1955

Synthesis and orientation of some derivatives of thianthrene

Dhairyasheel R. Swayampati
Iowa State College

Recommended Citation

Swayampati, Dhairyasheel R., "Synthesis and orientation of some derivatives of thianthrene" (1955). *Retrospective Theses and Dissertations*. 15208.
https://lib.dr.iastate.edu/rtd/15208

SYNTHESIS AND ORIENTATION OF SOME DERIVATIVES OF THIANTHRENE

by

Dhairyasheel R. Swayampati

45

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1955

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

1126-90

TABLE OF CONTENTS

INTRODUCTION

Thianthrene (I) was first prepared by Stenhouse[1] in the year 1869 by distilling thiophenol from a copper retort. Several other workers prepared the compound by different reactions in the following twenty years,[2-6] but its structure was established for the first time in the year 1889.[7] The name thianthrene was given to the compound in 1896 from its structural analogy with anthracene.[8] The other name commonly used for thianthrene is diphenylene disulfide.

Since then a large number of derivatives of thianthrene have been made, but in spite of the considerable amount of work done in this field, the chemical knowledge of thianthrene, at present, is fragmentary. The investigations described in this thesis were undertaken with a view to collect, systematize and extend the knowledge of the syntheses and orientation in

---

[1] J. Stenhouse, Ann., 149, 252 (1869).

[2] C. Graebe, Ber., 7, 50 (1874).

[3] C. Graebe, Ann., 179, 180 (1875).

[4] E. B. Schmidt, Ber., 11, 1173 (1878).

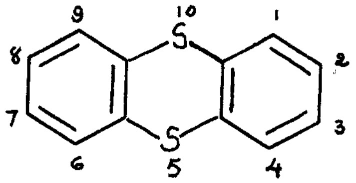
[5] C. Friedel and J. M. Crafts, Ann. chim. phys., 1, 530 (1884).

[6] C. Friedel and J. M. Crafts, Ann. chim. phys., 14, 433 (1888).

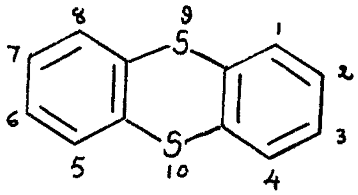
[7] P. Jacobson and E. Ney, Ber., 22, 904 (1889).

[8] F. Kraft and R. E. Lyons, Ber., 29, 435 (1896).

the thianthrene system.



Ia



Ib

Thianthrene and its derivatives have been used in the preparation of vat dyes, disinfectants, insecticides, antioxidants and plasticizers. In contrast to dibenzothiophene, dibenzo-p-dioxin and phenoxathiin, thianthrene has the additional, interesting aspect of being non-planar, which adds to the possibility of stereoisomerism. Further, the presence of the two sulfur atoms in thianthrene greatly increases the possibility of making a large number of derivatives by oxidation to the sulfoxide, disulfoxide, monosulfone, sulfone-sulfoxide and disulfone. The meta-directing influence of the sulfoxide or sulfone group toward electrophilic attack is in contrast to the ortho-, and para-directing influence of the sulfide group. The possibility of preparing selected derivatives by direct substitution is, therefore, increased by the presence of these groups in the thianthrene molecule.

The numbering system (Ia) employed in this thesis is that recommended by Patterson[9], and which is used by the current

---

[9] A. M. Patterson and L. T. Capell, "The Ring Index", Reinhold Publishing Corporation, New York, N. Y., 1940, p. 262.

Chemical Abstracts. The other numbering system widely used is (Ib).

The numbering of all thianthrene compounds has been adjusted to conform to the style (Ia) where necessary. The oxidation products of thianthrene compounds, which are often described in the literature as sulfoxide, disulfoxide, monosulfone, sulfoxide-sulfone and disulfone have been described in the following pages as -5-oxide, -5,10-dioxide, -5-dioxide, -5,5,10-trioxide and -5,10-tetraoxide, respectively.

HISTORICAL

Thianthrene was used for the first time in this laboratory in a comparative study on the orientation influence of the hetero atoms, oxygen and sulfur, in metalation reactions.[10] Later work on thianthrene was restricted to the preparation of a few derivatives.[11-14]

Although detailed information about the chemistry of

---

[10] H. Gilman and C. G. Stuckwisch, J. Am. Chem. Soc., 65, 1461 (1943).

