[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Metalation of Thianthrene-5-dioxide by *n*-Butyllithium and by Phenyllithium and Cleavage of Thianthrene-5,5,10-trioxide by *n*-Butyllithium

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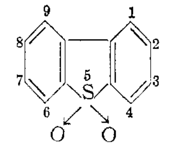
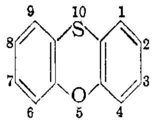
Thianthrene-5-dioxide was metalated in the 4- and/or 4,6-positions by *n*-butyllithium. Phenyllithium metalated the sulfone in the 4,6-positions. Metalation of thianthrene was checked and 1-thianthrenecarboxylic acid and 1-aminothianthrene were obtained in greater purity, and the orientation of the lithium atom in the thianthrenyllithium was established by an independent method. Thianthrene-5,5,10-trioxide was cleaved by *n*-butyllithium to give, upon carbonation, 2,2′-dicarboxydiphenyl sulfone and dibenzothiophene-5-dioxide.

Aromatic sulfoxides and sulfones are more reactive to the action of *n*-butyllithium than the corresponding sulfides or ethers, but whereas the sulfoxides invariably undergo reduction,[1] cleavage,[2] or even complete elimination,[2,3] during treatment with *n*-butyllithium, the sulfones are stable under these conditions and metalate with great ease giving, upon carbonation, unreduced carboxylic acids. Like the sulfides and ethers the sulfones orient the lithium atom in the *ortho* positions. Thus, dibenzothiophene-5-dioxide (I) is metalated by *n*-butyllithium in the 4- and/or 4,6-positions.[4] Similarly, treatment of diphenyl sulfone with *n*-butyllithium followed by carbonation gave 2-carboxy- and/or 2,2′-dicarboxydiphenyl sulfone.[4] Phenoxathiin (II) is metalated by *n*-butyllithium in the 4-position,[5] but phenoxathiin-10-dioxide is metalated in the 1- and/or 1,9-positions.[6,7]



I



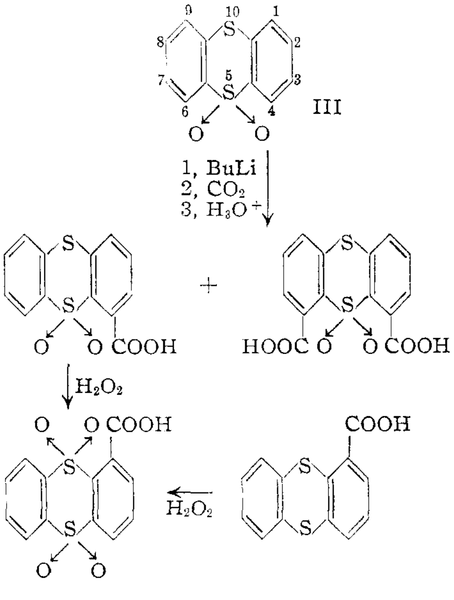
II

The object of the present investigation was to study the action of *n*-butyllithium on thianthrene-5-dioxide (III) and on thianthrene-5,5,10-trioxide (IV). At −70° the action of *n*-butyllithium on III was limited to monometalation to give, upon carbonation, a 41% yield of a monocarboxythianthrene-5-dioxide. At higher temperatures mixtures of mono- and dicarboxythianthrene-5-dioxide were obtained. In all the four experiments in which the metalation of the sulfone was carried out with *n*-butyllithium at temperatures ranging from −70 to 25°, fair amounts of the unreacted III were recovered. This fact illustrates the great stability of the sulfone as compared with the sulfoxide group toward *n*-butyllithium.

Phenyllithium metalated III at room temperature to give, upon carbonation, a dicarboxythianthrene-5-dioxide which was identical with the dicarboxythianthrene-5-dioxide obtained from the reaction of III with *n*-butyllithium. The yield of the dicarboxylic acid obtained from the metalation of III with phenyllithium was 54%, a fact which shows that phenyllithium may prove valuable in metalating other sulfones.

