5-nitrobenzoyl chloride was dissolved in benzene (200 cc.), and stannic chloride (29 g.) was added at 0–5° in one hour. The temperature of the charge was raised to 20° in four hours and agitation at 20–25° was continued for 18 hours. The reaction mass was then poured into dilute hydrochloric acid and steam distilled to remove the benzene. The filtered and washed solid residue was stirred at 20–25° for 24 hours in a solution of sodium hydroxide (5 g.) in 33% ethanol (100 cc.). The insoluble residue was filtered off and the crude 5-nitro-2-(2-thenoyl)-benzoic acid was precipitated from the filtrate with hydrochloric acid (17 g., yield 61.3%), m.p. about 170°. When crystallized from chlorobenzene it melted at 189–190° and was identical with the 5-nitro-2-(2-thenoyl)-benzoic acid obtained by the Grignard reaction.

Anal. Calcd. for $C_{12}H_7NO_5S$: N, 5.05; S, 11.55. Found: N, 5.27; S, 11.34.

4-Amino-2-(2-thenoyl)-benzoic Acid.—A solution of 4-nitro-*o*-(2-thenoyl)-benzoic acid (14 g.) in thiophene-free benzene (200 cc.) was hydrogenated at 100° and 600 lb. of hydrogen pressure, using reduced nickel as the catalyst. The crude product obtained upon evaporation of the filtered reduction mass was extracted with chlorobenzene and crystallized from the same solvent. 4-Amino-2-(2-thenoyl)-benzoic acid (2.5 g.) was obtained, m.p. 218–219°.

Anal. Calcd. for $C_{12}H_9NO_3S$: N, 5.67; S, 12.95. Found: N, 5.64; S, 12.71.

3-Chloro-2-(2-thenoyl)-benzoic Acid from 3-Amino-2-(2-thenoyl)-benzoic Acid.—3-Amino-2-(2-thenoyl)-benzoic acid (2.8 g.) was dissolved in water (10 cc.) and the minimum amount of sodium hydroxide necessary to dissolve it was added. The solution was poured on ice (20 g.) and concd. hydrochloric acid (20 cc.), and was diazotized with 21 cc. of a 0.54 *N* sodium nitrite solution. The diazotized mass formed a thick white crystalline slurry. It was poured into a solution of cuprous chloride (3 g.) in concd. hydrochloric acid (25 cc.) at 25–29°. The flocculent precipitate changed to a crystalline form when the charge was heated to 100°. It was filtered, washed, dissolved in dilute sodium hydroxide, clarified and reprecipitated with hydrochloric acid. 3-Chloro-2-(2-thenoyl)-benzoic acid (2.4 g., 80% yield) was obtained, m.p. 236–238°. Crystallized from chlorobenzene it melted at 238°. It was identical with the 3-chloro-2-(2-thenoyl)-benzoic acid obtained by the Grignard reaction.

Anal. Calcd. for $C_{12}H_7ClO_3S$: Cl, 13.23. Found: Cl, 13.21.

It was observed that it was necessary to carry out the reaction in highly concentrated acid and in small dilutions. Otherwise low melting products were obtained from which the pure 3-chloro-2-(2-thenoyl)-benzoic acid could be isolated only with difficulty.

4-Chloro-2-(2-thenoyl)-benzoic Acid from 4-Amino-2-(2-thenoyl)-benzoic Acid.—4-Amino-2-(2-thenoyl)-benzoic acid (1 g.) was dissolved in dilute sodium hydroxide (5 cc.) and poured into concd. hydrochloric acid (10 cc.) and ice (10 g.). It was diazotized with 7.5 cc. of 0.54 *N* sodium nitrite solution (the diazonium salt remained in solution) and was then poured into a solution of cuprous chloride (1 g.) in concd. hydrochloric acid (10 cc.) at 20–30° in about 30 minutes. Heating to 100° changed the amorphous precipitate to a crystalline form. 4-Chloro-2-(2-thenoyl)-benzoic acid (1 g., 93% yield), m.p. 215–220° was obtained. Crystallized from chlorobenzene it melted at 225–226° and was identical with the 4-chloro-2-(2-thenoyl)-benzoic acid obtained by the Grignard reaction.