[11] G. A. Martin, Jr., Unpublished Ph.D. Thesis, Iowa State College Library, 1945.

[12] G. A. Martin, Jr., Iowa State Coll. J. Sci., 21, 38 (1946).

[13] D. L. Esmay, Unpublished Ph. D. Thesis, Iowa State College Library, 1951.

[14] H. Gilman and D. L. Esmay, J. Am. Chem. Soc., 76, 5787 (1954).

the sulfur-containing heterocycles, dibenzothiophene,[13,15-20] phenoxathiin[21] and phenothiazine[22-26] can be obtained from several works, no attempt has been made to compile and systematize the available knowledge of thianthrene.

The historical section of this thesis includes the known

---

[15] S. Avakian, Unpublished Ph. D. Thesis, Iowa State College Library, 1944.

[16] R. K. Ingham, Unpublished Ph. D. Thesis, Iowa State College Library, 1952.

[17] A. L. Jacoby, Unpublished Ph. D. Thesis, Iowa State College Library, 1938.

[18] J. F. Nobis, Unpublished Ph. D. Thesis, Iowa State College Library, 1948.

[19] D. K. Fukushima in R. C. Elderfield, "Heterocyclic Compounds", John Wiley and Sons, Inc., New York, N. Y., 1950, Vol. 2, p. 164-172.

[20] H. D. Hartough and L. S. Meisel, "The Chemistry of Heterocyclic Compounds", "Compounds with Condensed Thiophene Rings", Interscience Publishers, Inc., New York, N. Y., 1954 p. 225-282.

[21] C. L. Deasy, Chem. Revs., 32, 173 (1943).

[22] J. F. Champaigne, Unpublished Master's Thesis, Iowa State College Library, 1952.

[23] J. W. Diehl, Unpublished Master's Thesis, Iowa State College Library, 1953.

[24] S. P. Massie, Chem. Revs., 54, 797 (1954).

[25] R. D. Nelson, Unpublished Ph. D. Thesis, Iowa State College Library, 1951.

[26] D. A. Shirley, Unpublished Ph. D. Thesis, Iowa State College Library, 1943.

methods for the preparation of, and the general reactions of thianthrene and its derivatives. References on thianthrene itself are listed separately in a bibliography at the end of the historical section. The known derivatives of thianthrene have been grouped in tables I-VII. The literature has been covered completely through the year 1953, and as completely as possible through May, 1955.

Steric Factors

The non-planar character of the thianthrene molecule, first shown by Bergmann and Tschudnowsky[27] from the dipole-moment determination, makes its chemistry interesting and somewhat complicated. The reported values for its dipole moment range from 1.41 - 1.57D,[27-30] which are all too high for a planar molecule. Crystallographic studies have confirmed the folded structure of thianthrene, and the angle of the fold has been determined as about 140°.[31] Further, in

---

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

[28] G. M. Bennett and S. Glasstone, J. Chem. Soc., 128 (1934).

[29] I. G. M. Campbell, C. G. LeFèvre, R. J. W. LeFèvre and E. E. Turner, J. Chem. Soc., 404 (1938).

[30] W. S. Walls and C. P. Smyth, J. Chem. Physics, 1, 337 (1933).

[31] R. G. Wood and J. E. Crackston, Phil. Mag., 31, 62 (1941).

agreement with the rule that "analogously constituted derivatives of elements of similar type form solid solutions, provided that their spatial structures are also alike", thianthrene forms solid solutions with the other non-planar heterocycles, phenothiazine and selenanthrene, but forms only eutectic mixtures with the planar heterocycles, phenoxazine and dibenzo-p-dioxin.[32,33] The molecule has an axis of symmetry through the two sulfur atoms.[27-30,34]

In view of the folded structure of the molecule it may be expected that a single substituent on one of the two rings of thianthrene would destroy the symmetry of the molecule, giving rise to optical isomerism. However, attempts to resolve 2-thianthrenecarboxylic acid[35] and 2-aminothianthrene[35,36] have proved unsuccessful. From this Keats has concluded that the thianthrene molecule oscillates so rapidly through a mean planar position that it virtually possesses a plane of

---

[32] N. M. Cullinane and W. T. Rees, Trans. Faraday Soc., 36, 507 (1940).

[33] N. M. Cullinane and C. A. J. Plummer, J. Chem. Soc., 63 (1938).