The structure of the monocarboxylic acid was established as 4-carboxythianthrene-5-dioxide from the fact that, upon oxidation with hydrogen peroxide, it gave an acid which was identical with authentic 1-carboxythianthrene-5,10-tetroxide obtained from the oxidation of 1-thianthrenecarboxylic acid with hydrogen peroxide. This fact proved that the monometalation of III must have taken place either in the 1- or the 4-position. The 4-position, which is *ortho* to the sulfone group, is far more reactive than the 1-position, which is *ortho* to the sulfide group. Dibenzothiophene-5-dioxide can be metalated at −30°,[4] but dibenzothiophene can be recovered almost quantitatively if allowed to react with *n*-butyllithium at −10°.[1] Thianthrene, which has two sulfide groups, did not react with *n*-butyllithium at −70°, a condition under which thianthrene-5-dioxide gave a 41% yield of the monocarboxythianthrene-5-dioxide. The sulfone group has a greater activating effect on the *ortho* position than the ether group, which in turn is greater than the sulfide group, as is illustrated by the metalation of phenoxathiin[5] and of phenoxathiin-10-dioxide.[6,7] Therefore, the monometalation of III is likely to have occurred in the 4-position and not in the 1-position.

The infrared spectrum of the dicarboxythianthrene-5-dioxide indicated that substitution had



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[1] H. Gilman and D. L. Esmay, THIS JOURNAL, **74**, 266 (1952).

[2] H. Gilman and D. R. Swayampati, *ibid.*, **77**, 3387 (1955).

[3] Unpublished studies of D. L. Esmay.

[4] H. Gilman and D. L. Esmay, THIS JOURNAL, **75**, 278 (1953).

[5] H. Gilman, M. W. Van Ess, H. B. Willis and C. G. Stuckwisch, *ibid.*, **62**, 2606 (1940).

[6] D. A. Shirley and E. A. Lehto, *ibid.*, **77**, 1841 (1955).

[7] Unpublished studies of S. Eidt.

taken place in both of the benzene rings. One of the two carboxyl groups must be in the 4-position since monometalation must have preceded dimetalation. The other carboxyl group must be substituted in the other *ortho* position to the sulfone group since other sulfones, such as diphenyl sulfone,[4] dibenzothiophene-5-dioxide[4] and phenoxathiin-10-dioxide,[6,7] undergo heteronuclear dimetalation in positions *ortho* to the sulfone group. The structure of the dicarboxylic acid obtained from the dimetalation of III is therefore considered to be 4,6-dicarboxythianthrene-5-dioxide.

The structure of the 4-carboxythianthrene-5-dioxide was based partly on that of 1-thianthrenecarboxylic acid, which has been obtained from the metalation of thianthrene followed by carbonation.[8] It was therefore considered necessary to check the metalation of thianthrene. The structure of the 1-thianthrenecarboxylic acid had been proved by its synthesis from 1-bromothianthrene by a halogen–metal interconversion reaction followed by carbonation.[8] However, the melting point, 145°, of the 1-bromothianthrene, which had been prepared by a Friedel–Crafts type of reaction, does not fall in line with the melting points of some other halothianthrenes, such as 1-chlorothianthrene, 2-chlorothianthrene[9] and 2-bromothianthrene.[10] The melting points of the four halothianthrenes are compared in Table I. For these reasons an independent proof of the structure of the 1-thianthrenecarboxylic acid was thought desirable.

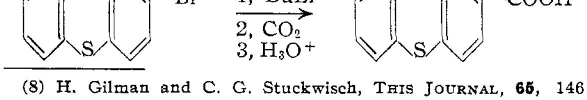
TABLE I

MELTING POINTS OF CHLORO- AND BROMOTHIANTHRENES

Halothianthrene	M.p., °C.
1-Chlorothianthrene	85–85.5[a]
2-Chlorothianthrene	84
1-Bromothianthrene	145
2-Bromothianthrene	89–90

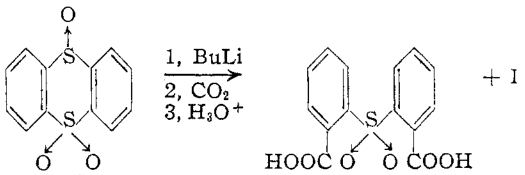
[a] See Experimental part.

2-Bromothianthrene[10] was allowed to react with *n*-butyllithium and the reaction mixture was carbonated to give a white thianthrenecarboxylic acid, which was different from the yellow thianthrenecarboxylic acid obtained from the metalation of thianthrene. It has been established that the lithium atom which has displaced bromine from 2-bromothianthrene does not undergo subsequent migration to another position.[10] Hence the acid obtained from 2-bromothianthrene by the halogen–metal interconversion reaction is 2-thianthrenecarboxylic acid. Since there are only two monocarboxylic acids of thianthrene, the other acid, obtained from the metalation of thianthrene, must be the 1-thianthrenecarboxylic acid. The melting point of the 1-isomer has been reported as 217–218°,[8] but we found that further recrystallization of the product raised its melting point to 224–225°.