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 110 FROM JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND CO.]

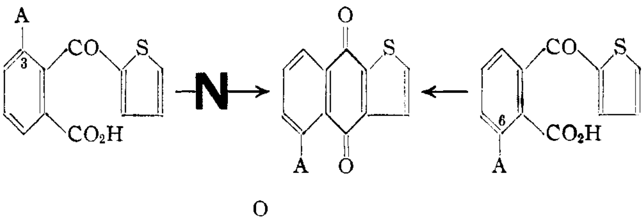
The Synthesis of Thiophanthraquinones from Thenoyl and Thenylbenzoic Acids

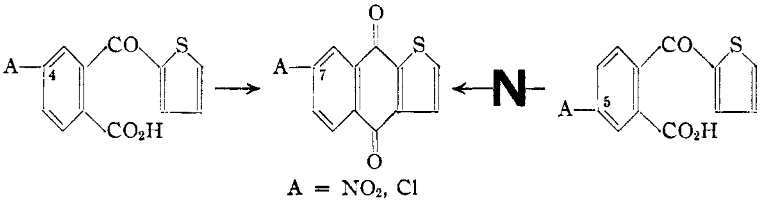
BY H. E. SCHROEDER AND V. WEINMAYR

RECEIVED AUGUST 24, 1951

The structures of the thiophanthraquinones substituted in the benzene ring by amino, chloro and nitro groups have been established beyond doubt. Ring-closure of the chloro- and nitro-thenoylbenzoic acids proceeds normally when the substituent is meta to the thenoyl group but with rearrangement when in any ortho or para position. Conversely the amines cyclize normally when ortho or para but rearrange when meta to the thenoyl group.

The normal procedures for ring-closure of benzene substituted 2-(2-thenoyl)-benzoic acids,[1] did not give expected isomeric substituted thiophanthraquinones. Since there are many known cases of rearrangement on ring-closure of substituted *benzoyl*benzoic acids,[2,3] the situation has been clarified by use of the excellent method of Fieser and Hershberg, involving cyclization of benzylbenzoic acids to anthranylacetates,[4] followed by oxidation to the quinones. Synthetic routes have been developed for the preparation of the pure isomers, particularly those which are inaccessible by ring-closure of 2-(2-thenoyl)-benzoic acids because of rearrangements, *i.e.*, 8- and 6-chlorothiophanthraquinones, and 6- and 5-aminothiophanthraquinones. These have shown that when nitro or chloro groups are in a meta position with respect to the thenoyl group the thenoyl benzoic acids cyclize normally but when either ortho or para they cyclize only with rearrangement





A = NO_2, Cl

Conversely, in the case of the aminothenoylbenzoic acids, the amino derivatives ortho and para to the thenoyl group cyclize normally while the meta derivatives rearrange as shown.

These rearrangements are independent of the condensing agent, *e.g.*, sulfuric acid, hydrogen fluoride, aluminum chloride, etc. yield the same isomer.

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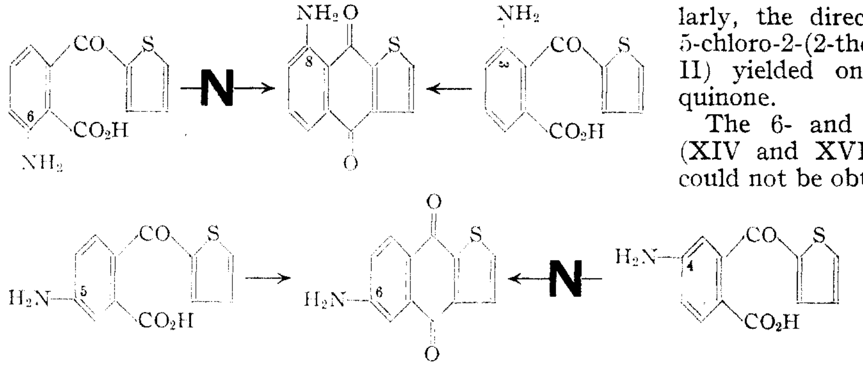
(1) V. Weinmayr, THIS JOURNAL, 74, 4353 (1952).