[34] M. Prasad, J. Shanker and B. H. Peermohamed, J. Indian Chem. Soc., 14, 177 (1937).

[35] G. M. Bennett, M. S. Lesslie and E. E. Turner, J. Chem. Soc., 444 (1937).

[36] G. H. Keats, ibid., 1592 (1937).

symmetry.[36] The valence angle of the sulfur atoms has been shown to be about 110°,[37] while in a planar form the angle would be 120°. The energy required for the conversion from a non-planar to a planar form would be only about 7000 calories. It is, therefore, very easy for the thianthrene molecule to assume the planar form. Optical activity is observable only when the heat of racemization is more than 20,000 calories per mole.[36]

The net effect of the oscillation, and therefore only a slight resultant deviation from planarity, accounts for the fact that the dipole moment of 2,7-dichlorothianthrene, 1.37 D, is not much different from that of thianthrene, since the two C-Cl moments would cancel each other more or less completely.[38]

Thianthrene and a number of its derivatives give two isomeric disulfoxides. The higher-melting disulfoxide is designated as the α- and the other, the β- form. The two forms of thianthrene-5,10-dioxide melt at 284° and 249°,

---

[37] L. E. Sutton and G. C. Hampson, Trans. Faraday Soc., 31, 945 (1935).

[38] E. Bergmann and A. Weizmann, Chemistry & Industry, 364 (1938).

respectively.[27,39-43] A third reported form, m.p., 229°,[8,44] has been shown by Fries and Vogt[41] to be an equimolecular mixture of the α- and the β- form. It has been found that in the preparation of one form, the other is always present, and that the β- form is more than three times as soluble as the α- form.[39] Bergmann and Tschudnowsky[27] determined the dipole moments of the two forms, and found the values as 1.7 D for the α-, and 4.2 D for the β- form. These authors concluded from this that the α- has a trans, and the β- has a cis configuration. However, Taylor[43] has shown that in view of the folded structure of the molecule, the cis form is more symmetrical than the trans form. He has, therefore, assigned the cis structure to the α- form, and the trans, to the other.

The two forms of the disulfoxides have been prepared for 2,7-dichlorothianthrene-5,10-dioxide, 2,7-dimethoxythianthrene-5,10-dioxide and 2,7-dimethylthianthrene-5,10-dioxide.[39]

---

[39] H. Baw, G. M. Bennett and P. Dearns, J. Chem. Soc., 680,(1934).

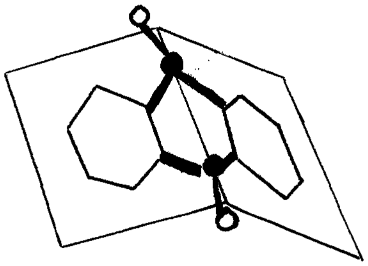
[40] J. Böeseken and A. T. H. Van der Meulen, Rec. trav. chim., 55, 925 (1936).

[41] K. Fries and W. Vogt, Ber., 44, 756 (1911).

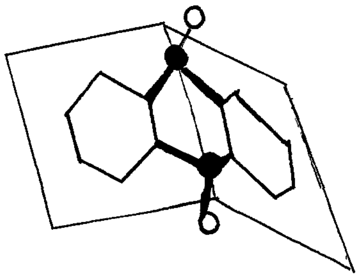
[42] O. Hinsberg, J. prakt. Chemie, 93, 302 (1916).

[43] T. W. J. Taylor, J. Chem. Soc., 625 (1935).

[44] J. J. B. Deuss, Rec. trav. chim., 27, 145 (1908).



cis



trans

Condensation Reactions

Condensations in the presence of anhydrous aluminum chloride

The use of anhydrous aluminum chloride as a catalyst in various organic reactions has been adequately reviewed elsewhere.[45] Only those reactions of immediate interest will be discussed here.

Thianthrene has been prepared by condensing benzene and sulfur,[6,42,46-48] benzene and sulfur monochloride,[5,40,49-51]

---

[45] C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry", Reinhold Publishing Corporation, New York, N. Y., 1941.

[46] I. Boeseken, *Rec. trav. chim.*, *24*, 209 (1905).

[47] P. Genvresse, *Bull. soc. chim. France*, *15*, 1038 (1896).

[48] G. Dougherty and P. D. Hammond, *J. Am. Chem. Soc.*, *57*, 117 (1935).

