181–183° was recovered. However 10 g. of 3-nitro-2-(2-thenoyl)-benzoic acid added to 100 g. of 100% sulfuric acid *at 70°* and drowned after 30 minutes yielded 6 g. of rearranged acid, m.p. 188–190° or 190.5–191.5° after reclarification.

Although it analyzed as a nitro-2-(thenoyl)-benzoic acid it gave a strong mixed melting point depression with both the 3-nitro-2-(2-thenoyl)-benzoic acid and the 6-nitro-2-(2-thenoyl)-benzoic acid.

Since ring-closure of this product (followed by reduction) produced pure 5-aminothiophanthraquinone it was probably a substance which would ring-close cleanly, *i.e.*, 3-nitro-2-(3-thenoyl)-benzoic acid (XXI).

The following table shows that rearrangement may occur at temperatures as low as 50°, that 100% sulfuric acid is required, and that weaker acid under comparable conditions yields only the starting material. 3-Nitro-2-(2-thenoyl)-benzoic acid (10 g.) was added to the sulfuric acid (100 g.) at the temperatures indicated, held for the specified time, drowned, filtered, dissolved in alkali, clarified and precipitated with acid.

H_2SO_4, %	Temp., °C.	Time, min.	Yield, g.	M.p., °C.
100	50	30	4.58	169–175
100	60	30	3.77	179–189
100	70	30	6.0	188–190
100	80	15	4.18	188–190
100	90	15	3.72	188–190
95.5	70	30	5.79	214–215
90.0	70	30	7.09	213-214
85.0	70	30	7.56	213-214
80.0	Insoluble			

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 109 FROM JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND CO.]

4,5- and 8,9-Benzthiophanthrones

BY V. WEINMAYR, F. S. PALMER AND A. A. EBERT, JR.

RECEIVED AUGUST 24, 1951

The constitution of the two possible benzthiophanthrones has been determined. The two benzthiophanthrones previously described have been shown to have structures different from those originally assigned.

Thiophanthraquinone (I) can form two isomeric benzthiophanthrones, a 4,5-benzthiophanthrone (II) and a 8,9-benzthiophanthrone (III).

Scholl[1] prepared an impure benzthiophanthrone melting at about 210° by fusing 1-(2-thenoyl)-naphthalene (IV) with aluminum chloride. It was natural to assume that the 4,5-benzthiophanthrone was obtained. Scholl's experiment was repeated and a pure benzthiophanthrone, m.p. 215–217°, was obtained in a low yield. It was soluble in 96% sulfuric acid with an orange color but was insoluble in 34–36% hydrochloric acid.

A different benzthiophanthrone, m.p. 140°, was prepared from thiophanthraquinone with glycerol and iron in sulfuric acid in yields of 60–70% by the method used for the preparation of benzanthrone from anthraquinone.[2] Because this isomer was soluble with an orange color both in 96% sulfuric acid and 36% hydrochloric acid, and because mixed melting points between the two isomers showed a strong depression, it was assumed to be the new isomeric 8,9-benzthiophanthrone.[3]

Oxidation of the benzthiophanthrone m.p. 140° gave a thiophanthraquinone carboxylic acid. Examination of the infrared spectrum of this thio-

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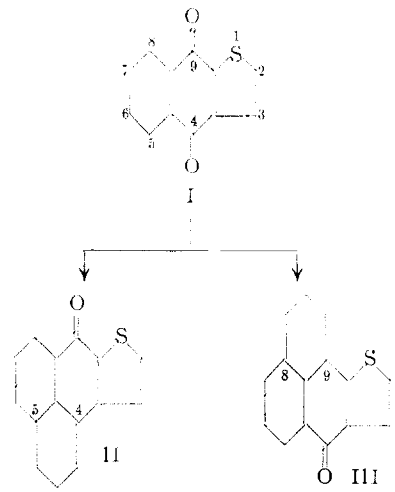
(1) R. Scholl and Ch. Seer, *Ann.*, **394**, 131, 175 (1912).

(2) A. J. Wuertz, U. S. Patent 1,896,147 (1933), *C. A.*, **27**, 2459 (1933).