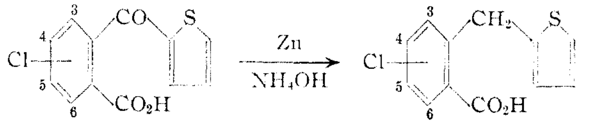
(2) M. Hazaski, *J. Chem. Soc.*, 1520, 1524 (1930).

(3) R. B. Sandin and L. F. Fieser, THIS JOURNAL, 62, 3098 (1940).

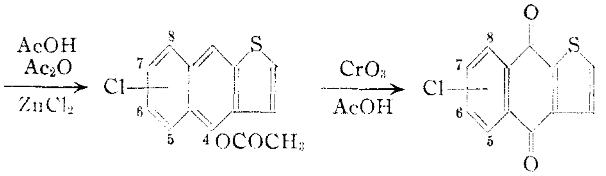
(4) L. F. Fieser and E. B. Hershberg, *ibid.*, 59, 1028 (1937); 60, 1893 (1938).



A. The Chloro Derivatives.—The four possible isomeric mono chlorothiophanthraquinones were prepared from the chloro-2-(2-thenoyl)-benzoic acids *via* the chloro-2-(2-thenyl)-benzoic acids, and the chloroacetoxythiophanthrenes



chloro-2-(2-thenoyl)-benzoic acids	chloro-2-(2-thenyl)-benzoic acids
I, 6-Cl; m.p. 129°	V, 6-Cl; m.p. 114°
II, 5-Cl; m.p. 155°	VI, 5-Cl; m.p. 155°
III, 4-Cl; m.p. 226°	VII, 4-Cl; m.p. 134°
IV, 3-Cl; m.p. 239°	VIII, 3-Cl; m.p. 114°



4-acetoxychlorothiophanthrenes	chlorothiophanthraquinones
IX, 5-Cl; m.p. 188°	XIII, 5-Cl; m.p. 226°
X, 6-Cl; m.p. 156°	XIV, 6-Cl; m.p. 214°
XI, 7-Cl; m.p. 155°	XV, 7-Cl; m.p. 190°
XII, 8-Cl; m.p. 88°	XVI, 8-Cl; m.p. 172°

Direct ring-closure of the 3- and 6-chloro-2-(2-thenoyl)-benzoic acids (IV and I) actually yielded only 5-chlorothiophanthraquinone (XIII). Similarly, the direct ring-closure of the 4- and 5-chloro-2-(2-thenoyl)-benzoic acids (III and II) yielded only the 7-chlorothiophanthraquinone.

The 6- and 8-chlorothiophanthraquinones (XIV and XVI) melting at 214° and 172° could not be obtained by direct ring-closure of chloro-2-(2-thenoyl)-benzoic acids.

B. The Amino and Nitrothiophanthraquinones. a. The α-(5- and 8-)-isomers.—The 5-aminothiophanthraquinone and the 8-aminothiophanthraquinone were synthesized from the authentic chlorothiophanthraquinones by amination with toluenesulfonamide followed by hydrolysis.

The aminothiophanthraquinones obtained by ring-closure of both 3- and 6-amino-2-(2-thenoyl)-benzoic acids gave toluenesulfonamides melting at 221°, and 2-thenoylamides melting at 275°, and were both therefore 8-aminothiophanthraquinone (XX).

The supposed 5- and 8-nitrothiophanthraquinones obtained by ring-closure of the 3- and 6-nitro-2-(2-thenoyl)-benzoic acids gave amines melting at 233°. The latter yielded toluenesulfonamides melting at 250°, and 2-thenoylamides melting at 260° and were both therefore 5-aminothiophanthraquinone (XVIII), probably contaminated with a trace of 8-aminothiophanthraquinone.