Another way to show that the metalation of thianthrene takes place in the 1-position is through the conversion of the intermediate, thianthrenyllithium, to the aminothianthrene. We found that the aminothianthrene obtained from the metalation of thianthrene by *n*-butyllithium, followed by treatment with methoxylamine, melted at 121–122° instead of at 139° as has been reported.[8] A close examination of the reference revealed that the analysis of the reported 1-aminothianthrene[8] was far from satisfactory, and the product must have been, therefore, impure. The aminothianthrene, m.p. 121–122°, was found to be different from the 2-aminothianthrene.[10] Again, since there are only two possible monoaminothianthrenes, the one obtained from the metalation of thianthrene must be the 1-aminothianthrene. The infrared spectra of the two aminothianthrenes also substantiate the structures assigned to them.

Thianthrene-5,5,10-trioxide was considered a very interesting molecule for studying its reaction with *n*-butyllithium since it contains the two very reactive sulfoxide and sulfone groups. The sulfoxide group could undergo reduction, cleavage or elimination. The elimination of the sulfoxide group may be accompanied by a ring-closure reaction to give a dibenzothiophene derivative in a manner analogous to the conversion of thianthrene-5-oxide to dibenzothiophene.[2] The stable sulfone group could orient substitution of the lithium atom in the 4- and/or 4,6-positions, or it could assist the elimination of the sulfoxide group to form 2,2′-dilithiodiphenyl sulfone in view of its *ortho*-directing influence. We found that the treatment of IV with *n*-butyllithium at −70° resulted in cleavage, elimination of the sulfoxide group and the ring-closure reaction, to give upon carbonation 2,2′-dicarboxydiphenyl sulfone and dibenzothiophene-5-dioxide.



IV

In the reaction of thianthrene-5-oxide with *n*-butyllithium at low temperatures the main product was dibenzothiophene (53% yield) and the acid, 2,2′-dicarboxydiphenyl sulfide, formed as a result of the elimination of the sulfoxide group, was obtained only in very small amount (1%).[2] With IV the situation was reversed. The main product of the reaction was the acid, 2,2′-dicarboxydiphenyl sulfone (17%), and the corresponding dibenzothiophene derivative I, was formed to the extent of only 5%. This is attributed to the *ortho*-directing influence of the sulfone group which would assist the elimination of the sulfoxide group by directing lithium atoms in the positions where the carbon atoms are holding the sulfoxide group.

The mechanism of this reaction probably involves the initial cleavage of IV by *n*-butyllithium to give the intermediate V. The carbanion of the intermediate may attack the carbon atom holding

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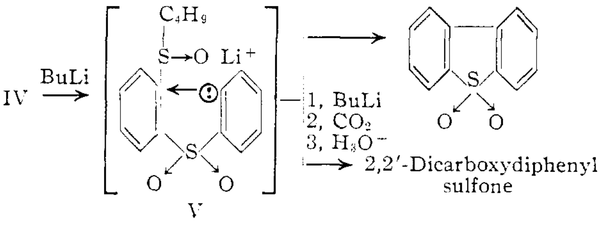
[8] H. Gilman and C. G. Stuckwisch, THIS JOURNAL, **65**, 1461 (1943).

[9] K. Fries and W. Vogt, *Ann.*, **381**, 312 (1911).

[10] H. Gilman and D. R. Swayampati, THIS JOURNAL, **77**, 5944 (1955).

the butylsulfinyl group. This intramolecular elimination reaction of V would form the dibenzothiophene-5-dioxide. The intermediate, however, can be further attacked by additional *n*-butyllithium, resulting in the elimination of the butylsulfinyl group and formation of 2,2'-dilithiodiphenyl sulfone, which, upon carbonation, would give the 2,2'-dicarboxydiphenyl sulfone. Obviously, the second reaction takes place at a greater rate than the first since the yield of the acid, 2,2'-dicarboxydiphenyl sulfone, was more than three times the yield of the dibenzothiophene-5-dioxide.