(3) H. R. Lee and V. Weinmayr, U. S. Patent 2,480,746 (1949), *C. A.*, **43**, 9467 (1949). Note: The patent is erroneously abstracted as dealing with a benzthiophanthrene. It should read benzthiophanthrone.



phanthraquinone carboxylic acid showed that it was identical with the spectrum shown by the thiophanthraquinone-5-carboxylic acid and was very much different from the spectrum of the thiophanthraquinone-8-carboxylic acid.

Both thiophanthraquinone carboxylic acids had been prepared from the corresponding aminothiophanthraquinones by the Sandmeyer reaction.

It must be assumed that the 1-(2-thenoyl)-naphthalene (IV) had rearranged during the aluminum chloride fusion to a 1-(3-thenoyl)-naphthalene (V) which then ring closed to 8,9-benzthiophanthrone (III).

Such rearrangements have been observed when chloro-2-(2-thenoyl)-benzoic acids, and nitro-2-(2-thenoyl)-benzoic acids were ring closed to the substituted thiophanthraquinones.[4]

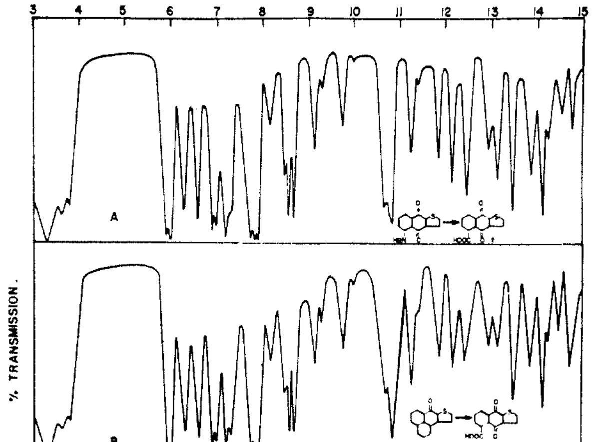
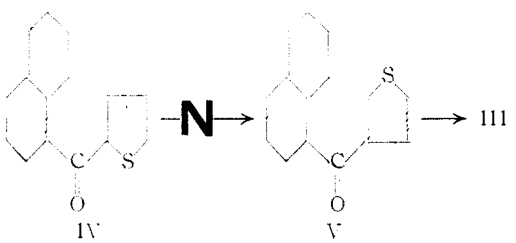


Fig. 1.



Thus the Scholl benzthiophanthraquinone, m.p. 215–217°, is the 8,9-benzthiophanthraquinone, and the compound of reference (3) is the 4,5-benzthiophanthrone. Figure 1 shows the infrared data of the thiophanthraquinone carboxylic acids obtained from the 5-aminothiophanthraquinone and from the 8-aminothiophanthraquinone, and the curve obtained from the thiophanthraquinone carboxylic acid formed upon the oxidation of the benzthiophanthrone formed from thiophanthraquinone.

Figure 2 shows the infrared curve of unsubstituted thiophanthraquinone.[5]

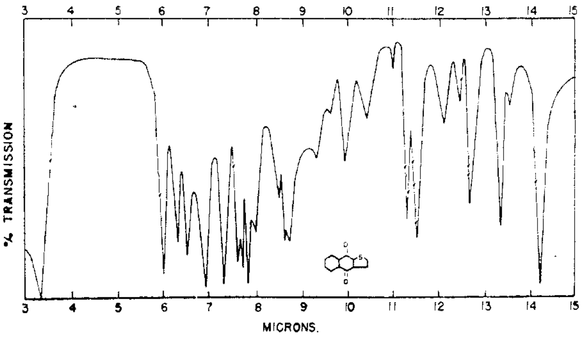


Fig. 2.

Experimental

8,9-Benzthiophanthrone (III).—1-(2-Thenoyl)-napththalene (36 g.)[6] was added at 118–123° in ten minutes to a fusion mass of anhydrous aluminum chloride (290 g.), sodium chloride (40 g.) and potassium chloride (34 g.), and the reaction mass was stirred at 120° for 15 minutes. It was then poured into cold water, the precipitate was filtered, washed and dried. Crude 8,9-benzthiophanthrone (45 g.) was obtained. The product was extracted with chlorobenzene in a Soxhlet apparatus, and the extract (500 cc.) was chromatographed on a 24 × 1.5 in. column of alumina which had been activated at 325–350°. Two layers were obtained, a dark brown top layer and a yellow lower layer, but the line of separation was not very sharp. The center section of the yellow band was separated and extracted with ethanol, and the alcoholic solution was evaporated to dryness.