Thus 3-amino-2-(2-thenoyl)-benzoic acid ring-closed normally while the 6-amino-2-(2-thenoyl)-benzoic acid rearranged. This behavior was the opposite of that noted in the chloro-2-(2-thenoyl)-benzoic acids.

Conversely, 3-nitro-2-(2-thenoyl)-benzoic acid rearranged while the 6-nitro-2-(2-thenoyl)-benzoic acid cyclized normally. This paralleled the behavior of the chloro derivatives.

b. The β-(6- and 7-)-Isomers.—Attempts to convert the known β-chlorothiophanthraquinones to the β-aminothiophanthraquinones were unsuccessful. The β-aminothiophanthraquinones obtained from ring-closures of 4- and 5-amino-2-(2-thenoyl)-benzoic acid and 4- and 5-nitro-2-(2-thenoyl)-benzoic acids were therefore converted to the chlorothiophanthraquinone by the Sandmeyer method and compared with authentic chlorothiophanthraquinones with the following results: (1) The 4- and 5-amino-2-(2-thenoyl)-benzoic acids yielded largely 6-aminothiophanthraquinone (contaminated with some 7-aminothiophanthraquinone). Thus the 5-amino-2-(2-thenoyl)-benzoic acid ring-closed directly, while the 4-amino-2-(2-thenoyl)-benzoic acid rearranged. (2) The 4- and 5-nitro-2-(2-thenoyl)-benzoic acids both yielded largely the 7-nitrothiophanthraquinone, but often contaminated with some 6-nitrothiophanthraquinone. Thus the 4-nitro-2-(2-thenoyl)-benzoic acid ring-closed directly, while the 5-nitro-2-(2-thenoyl)-benzoic acid rearranged.

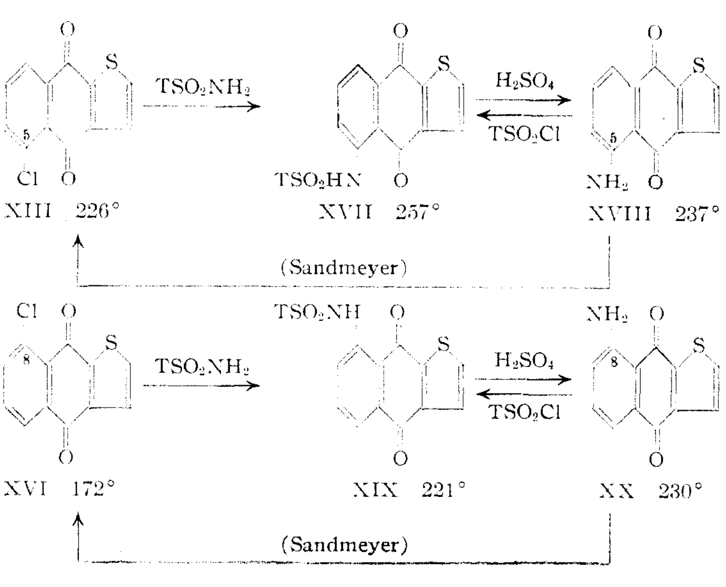


TABLE I

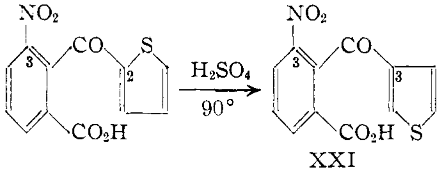
Compound, benzoic acid	M.p., °C.	Yield, %	Formula	Analyses, % Calculated C	H	Cl	Found C	H	Cl
4-Chloro-2-(2-thenyl)- VII	134	92	$C_{12}H_9ClO_2S$	57.00	3.56	14.07	56.80	3.62	13.99
5-Chloro-2-(2-thenyl)- VI	155	89	$C_{12}H_9ClO_2S$	57.00	3.56	14.07	56.79	3.44	14.07
6-Chloro-2-(2-thenyl)- V	117	95	$C_{12}H_9ClO_2S$	57.00	3.56	14.07	57.43	3.77	13.86
o-(2-Thenyl)-	109	94	$C_{12}H_{10}O_2S$	66.15	4.57	S, 14.67	66.41	4.15	S, 14.29