[49] P. Genvresse, *Bull. soc. chim. France*, *15*, 409 (1896).

[50] K. Fleischer and J. Stemmer, *Ann.*, *422*, 265 (1921).

[51] W. W. Hartman, L. A. Smith and J. B. Dickey, *Ind. Eng. Chem.*, *24*, 1317 (1932).

benzene and sulfur dichloride,[5,52] diphenyl sulfide [53,55] and thiophenol,[44] using anhydrous aluminum chloride as the catalyst in each case. The preparation from benzene and sulfur monochloride has been particularly recommended by Fleischer and Stemmer[50] who obtained thianthrene from the reaction in 66.5% yield. Martin found that, for some unexplained reason, the yields ranged from 35-60%,[13] while Shirley has reported the yields as 25-30%.[54] The main by-products of the reaction are thiophenol, diphenyl sulfide and diphenyl disulfide. Dougherty and Hammond have worked out conditions favorable for the formation of either thianthrene or diphenyl sulfide as the main product of the reaction between benzene and sulfur in the presence of the catalyst.[48]

The methods involving the use of sulfur monochloride or sulfur dichloride have been extended to prepare some disubstituted thianthrene derivatives of unknown structures from chlorobenzene,[52] nitrobenzene[49] and toluene.[49,50]

Some other catalysts such as selenium,[8] zinc[4] and aluminum

---

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

[53] J. J. B. Deuss, Rec. trav. chim., 28, 136 (1909).

[54] D. A. Shirley, "Preparation of Organic Intermediates", John Wiley and Sons, Inc., New York, N. Y., 1951, p. 276.

[55] E. E. Turner and A. B. Sheppard, J. Chem. Soc., 127, 544 (1925).

amalgam[56,57] have been used with sulfur and sulfur monochloride in the preparation of thianthrene. The aluminum amalgam had been used first by Cohen and Skirrow[56] in the condensation of benzene, and toluene with sulfur monochloride to yield thianthrene, and dimenthylthianthrene, respectively. The interest in this catalyst was revived by Ray, who used it in devising a general method for the preparation of di- and tetrasubstituted derivatives of thianthrene.[57] The method has been successfully used in the condensation of acetanilide, acetylbenzene, benzoyl chloride, chlorobenzene, o-chlorotoluene, p-chlorotoluene, diphenylmethane and methoxylbenzene,[58] and with 2-hydroxytoluene and p-xylene[59] to yield the corresponding di- and tetrasubstituted thianthrenes. In most cases the structures of the derivatives remain unestablished.

Thianthrene can undergo the Friedel-Crafts reaction with acetyl chloride,[60] chloroacetyl chloride,[60] diethylmalonyl chloride[50] and phthallic anhydride[61] to give 2,7-diacetylthianthrene, 2,7-bis(β-chloroacetyl)thianthrene, 2,2-diethylthianthrenindan-1,3-dione (50% yield), and thianthrene-

---

[56] J. B. Cohen and F. W. Skirrow, ibid., 75, 887 (1899).

[57] J. N. Ray, ibid., 117, 1335 (1920).

[58] J. N. Ray, ibid., 119, 1962 (1921).

[59] M. Sen and J. N. Ray, ibid., 1139 (1926).

[60] M. Tomita, J. Pharm. Soc. Japan, 58, 517 (in German, 139) (1938) [C. A., 32, 7463 (1938)].

[61] R. Scholl and Chr. Seer, Ber., 44, 1233 (1911).

diphthaloylic acid (47% yield), respectively. The last mentioned compound is interesting in that it can give, through ring closure, a polynuclear heterocycle with a thianthrene skeleton.[61] γ-Oxo-2-thianthrenebutyric acid, obtained from the condensation of thianthrene with succinic anhydride in the presence of anhydrous aluminum chloride, has been found to be effective as a choleretic.[61a]

Dimethylthianthrene also reacts with phthallic anhydride in the presence of aluminum chloride to give 2,7-dimethylthianthrene-3,8-diphthaloylic acid in 73% yield.[61]

Miscellaneous Methods of Syntheses

Reaction between phenol and phosphorus pentasulfide

Some early methods for the preparation of thianthrene employed phenol and phosphorus pentasulfide.[2,3] A mixture of the two reagents was distilled to give thiophenol, diphenyl sulfide, diphenyl disulfide and thianthrene. The usefulness of the method cannot be evaluated from the references, and no attempt to extend the method to substituted phenols has been reported.