The 8,9-benzthiophanthrone (4.4 g.) was obtained as bright yellow crystals, m.p. 180–205°. After several crystallizations from glacial acetic acid (450 cc.), it melted at 215–217° (recovery 2 g.). It was soluble in 96% sulfuric acid with an orange color without fluorescence, but was insoluble in 36% hydrochloric acid.

Anal. Calcd. for $C_{15}H_8OS$: S, 13.56. Found: S, 13.16.

4,5-Benzthiophanthrone (II).—Thiophanthraquinone (107 g., 0.5 mole) (m.p. 229–230°) was dissolved in 96% sulfuric acid (825 g.). Water (131 g.) containing copper sulfate (2 g.) was added through a dropping funnel to the well-agitated, deep red solution, allowing the temperature to rise to 110°. The thiophanthraquinone remained in solution in this 82.5% sulfuric acid. Glycerol (95 g., 1.03 *M*) and iron filings (49 g., 0.87 mole) were added uniformly over a period of three hours at a reaction temperature of 110–117°.

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[4] H. E. Schroeder and V. Weinmayr, This Journal, **74**, 4357 (1952).

[5] The samples were run as Nujol (white mineral oil) mulls in a 0.025 mm. cell using a Perkin-Elmer Model 12-C spectrometer.

[6] R. Scholl and Ch. Seer, *Ann.*, **394**, 111 (1912).

This reaction temperature was maintained one hour longer, then a few cc. of the reaction mass was poured into water, the precipitate was filtered, washed and slurried in dilute alkali containing sodium hydrosulfite. The absence of an orange vat indicated completion of the reaction.

The reaction mass was poured into water (3 l.) and the charge was heated to boiling where the reaction product formed a lump of tar. After washing by decantation with cold water, it was slurried in warm water (3 l.) containing an excess of sodium hydroxide, where it dispersed to a very fine powder that caused difficulty in filtration. The slurry was therefore again acidified cold with hydrochloric acid, and the precipitate was filtered, washed and dried. Crude, greenish-black 4,5-benzthiophanthrone (130 g.) was isolated. Upon Soxhlet extraction with benzene, and evaporation of the benzene extract, a bright yellow 4,5-benzthiophanthrone (75 g.), m.p. 139–140°, was obtained, equal to a 63.5% yield from thiophanthraquinone. After crystallization from "Dependip" (3500 cc.) (a high boiling gasoline), it formed yellow needles, m.p. 140° (recovery 50 g.). It could be distilled at atmospheric pressure without decomposition, and was soluble in 96% sulfuric acid as well as in 36% hydrochloric acid.

Anal. Calcd. for $C_{15}H_8O_5$: S, 13.56. Found: S, 13.43.

Thiophanthraquinone-5-carboxylic Acid by Oxidation of 4,5-Benzthiophanthrone.—4,5-Benzthiophanthrone (5 g.) was dissolved in glacial acetic acid (50 cc.). A solution of chromic acid (25 g., CrO_3) in water (25 cc.) and acetic acid (25 cc.) was added in three hours during which time the reflux temperature dropped from 120 to 105°. After refluxing for one hour, water (700 cc.) was added and the precipitate which formed was filtered, washed first with 10% sulfuric acid, then with water. The crude thiophanthraquinone-5-carboxylic acid was dissolved in aqueous sodium carbonate (100 cc.), filtered from a small amount of insoluble matter, and precipitated again with hydrochloric acid; (yield 1.05 g.), m.p. 255–268°. After two crystallizations from nitrobenzene (9 cc.), thiophanthraquinone-5-carboxylic acid (0.8 g.) was obtained, m.p. 283–284°. Its solutions in aqueous sodium hydroxide turned deep red upon the addition of sodium hydrosulfite.

Anal. Calcd. for $C_{13}H_6O_4S$: C, 60.45; H, 2.32; S, 12.40. Found: C, 60.48; H, 2.40; S, 12.46.