TABLE II

Compound, thiophanthrene	M.p., °C.	Yield, %	Formula	Analyses, % Calculated C	H	Cl	S	Found C	H	Cl	S
4-Acetoxy-5-chloro- (IX)	188[a]	85	$C_{14}H_9ClO_2S$	60.75	3.25	12.83		60.90	3.30	12.79	
4-Acetoxy-6-chloro- (X)	156	83	$C_{14}H_9ClO_2S$	60.75	3.25	12.83	11.58	60.89	2.97	13.14	11.54
4-Acetoxy-7-chloro- (XI)	155	78	$C_{14}H_9ClO_2S$			12.83	11.58			13.06	11.78
4-Acetoxy-	122	93	$C_{14}H_{10}O_2S$	69.30	4.13		13.20	69.43	3.78		12.99

[a] All Compounds of Table II were crystallized from ethanol.

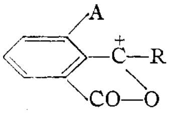
Course of the Rearrangement.—In the case of the α-isomers the rearrangement apparently involved a shift of the entire nitrophthaloyl radical from the 2- to the 3-position in the thiophene. 3-Nitro-2-(2-thenoyl)-benzoic acid when treated with 100% sulfuric acid at 70–90° was rapidly rearranged (five minutes) to form the presumed 3-nitro-2-(3-thenoyl)-benzoic acid



XXI

m.p. 217° m.p. 191.5°

The only other possibility, 2-nitro-6-(3-thenoyl)-benzoic acid, is considered extremely unlikely since ring closure would then involve a second rearrangement, which would presume a shift of the thienyl radical from a relatively unhindered position to the 2,6-disubstituted position. The known stability of ions of the type in 100% sulfuric acid affords a



reasonable mechanism leading to the product indicated as XXI. There is some evidence that the 3-chloro isomer behaved similarly. Attempts to effect the same reaction with the beta isomers were unsuccessful since they yielded only starting material or the thiophanthraquinones.

Acknowledgments.—The authors wish to express their grateful appreciation to Dr. Louis F. Fieser for his many helpful suggestions throughout the course of this work.

Experimental

3-Chloro-2-(2-thenyl)-benzoic Acid (VIII).—A mixture of pure 3-chloro-2-(2-thenoyl)-benzoic acid (IV) (20 g.) m.p. 239°, 28% aqueous ammonia (1000 cc.), copper sulfate (0.5 g.), and zinc dust (50 g.) was refluxed for 36 hours while 28% ammonia (50 cc.) was added every six hours. The charge was filtered, the colorless filtrate was acidified hot and upon cooling 3-chloro-2-(2-thenyl)-benzoic acid (19 g.), m.p. 113–114°, was obtained (mixed m.p. with the 6-isomer (V) 94–105°).

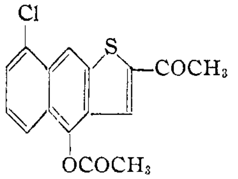
Anal. Calcd. for $C_{12}H_9ClO_2S$: Cl, 14.07. Found: Cl, 13.82.

The *o*-(2-thenyl)-benzoic acids of Table I were obtained in a similar manner from the corresponding *o*-(2-thenoyl)-benzoic acids.

4-Acetoxy-8-chlorothiophanthrene (XII).—A solution of 3-chloro-2-(2-thenyl)-benzoic acid (VIII) (19 g.) and freshly fused zinc chloride (1.5 g.) in glacial acetic acid (114 g.) and acetic anhydride (76 g.) was refluxed for 90 minutes and then, while still hot, carefully diluted to about double its volume with water. The 4-acetoxy-8-chlorothiophanthrene (15 g.), m.p. 80–85°, thus obtained was crystallized from methanol and melted then at 87–88°.