V

The other sulfoxide of thianthrene, thianthrene-5,10-dioxide, did not react to any appreciable extent with *n*-butyllithium due probably to the extreme insolubility of the product in ether at low temperatures. Substantial amounts of the 5,10-dioxide were recovered. The only acidic material obtained following carbonation of the reaction mixture was a yellow oil which did not harden upon standing. Both the α- and the β-form of the 5,10-dioxide[11] were employed successively in the reaction, but no appreciable difference in their reactivity was observed, although the α-form is much more polar than the β-form.[11]

Experimental[12]

Thianthrene-5-dioxide (III) and *n*-Butyllithium. Run I.—To a stirred suspension of 9.92 g. (0.04 mole) of III[10] in 200 ml. of anhydrous ether was added, over a period of 15 minutes, 44 ml. (0.044 mole) of an ethereal solution of *n*-butyllithium.[13] The reaction flask was immersed in an ice-bath during the addition of the *n*-butyllithium solution and for a subsequent period of 2 hours. The color of the suspension changed to orange during this period. The ice-bath was removed, and the mixture was stirred for an additional period of 30 minutes. Carbonation was effected by the jet-wise addition of the suspension to a stirred slurry of Dry Ice and ether. When all the carbon dioxide had evaporated, the mixture was warmed on the steam-plate to remove the ether.

The dry residue was treated with water and filtered. The yellowish solid was washed and dried to give 3.7 g. (37%) of the crude III melting over the range 150–170°. Recrystallization from acetic acid gave 2.1 g. (21%) of pure III, m.p. and mixed m.p. 167–168°.

The filtrate from the above was treated with Norit-A, filtered and acidified with 10% hydrochloric acid. A grey, sticky product separated and hardened upon standing. The material was filtered, washed and dried to yield 7.8 g. of a white product. A part of it melted over the range 230–235° and the remainder melted between 290 and 300°. The separation of the mono- and the dicarboxylic acids was effected by fractional crystallization from methanol. The crude monocarboxylic acid was finally recrystallized from aqueous acetone to give 2.0 g. (21.7%) of the pure product, melting at 255–256°. The yield of the monocarboxythianthrene-5-dioxide is based on the unrecovered III.

The infrared spectrum showed absorption bands at 5.9, 8.7 and 13.8 μ, indicative of the carbonyl group, the sulfone group and 1,2-substitution, respectively.

Anal. Calcd. for $C_{13}H_8O_4S_2$: neut. equiv., 292; S, 21.92. Found: neut. equiv., 296, 296; S, 22.35, 22.19.

The product, upon oxidation with hydrogen peroxide, gave an acid which was identical with the 1-carboxythianthrene-5,10-tetroxide, obtained from the oxidation of 1-thianthrenecarboxylic acid with hydrogen peroxide. From these considerations and the greater reactivity of the sulfone over the sulfide group, the monocarboxythianthrene-5-dioxide is considered to be 4-carboxythianthrene-5-dioxide.

The other pure product obtained from the fractional crystallization was a dicarboxythianthrene-5-dioxide. The yield of the dicarboxylic acid, which melted at 364° with decomposition, was 0.25 g. (2%, based on the unrecovered III).

Anal. Calcd. for $C_{14}H_8O_6S_2$: neut. equiv., 168; S, 19.03. Found: neut. equiv., 167, 167; S, 19.02, 18.98.

The infrared spectrum showed absorption bands at 5.9 and 8.7 μ, indicative of the carbonyl and the sulfone groups, respectively. The absence of a band between 13 and 14 μ showed that substitution had taken place in both of the benzene rings.

From considerations applied to the structure of the 4-carboxythianthrene-5-dioxide, and by comparison with the dimetalation of diphenyl sulfone,[4] I[4] and phenoxathiin-10-dioxide,[6,7] the dicarboxylic acid is considered to be 4,6-dicarboxythianthrene-5-dioxide.

Run II.—To a stirred suspension of 24.8 g. (0.1 mole) of III in 200 ml. of anhydrous ether at −40 to −45° was added 261 ml. (0.3 mole) of an ethereal solution of *n*-butyllithium. The mixture was stirred at the low temperature for a period of 5 hours. Color Tests I[14] and II[15] were positive at the end of this period. The reaction mixture was carbonated and worked up as in Run I. The yield of the pure III recovered was 7.7 g. (31%).

The aqueous layer, upon acidification, gave 15.3 g. of acidic material. Fractional crystallization of the crude product gave 3.1 g. of the pure 4,6-dicarboxythianthrene-5-dioxide, melting at 364° with decomposition. The yield of the dicarboxylic acid, based on the unrecovered thianthrene-5-dioxide, was 12%.