Thermal decomposition of benzothiadiazoles

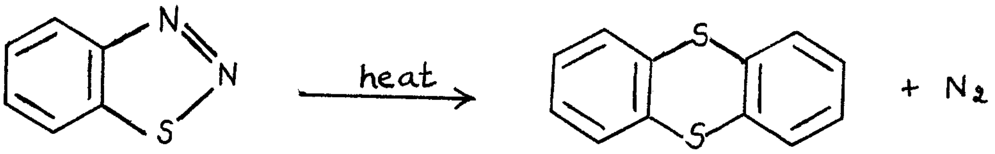
An interesting method of more general application employes a benzothiadiazole, which, upon heating, loses nitrogen and forms thianthrene.[7,62] The starting material is obtained

---

[61a] U. S. Patent 2,480,220 [C. A., 44, 1142 (1950)].

[62] P. Jacobson and E. Ney, Ann., 277, 232 (1893).

from an ortho-aminothiophenol by the action of nitrous acid.



Thianthrene,[62] 2,7-dimethoxythianthrene,[63] 2,7-dimethylthianthrene[7,62] and 1,3,6,8-tetramethylthianthrene[7,62] have been prepared by this method.

Action of sulfuric acid on thiophenols

Sulfuric acid reacts with a thiophenol to yield a thianthrene derivative and sulfur dioxide. The method was first introduced by Fries and Vogt[64] who obtained thianthrene derivatives in 10-20% yield by treating thiophenol, p-thiocresol, β-thionaphthol, and 2,4-dichloro-3-hydroxythiophenol with fuming sulfuric acid. Later workers have successfully employed the method with p-chlorothiophenol,[39] 3,4-dimethoxythiophenol,[65] 4-methoxythiophenol,[66] and p-thiocresol.[66] In the case of p-chlorothiophenol and p-thiocresol the yields were as high as 50%.

---

[63] K. Fries and E. Engelbertz, Ann., 407, 194 (1915).

[64] K. Fries and W. Volk, Ber., 42, 1170 (1909).

[65] K. Fries, H. Koch and H. Stukenbrock, Ann., 468, 162 (1929).

[66] P. Rumpf, Bull. soc. chim. France, 7, 632 (1940).

The main advantage of the reaction is that it leaves no doubt as to the structure of the thianthrene derivative obtained.

Litharge has been used in the reaction in the place of sulfuric acid, but the yield of thianthrene was very small.[67]

Krishna's method

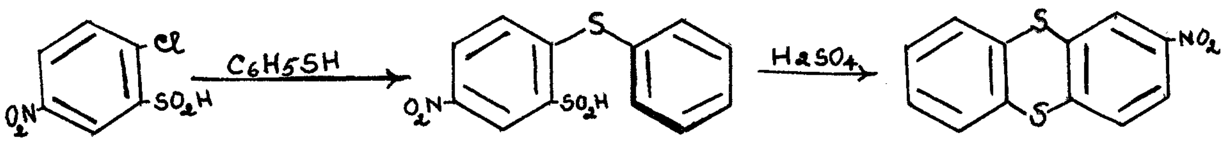
All of the foregoing methods give thianthrene derivatives with an even number of substituents. A method devised by Krishna yields thianthrene compounds with one or more substituents.[68] The intermediate used in the synthesis is 2-chloro-5-nitrobenzenesulfinic acid which is first condensed with a thiophenol by refluxing the aqueous solution of the sodium salts of the two reagents for about twenty minutes. The resulting disulfide undergoes ring closure when it is treated with sulfuric acid for 30 minutes.[69] The resulting sulfoxide is reduced immediately to the thianthrene derivative during the reaction. In some cases the ring closure and reduction takes place in 3 hours.[69]

---

[67] V. N. M. Cullinane and H. J. H. Padfield, J. Chem. Soc., 134 (1935).

[68] S. Krishna, J. Chem. Soc., 123, 156 (1923).

[69] S. Krishna, ibid., 123, 2786 (1923).



The starting material is obtained from 2-chloro-5-nitrobenzene-sulfonic acid which is converted to the sulfonyl chloride by treatment with phosphorus pentachloride. The sulfonylchloride is reduced to the sulfinic acid by the action of sodium sulfite.