Anal. Calcd. for $C_{14}H_9ClO_2S$: C, 60.75; H, 3.25; Cl, 12.83; S, 11.58. Found: C, 60.85; H, 3.50; Cl, 12.62; S, 11.40.

This preparation frequently yielded a small amount (5%) of a higher melting product, m.p. 211–212°, which was quite insoluble in methanol and was easily separated. By analysis it corresponded to



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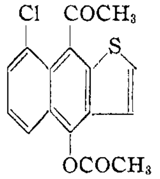

XXII XXIII

Anal. Calcd. for $C_{16}H_{11}ClO_3S$: Cl, 11.10; S, 10.04. Found: Cl, 10.90; S, 9.94.

Oxidation with chromic acid yielded a substance that appeared to be an acetylchlorothiophanthraquinone, m.p. 328–329° (from alcohol).

Anal. Calcd. for $C_{14}H_7ClO_3S$: Cl, 12.30. Found: Cl, 12.20.

Formula XXII is probably correct since compound XXIII should have yielded 8-chlorothiophanthraquinone on oxidation.

The acetoxythiophanthrenes of Table II were prepared in a similar manner from the corresponding *o*-(2-thenyl)-benzoic acids.

8-Chlorothiophanthraquinone (XVI).—To a suspension of 4-acetoxy-8-chlorothiophanthrene (5 g.) in glacial acetic acid (100 cc.) was added a trace of chromic acid (0.05 g.). The mixture was then heated to 80° over a period of ten minutes. The color of the chromic acid had changed to green. The remainder of the chromic acid (total 5 g.) was added portion-wise fairly quickly, causing the temperature to rise to the boiling point of the mixture. After five minutes of refluxing 35% hydrochloric acid (10 cc.) was added, and after five more minutes of boiling the charge was diluted with water (100 cc.). The white solid which precipitated was filtered cold (0°) (yield 85% of product, m.p. 161–163°). It was vatted, and recrystallized twice (Nuchar) from methanol, m.p. 171.5–172.5°.

Anal. Calcd. for $C_{12}H_5ClO_2S$: Cl, 14.28; C, 57.95; H, 2.02. Found: Cl, 14.50; C, 57.87; H, 2.12.

The chlorothiophanthraquinones of Table III were obtained in a similar manner from the corresponding 4-acetoxychlorothiophanthrenes.

TABLE III

Compound, thiophanthraquinone	M.p., °C.	Formula	Analyses, % Calculated C	 H	 Cl	 Found C	 H	 Cl
5-Chloro- (XIII)	226[a]	$C_{12}H_5ClO_2S$	57.95	2.01	14.28	57.77	2.17	14.47
6-Chloro- (XIV)	214[a]	$C_{12}H_5ClO_2S$	57.95	2.01	14.28 S, 12.88	57.94	2.01	14.29 S, 13.12
7-Chloro- (XV)	190[b]	$C_{12}H_5ClO_2S$	57.95	2.01		57.82	2 10	

[a] From acetic acid. [b] From chlorobenzene.

5-Chlorothiophanthraquinone from the 3- and 6-Chloro-2-(2-thenoyl)-benzoic Acids.—A solution of 6-chloro-2-(2-thenoyl)-benzoic acid (2 g.), m.p. 129°, in 96% sulfuric acid (10 cc.) was heated to 170–175° in one minute and held there for about half a minute. The red brown solution was quickly cooled and carefully diluted by adding ice. The coarse crystalline precipitate was filtered, washed acid free, extracted with dilute sodium carbonate, and dissolved in alkaline sodium hydrosulfite (vatted). After filtration and oxidation with air 5-chlorothiophanthraquinone, m.p. 194–200° (1.15 g., 61.8%) was obtained. After one crystallization from chlorobenzene (25 cc.) it melted at 225–226°.

Anal. Calcd. for $C_{12}H_5ClO_2S$: Cl, 14.28; S, 12.88. Found: Cl, 14.28; S, 13.00.