Run III.—To a stirred suspension of 22.3 g. (0.09 mole) of III in 200 ml. of anhydrous ether at room temperature was added, over a period of 15 minutes, 75 ml. (0.099 mole) of an ethereal solution of *n*-butyllithium. At the end of 1 hour, Color Test I was positive and Color Test II was negative.

The reaction mixture was carbonated and worked up as in Run I. The yield of the pure III recovered was 13 g. (58.3%). The aqueous layer, upon acidification, gave 4.0 g. (36.5%) of the crude 4-carboxythianthrene-5-dioxide, melting over the range 235–240°. Recrystallization of the crude product from aqueous acetone gave 2.5 g. (22.7%) of the pure acid, m.p. 255–256°.

Run IV.—This run differed from Run II in that the reaction mixture was stirred at −70° for a period of 16 hours. The yield of the pure III recovered was 11.95 g. (48.2%). The aqueous layer, upon acidification, gave 8.2 g. of crude 4-carboxythianthrene-5-dioxide, melting over the range 230–246°. Recrystallization of the product from ethanol gave 6.15 g. of the pure product, melting at 255–256°. The yields of the crude and pure 4-carboxythianthrene-5-dioxide, based on unrecovered III, were 54 and 41%, respectively.

Thianthrene-5-dioxide and Phenyllithium.—To a stirred suspension of 4.96 g. (0.02 mole) of powdered III in 50 ml. of anhydrous ether was added 50 ml. (0.04 mole) of an ethereal solution of phenyllithium.[16] The reaction flask was immersed in an ice-bath for 1 hour, and the stirring was continued for an additional period of 3 hours at room temperature. Carbonation was effected by adding the suspension to a stirred slurry of Dry Ice and ether. When all the carbon dioxide had evaporated water was added and the layers were separated. The ethereal layer, upon

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[11] E. Bergmann and M. Tschudnowsky, *Ber.*, **65**, 457 (1932).

[12] All melting points reported herein are uncorrected. Reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen.

[13] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949).

[14] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

[15] H. Gilman and J. Swiss, *ibid.*, **62**, 1847 (1940).

[16] J. C. W. Evans and C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 518.

evaporation, left a small amount of a brown oil which was discarded.

The aqueous layer was warmed to expel the dissolved ether, subsequently treated with Norit-A, filtered, cooled and acidified with 10% hydrochloric acid. The white product which separated was filtered, washed and dried to yield 4.2 g. (62%) of crude 4,6-dicarboxythianthrene-5-dioxide, melting over the range 350–360° with decomposition. The product was refluxed with acetic acid, filtered and dried to give 3.6 g. (54%) of pure acid, melting at 364° with decomposition. The infrared spectrum of the acid was identical with that of the 4,6-dicarboxythianthrene-5-dioxide, obtained from the dimetalation of III with *n*-butyllithium. A mixture of the two acids melted undepressed. No III was recovered from this reaction.

4-Carboxythianthrene-5-dioxide and Hydrogen Peroxide.—To a hot solution of 1.46 g. (0.005 mole) of 4-carboxythianthrene-5-dioxide in 20 ml. of glacial acetic acid was added 9.0 g. of 30% hydrogen peroxide in 10 ml. of glacial acetic acid. The resulting solution was refluxed for a period of 2 hours. The white product which separated upon cooling was filtered and dried to yield 1.35 g. of an acid melting at 306–307°.

The mother liquor was concentrated to a volume of 25 ml. and allowed to cool. The white product which separated was filtered and dried to give 0.25 g. of the acid melting at 307–308°. The total yield of the pure acid, identified as 1-carboxythianthrene-5,10-tetroxide, was 1.60 g. (99%).

The acid did not depress the melting point of authentic 1-carboxythianthrene-5,10-tetroxide, obtained from the oxidation of 1-thianthrenecarboxylic acid with hydrogen peroxide. The identity was further established by a comparison of the infrared spectra.

2-Thianthrenecarboxylic Acid.—To a solution of 5.90 g. (0.02 mole) of 2-bromothianthrene[10] in 100 ml. of anhydrous ether at −70° was added, over a period of 5 minutes, 17 ml. (0.02 mole) of an ethereal solution of *n*-butyllithium. The reaction mixture was stirred at the low temperature for 20 minutes. Color Test II was negative at the end of this period. The mixture was carbonated and worked up as before. The ethereal layer, upon evaporation, left a white residue which was too small to work up.