Thiophanthraquinone-5-carboxylic Acid from 5-Aminothiophanthraquinone.—5-Aminothiophanthraquinone (2 g.) obtained by ring closing 6-nitro-2-(2-thenoyl)-benzoic acid to 5-nitrothiophanthraquinone and reducing the latter,[4] was dissolved in 96% sulfuric acid (11 g.), and diazotized at about 10° with finely powdered sodium nitrite (0.3 g.). The diazotization was finished by heating the solution to 40°. The diazonium salt was precipitated by carefully adding ice (10–15°) to the reaction mass. It was filtered, sucked as dry as possible and added to a solution of copper sulfate (4.5 g.), sodium bicarbonate (2.5 g.) and potassium cyanide (3.5 g.) in water (140 cc.). The reaction mass was held at room temperature overnight and then heated to 60° for 30 minutes. Crude 5-cyanothiophanthraquinone (1.19 g.), m.p. 200–215°, was separated by filtration.

This crude 5-cyanothiophanthraquinone was dissolved in 90% sulfuric acid (10 g.) and heated to 70–80° for 20 minutes. The hot solution was treated with sodium nitrite (0.3 g.). Upon dilution with water crude thiophanthraquinone-5-carboxylic acid (0.66 g.), m.p. 270–280°, was obtained. After recrystallizations from *o*-dichlorobenzene and from methanol it melted at 283–284° (0.36 g.).

Anal. Calcd. for $C_{13}H_6O_4S_2$: C, 60.45; H, 2.32; S, 12.40. Found: C, 60.26; H, 2.38; S, 12.10.

Thiophanthraquinone-8-carboxylic Acid from 8-Aminothiophanthraquinone.—In a manner similar to that described above, 8-aminothiophanthraquinone, prepared by ring closing 3-amino-2-(2-thenoyl)-benzoic acid,[4] was converted to the thiophanthraquinone-8-carboxylic acid. After several crystallizations from chlorobenzene, and from ethanol it melted at 273–274°.

Anal. Calcd. for $C_{13}H_6O_4S_2$: C, 60.45; H, 2.32; S, 12.40. Found: C, 59.99; H, 2.51; S, 11.92.

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[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY]

Tri-1-naphthylgermanium Compounds and Steric Hindrance[1]

BY ROBERT WEST

RECEIVED FEBRUARY 21, 1952

Tetra-1-naphthylgermane and several tri-1-naphthylgermanium compounds have been prepared. A comparison of the chemical properties of tri-1-naphthylgermanium compounds with those of the analogous silicon compounds shows a much lower degree of steric hindrance to the reactions of the germanium compounds.

Although tetra-2-naphthylsilane has been prepared from 2-naphthyllithium and silicon tetrachloride,[2] all attempts to prepare tetra-1-naphthylsilane have given only the tri-1-naphthylsilicon derivative. The results have been attributed to the large steric requirements of the 1-naphthyl groups.[3] The same investigators reported other evidence of steric hindrance to reactions occurring at a silicon atom bonded to three 1-naphthyl groups. Thus tri-1-naphthylchlorosilane can be hydrolyzed to the corresponding silanol only under relatively vigorous conditions; and tri-1-naphthylsilanol is not converted to the disiloxane by treatment with acid, nor does it react quantitatively with the Karl Fischer reagent, which can be used to titrate unhindered organosilicon hydroxides.[4] Also, tri-1-naphthylsilane is not hydrolyzed readily by bases, as unhindered organosilanes are.

Because of the slightly larger covalent bonding radius of germanium than that of silicon,[5] a comparative study of the reactions of tri-1-naphthylgermanium compounds is of interest. The results of this study indicate much less steric hindrance to most reactions occurring at a germanium atom bonded to three 1-naphthyl groups. If it is assumed that analogous organic compounds of silicon and germanium react by similar mechanisms, this confirms the explanation offered by Gilman and Brannen for the behavior of the tri-1-naphthylsilicon compounds.

Attempts to prepare tetra-1-naphthylgermane directly from germanium tetrabromide, either with 1-naphthyllithium or with 1-naphthylmagnesium bromide, were unsuccessful; but interaction of

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[1] This work was partly supported by a grant from the Office of Naval Research.

[2] H. Gilman and C. G. Brannen, THIS JOURNAL, **72**, 4280 (1950).

[3] H. Gilman and C. G. Brannen, *ibid.*, **73**, 4640 (1951).

[4] H. Gilman and L. S. Miller, *ibid.*, **73**, 2367 (1951).

[5] 1.17 Å. for silicon and 1.22 Å. for germanium: L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 164.