Upon ring-closure of 3-chloro-2-(2-thenoyl)-benzoic acid m.p. 239° in a similar manner the same 5-chlorothiophanthraquinone m.p. 226° was obtained in the same yield.

Ring-closures of both isomeric 3- and 6-chloro-2-(2-thenoyl)-benzoic acids in nitrobenzene with phosphorus pentoxide, or with aluminum chloride (at 130°) gave the same 5-chlorothiophanthraquinone, m.p. 226°.

Anal. Calcd. for $C_{12}H_6ClO_2S$: S, 12.88. Found: S, 12.80.

7-Chlorothiophanthraquinone from 4- and 5-Chloro-2-(2-thenoyl)-benzoic Acids.—A solution of 5-chloro-2-(2-thenoyl)-benzoic acid (4 g.), m.p. 155°, and aluminum chloride (12 g.) in nitrobenzene (60 cc.) was heated to 130° for 20 hours. The solution was then poured into dilute hydrochloric acid, the nitrobenzene was removed with steam and the crude 7-chlorothiophanthraquinone was purified by vatting with alkaline hydrosulfite. Upon oxidation of the filtrate with air 7-chlorothiophanthraquinone, m.p. 190°, (2.66 g.) was obtained. It was crystallized from a high boiling gasoline fraction, m.p. 190–191°.

Anal. Calcd. for $C_{12}H_5ClO_2S$: Cl, 14.28; S, 12.88. Found: Cl, 14.7; S, 13.09.

Ring-closure of the isomeric 4-chloro-2-(2-thenoyl)-benzoic acid, m.p. 226°, gave the identical 7-chlorothiophanthraquinone, m.p. 190–191°, in a comparable yield.

Anal. Calcd. for $C_{12}H_5ClO_2S$: Cl, 14.28; S, 12.88. Found: Cl, 14.51; S, 12.75.

The α-Aminothiophanthraquinones. 8-Aminothiophanthraquinone (XX).—8-Chlorothiophanthraquinone (2.1 g.), *p*-toluenesulfonamide (2.1 g.), sodium carbonate (1.25 g.), cuprous chloride (0.1 g.) and dry distilled nitrobenzene (20 cc.), were heated with agitation to 200–205° for five hours. The mixture was cooled, diluted with an equal volume of methanol, filtered, and washed with methanol and water. The 8-*p*-toluenesulfonamidothiophanthraquinone (1.5 g.) thus obtained (XIX), m.p. 212–215°, was crystallized from ethanol and melted then at 220°.

To hydrolyze it to 8-aminothiophanthraquinone it was slurried for 30 minutes in 96% sulfuric acid at 5–7°. The initially blue-red solution turned brown, and finally yellow. The solution was then warmed to 25°, stirred for one hour and drowned in water to yield 8-aminothiophanthraquinone, m.p. 225–226° (0.77 g.). After two crystallizations from ethanol it melted at 229.5–230°; after a sublimation it melted at 230–230.5°.

Part of this 8-aminothiophanthraquinone (0.040 g.) was converted to the *p*-toluenesulfonamide by boiling it for 90 minutes with *p*-toluenesulfonyl chloride (0.040 g.) in dry nitrobenzene (1 cc.) containing three drops of pyridine. The 8-toluenesulfonamidothiophanthraquinone thus obtained melted at 221°, after recrystallization from pyridine.

An 8-(2-thenoyl)-aminothiophanthraquinone prepared from the above 8-aminothiophanthraquinone melted at 275° (crystallized from dichlorobenzene).

5-Aminothiophanthraquinone (XVIII).—5-Chlorothiophanthraquinone (2.5 g.) was converted in a similar manner as above to the 5-toluenesulfonamidothiophanthraquinone (XVII) (yield 2.865 g.), m.p. 256.5–257°, crystallized from ethanol. On hydrolysis it afforded 5-aminothiophanthraquinone (1.4 g.) (XVIII), m.p. 230–231°. After crystallization and sublimation it melted at 237°.