The aqueous layer was warmed to expel the dissolved ether, subsequently treated with Norit-A, filtered, cooled and acidified with 10% hydrochloric acid. The white product which separated was filtered, washed and dried to yield 3.58 g. (70%) of the 2-thianthrenecarboxylic acid, melting at 226–228°. Recrystallization from glacial acetic acid gave the pure product melting at 227–228°. The white acid showed strong fluorescence under ultraviolet rays.

Anal. Calcd. for $C_{13}H_8O_2S_2$: neut. equiv., 260; S, 24.6. Found: neut. equiv., 258, 258; S, 24.4, 24.2.

A product, m.p. 224°, has been reported which may have been 2-thianthrenecarboxylic acid.[17]

2-Carboxythianthrene-5,10-tetroxide.—To a hot solution of 0.90 g. (0.0035 mole) of 2-thianthrenecarboxylic acid in 20 ml. of glacial acetic acid was added 5 ml. of 30% hydrogen peroxide. The solution became colorless in a few minutes. The mixture was refluxed for 2 hours. A white product which crystallized upon cooling was filtered and dried to yield 0.95 g. (87%) of 2-carboxythianthrene-5,10-tetroxide, melting at 302–303°.

Anal. Calcd. for $C_{13}H_8O_6S_2$: neut. equiv., 324; S, 19.75. Found: neut. equiv., 320, 319; S, 19.76, 19.61.

1-Thianthrenecarboxylic Acid.—To a stirred suspension of 43.2 g. (0.2 mole) of thianthrene[18] in 400 ml. of anhydrous ether was added 300 ml. (0.3 mole) of an ethereal solution of *n*-butyllithium, and the resulting mixture was stirred at room temperature for 40 hours, after which Color Test II was found to be negative. Color Test I was positive throughout the stirring period. Carbonation was carried out as before. The ethereal layer gave 3.0 g. (7% recovery) of thianthrene (mixed m.p.).

The aqueous layer was warmed to expel the dissolved ether, treated with Norit-A, filtered, cooled and acidified with 10% hydrochloric acid. The yellow product which separated was filtered, washed and dried to give 43.0 g. (83%) of crude acid, melting over the range 185–220°. The product was extracted three times with 500-ml. portions of hot benzene and the combined extract was allowed to cool. The product was recrystallized once again from benzene to yield 14.5 g. (28%) of the pure 1-thianthrenecarboxylic acid, melting at 224–225°. The values 257 and 258 obtained for the neutral equivalent are in agreement with the calculated value of 260 for the monocarboxylic acid. The acid was found to be different from the 2-thianthrenecarboxylic acid.

The 1-thianthrenecarboxylic acid has been prepared before, but its melting point was reported as 217–218°.[8]

1-Carboxythianthrene-5,10-tetroxide.—To a hot solution of 5.2 g. (0.02 mole) of 1-thianthrenecarboxylic acid in 50 ml. of glacial acetic acid was added a solution of 18 g. (0.16 mole) of 30% hydrogen peroxide in 20 ml. of glacial acetic acid. The yellow color of the solution disappeared in approximately 10 minutes. The colorless solution was refluxed for 3 hours and allowed to cool. The white, crystalline product which separated during a period of 24 hours was filtered and dried to yield 4.13 g. of the pure product melting at 306–307° with decomposition. The mother liquor upon dilution gave an additional 1.4 g. of the nearly pure acid, melting at 302–304° with decomposition. The total yield of the 1-carboxythianthrene-5,10-tetroxide was 5.53 g. (85.3%).

Anal. Calcd. for $C_{13}H_8O_6S_2$: neut. equiv., 324; S, 19.75. Found: neut. equiv., 327, 326; S, 19.39, 19.37.

1-Aminothianthrene.—To the thianthrenyllithium solution prepared, as described for 1-thianthrenecarboxylic acid, from 43.2 g. (0.2 mole) of thianthrene and 0.4 mole of *n*-butyllithium was added an ethereal solution of 9.4 g. (0.2 mole) of methoxylamine[19] in 60 ml. of anhydrous ether. The addition of the base was carried out at 0–5° over a period of 15 minutes. The reaction mixture was stirred for 1 hour after which Color Test I was found to be negative. Dilute hydrochloric acid was added until the aqueous layer was acidic. The ethereal layer was separated and dried over anhydrous sodium sulfate. Hydrogen chloride was bubbled through the reddish solution for 1 hour at the end of which period the precipitation of the hydrochloride was complete. The cream-colored product was filtered and dried to yield 23.0 g. of crude hydrochloride which softened at 220° and melted at 231° with decomposition.

The free base was obtained by warming the hydrochloride with 10% sodium hydroxide solution. The crude 1-aminothianthrene weighed 18.0 g. Recrystallization of the product from 70% ethanol gave 12.0 g. of pure 1-aminothianthrene melting at 120–121°. The melting point did not change upon further recrystallization.

Anal. Calcd. for $C_{12}H_9NS_2$: N, 6.06. Found: N, 6.03, 5.96.

The product was different from the 2-aminothianthrene,[10] m.p. 160.5–161°, as shown by the comparison of the infrared spectra of the two isomers.

From the original reaction mixture and the mother liquor left after the precipitation of the hydrochloride was recovered a total of 23.0 g. (53%) of thianthrene (mixed m.p.). The yields of the crude and pure 1-aminothianthrene, based on the unrecovered thianthrene, were 83 and 55%, respectively.

The reported 1-aminothianthrene, m.p. 139°,[8] must have been impure since its analysis was not very satisfactory.

1-Chlorothianthrene.—To a stirred suspension of 6.93 g. (0.03 mole) of 1-aminothianthrene, 7.5 ml. of hydrochloric acid and 15 ml. of water, cooled to 0°, was added a solution of 2.1 g. of sodium nitrite in 10 ml. of water. The temperature of the mixture was maintained at 0–5° during the addition of the sodium nitrite solution. After a period of 10 minutes, 30 ml. from a total of 90 ml. of a solution of cuprous chloride in hydrochloric acid was added to the mixture. The cuprous chloride solution was freshly prepared from 62.5 g. of copper sulfate in accordance with the procedure described by Vogel.[20] A vigorous reaction followed the addition of the catalyst, and the red diazotized

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(17) G. M. Bennett, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 444 (1937).

(18) K. Fleischer and J. Stemmer, *Ann.*, **422**, 265 (1921).

(19) The free base was obtained by the dropwise addition of a 50% sodium hydroxide solution to the hydrochloride. The reaction flask was immersed in a bath maintained at 60–70°, and the vapor was passed through potassium hydroxide pellets before being condensed.

(20) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Company, New York, N. Y., 1948, p. 186.

mixture turned brown. The voluminous mass was subsequently heated on the steam-bath for 30 minutes and allowed to cool. The supernatant liquid was decanted off, and the brown residue was treated with hydrochloric acid and washed.

The black tarry material obtained was sublimed under reduced pressure to give a total of 3.0 g. (40%) of crude 1-chlorothianthrene melting over the range 70–78°. Recrystallization from methanol (Norit-A) gave 1.4 g. (18.6%) of the nearly pure product melting at 79.5–81.5°. The pure product, m.p. 85–85.5°, was obtained by further recrystallization. The product gave a positive test for chlorine.

The infrared spectrum showed absorption bands at 13.0 and 13.4 μ, characteristic of 1,2,3- and 1,2-substitution, respectively.

Anal. Calcd. for $C_{12}H_7ClS_2$: S, 25.5. Found: S, 25.4, 24.9.

1-Chlorothianthrene-5,10-tetroxide.—To a hot solution of 0.25 g. (0.001 mole) of 1-chlorothianthrene in 2 ml. of glacial acetic acid was added 0.46 g. of 30% hydrogen peroxide in 2 ml. of glacial acetic acid, and the resulting solution was refluxed for 2 hours. The mixture was cooled, and the crystalline product which had separated was filtered and dried to yield 0.26 g. (84%) of 1-chlorothianthrene-5,10-tetroxide melting over the range 236–239°. Recrystallization from glacial acetic acid gave 0.20 g. (65%) of the pure product melting at 242°.

Anal. Calcd. for $C_{12}H_7ClO_4S_2$: S, 20.38. Found: S, 20.67.

1-Thianthreneboronic Acid.—The thianthrenyllithium solution prepared, as described for 1-thianthrenecarboxylic acid, from 54.0 g. (0.25 mole) of thianthrene and 0.25 mole of *n*-butyllithium was transferred to a graduated separatory funnel and subsequently added slowly to a stirred solution of 57.5 g. (0.25 mole) of tri-*n*-butyl borate[21] in 200 ml. of anhydrous ether at −70°. The low temperature was maintained for a period of 6 hours after which the mixture was allowed to warm up to room temperature.