Treated with *p*-toluenesulfone chloride, it gave the 5-toluenesulfonamidothiophanthraquinone, m.p. 256–257° (XVII). The 5-(2-thenoyl)-amidothiophanthraquinone made from it melted at 252°, resolidified, and then melted again at 259–260° (crystallized from benzene). When crystallized from *o*-dichlorobenzene it melted at 258–259°.

8-Aminothiophanthraquinone from 3-Amino-2-(2-thenoyl)-benzoic Acid.—3-Amino-2-(2-thenoyl)-benzoic acid, m.p. 180° (obtained by reducing 5 g. of 3-nitro-2-(2-thenoyl)-benzoic acid with iron sulfate[5]) was heated in 96% sulfuric acid (50 cc.) containing boric acid (10 g.) to 135° for five minutes. The solution was then poured into water (500 cc.) and 8-aminothiophanthraquinone (2.6 g.), m.p. 220–222° was obtained. After two crystallizations from chlorobenzene it melted at 231–232°.

Anal. Calcd. for $C_{12}H_7NO_2S$: N, 6.12; S, 13.98. Found: N, 6.23; S, 13.92.

It gave a toluenesulfonamide, m.p. 220°, and a 2-thenoylamide, m.p. 275°, and was therefore authentic 8-aminothiophanthraquinone.

5-Aminothiophanthraquinone from 3- and 6-Nitro-2-(2-thenoyl)-benzoic Acids.—A solution of 3-nitro-2-(2-thenoyl)-benzoic acid, m.p. 217° (2 g.) in 96% sulfuric acid (20 cc.) was quickly heated to 140–145° and after one minute poured into water. 5-Nitrothiophanthraquinone (0.6 g.), m.p. 230–231°, was obtained; after crystallization from chlorobenzene, m.p. 234–235°.

Anal. Calcd. for $C_{12}H_5NO_4S$: N, 5.41; S, 12.36. Found: N, 5.23; S, 12.32.

6-Nitro-2-(2-thenoyl)-benzoic acid, m.p. 170°, was ring-closed in a similar manner. This too was 5-nitrothiophanthraquinone, m.p. 235–236°.

When the nitrothiophanthraquinone prepared from either the 3- or the 6-nitro-2-(2-thenoyl)-benzoic acid was reduced with sodium hydrosulfite the 5-aminothiophanthraquinone was obtained as identified by the *p*-toluenesulfonamido and the 2-thenoylamido derivatives.

The β-Aminothiophanthraquinones.—A number of attempts to convert the β-chlorothiophanthraquinones to the β-aminothiophanthraquinones by condensations with *p*-toluenesulfonamide proved fruitless. Therefore the β-aminothiophanthraquinones prepared from the 4-amino-2-(2-thenoyl)-benzoic acid and from the 4- and 5-nitro-2-(2-thenoyl)-benzoic acid by the methods described for the α-aminothiophanthraquinones were converted to the chloro derivatives *via* the Sandmeyer reaction.

A solution of β-aminothiophanthraquinone (0.5 g.) in 96% sulfuric acid (5 cc.) was cautiously treated with sodium nitrite (0.140 g.). After the addition which required about 20 minutes at 10°, the solution was held at 15° until a test gave a clear yellow solution in water (no trace of red). The solution was poured on a little ice, filtered, and the filter-cake pressed well. It was then added to a solution of cuprous chloride (0.88 g.) in 36% hydrochloric acid (50 cc.). After the immediate reaction with evolution of nitrogen the suspension was stirred 15 minutes at room temperature, diluted with water (50 cc.) and heated to the boil. The hot solution was filtered and the precipitate was vatted in alkaline hydrosulfite and crystallized from ethanol. β-Chlorothiophanthraquinones were thus obtained. Comparisons were difficult since the melting points of the 6- and 7-chlorothiophanthraquinones depended upon the solvent from which they had been crystallized, on the time interval elapsed since they were crystallized, and on the rate of heating.

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(5) P. C. Mitter, *J. Indian Chem. Soc.*, 7, 625 (1930).

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

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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.