To the stirred, clear solution was added slowly 10% sulfuric acid until the aqueous layer was distinctly acidic (congo red). The ethereal layer was separated and extracted with a slight excess of 10% potassium hydroxide solution. The extract was washed with ether and subsequently warmed to expel the dissolved ether. It was observed that the product decomposed rapidly upon warming. The remaining, dissolved ether was removed by using the water-pump vacuum. The mixture was treated for a short time with Norit-A, filtered, cooled and acidified by the slow addition of 10% hydrochloric acid. A cream-colored product which separated was filtered and dried to give 40.5 g. (62.5%) of crude 1-thianthreneboronic acid. Recrystallization from benzene gave 17.5 g. of nearly pure product melting at 146–148°. Another recrystallization from the same solvent gave 14.4 g. (22.2%) of the pure 1-thianthreneboronic acid melting at 147–148°. The test for boron was positive.

Anal. Calcd. for $C_{12}H_9BO_2S_2$: neut. equiv., 260; S, 24.64. Found: neut. equiv., 263, 264; S, 24.45, 24.40.

1-Thianthrenyltriphenylsilane.—To the 1-thianthrenyllithium solution prepared, as described for 1-thianthrenecarboxylic acid, from 0.2 mole of thianthrene and 0.23 mole of *n*-butyllithium was added a solution of 68.7 g. (0.23 mole) of triphenylchlorosilane in 700 ml. of anhydrous ether. The mixture was stirred at room temperature for 48 hours after which Color Test I was found to be negative.

The suspension was cooled, treated with water and filtered. The residue was washed and dried to give 50.0 g. of a white product melting over the range 170–200°. Several recrystallizations, alternately from benzene and xylene, finally gave 9.0 g. (9.5%) of pure 1-thianthrenyltriphenylsilane melting at 190–191.5°.

Anal. Calcd. for $C_{30}H_{22}S_2Si$: Si, 5.91. Found: Si, 5.90, 5.90.

The other product obtained from the recrystallizations melted over the range 330–337° and was not identified.

Thianthrene-5,5,10-trioxide (IV) and *n*-Butyllithium.—To a stirred suspension of 26.4 g. (0.1 mole) of IV[10] in 200 ml. of anhydrous ether at −70° was added 300 ml. (0.3 mole) of an ethereal solution of *n*-butyllithium. The resulting mixture was stirred at the low temperature for 3 hours. Color Test I was positive and Color Test II, negative at the end of this period. The brown solution was carbonated by addition to a stirred slurry of Dry Ice and ether. When all the carbon dioxide had evaporated water was added and the layers were separated.

The ethereal layer upon evaporation left a white product which was crystallized from methanol to give 0.43 g. of white crystals melting at 234°. An admixture of the product with an authentic specimen of dibenzothiophene-5-dioxide melted undepressed. The infrared spectra of the two products were identical.

The ether-insoluble residue which was left in the reaction flask was recrystallized from 90% acetic acid to yield 0.65 g. of additional dibenzothiophene-5-dioxide, identified by its mixed melting point. The total yield of I from the reaction was 1.08 g. (5%).

The aqueous layer was warmed with Norit-A, filtered, cooled and acidified with 10% hydrochloric acid. A colorless oil separated, and upon standing for 7 days turned into a white, soft, sticky mass. The product was subjected to distillation under reduced pressure to remove a small amount of an oily material with which the acidic solid seemed to be contaminated. The reaction flask was immersed in a bath maintained at 100° during the distillation. The residue in the flask was washed with hot benzene and dried to yield 8.0 g. of a white powder melting over the range 213–217°. Recrystallization from water yielded 5.1 g. of the pure acid melting at 218–219°. Further recrystallization from water did not change the melting point, but recrystallization from glacial acetic acid raised the melting point to 220–221°.

The values obtained for the neutral equivalent, 155, 155, are in agreement with the calculated value, 153, for 2,2′-dicarboxydiphenyl sulfone. The infrared spectrum showed absorption bands at 5.9, 8.7 and 13.2 μ, characteristic of the carbonyl group, the sulfone group and 1,2-substitution, respectively.

The product did not depress the melting point of authentic 2,2′-dicarboxydiphenyl sulfone.[4] The infrared spectra of the two products were identical. The yields of the crude and pure 2,2′-dicarboxydiphenyl sulfone were 26 and 16.6%, respectively.

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[21] The reagent was kindly supplied by Mr. Ralph Ranck of this Laboratory.