The method has a very general application and has been successfully used in the syntheses of 2- nitro-8-acetamidothianthrene,[65] 2-nitro-8-chlorothianthrene,[69] 2-nitro-6,9-dichlorothianthrene,[69] 2-nitro-7,8-dimethoxythianthrene,[69] 2-nitro-6,8-dimethylthianthrene,[65,69] 2-nitro-6-methoxy-9-methylthianthrene[69] and 2-nitrothianthrene-7 (or 9)-carboxylic acid.[69] The nitro group can be reduced to the amino group which can be subsequently eliminated by diazotization and treatment with absolute ethanol.[68]

An interesting method for the preparation of thianthrene consists in heating tetraphenyltin with sulfur at 190° for 8 hours.[70] The yield of thianthrene is only about 20%, but

---

[70] R. W. Bost and P. Borgstrom, J. Am. Chem. Soc., 51, 1922 (1929).

tetra-p-totyltin, under similar treatment, gives an 80% yield of 2,7-dimethylthianthrene.[71]

Macallum has reported a synthesis which gives a high yield of thianthrene, and which also confirms the constitution of the heterocycle.[71a,b] A mixture of o-dichlorobenzene, calcium sulfide and sulfur is heated in a sealed glass tube, under vacuum, at about 300° for 20 hours. The reaction gave a 75% yield of thianthrene.

Oxidation Reactions

The presence of the two sulfur atoms in thianthrene gives, upon oxidation under suitable conditions, thianthrene-5-oxide, thianthrene-5-dioxide, thianthrene-5,10-dioxide, thianthrene-5,5,10-trioxide and thianthrene-5,10-tetraoxide. Since thianthrene-5,10-dioxide exists in two stereoisomeric forms, a total of six oxidation products can be obtained from each substitution product of thianthrene.

Chlorine[27,39-41,65] chromic acid,[3,6,11,39,49,58,68,72]

---

[71] R. W. Bost and H. R. Baker, *ibid.*, *55*, 1112 (1933).

[71a] A. D. Macallum, *J. Org. Chem.*, *13*, 154 (1948).

[71b] U. S. Patent 2,538,941 [*C. A.*, *45*, 5193 (1951)].

[72] V. V. Kozlov, E. P. Fruktova and O. M. Shemyakina, *J. Gen. Chem.* (*U. S. S. R.*), *10*, 1077 (1940) [Original not available for examination; abstracted in *C. A.*, *35*, 4028 (1941)].

hydrogen peroxide,[11,12,39,50,60,63-65,73] peracetic acid,[40] potassium permanganate[44,69] and nitric acid[27,40,44,49,52,56, 58-60,63-65,69,73a] have all been used in the oxidation of thianthrene and its derivatives. From a comparison of the different methods it appears that some of these oxidants are reagents of choice in the preparation of a particular oxide. Thus, nitric acid (sp. gr., 1.2), chlorine, and hydrogen peroxide (30%) are excellent reagents for the preparation of the 5-oxides, the 5,10-dioxides (α-form), and the 5,10-tetraoxides, respectively. Chromic acid has been used, almost exclusively, for the preparation of the 5,10-tetraoxides.

In the preparation of the 5,10-dioxides it has been found that oxidation with most chlorine gives the α-form in good yields,[27] while prolonged boiling with nitric acid (sp. gr., 1.2) yields the β-form in moderate yields.[40]

The action of chlorine on a thianthrene derivative in hot, aqueous acetic acid gives the 5,5,10-trioxide.[65] A similar method has been reported for the preparation of thianthrene-5-dioxide,[52] but later workers found the method to be unsuccessful.[40]

---

[73] S. Kambara, K. Okita and C. Muto, J. Soc. Rubber Ind. Japan, 21, 158 (1948) [Original not available for examination; abstracted in C. A., 43, 5622 (1949)].

[73a] M. Tomita and T. Ikeda, J. Pharm. Soc. Japan, 58, 780 (in German 231) (1938) [C. A., 33, 2526 (1939)].

Peracetic acid has been used in the preparation of thianthrene-5-oxide and the two forms of thianthrene-5,10-dioxide, but its use was not found to be advantageous.[40]

By using calculated quantities of hydrogen peroxide (30%) to give 1, 2, 3 or more gram atoms of oxygen, 5-oxides,[39,63,65,73] 5,10-dioxides,[39] 5-dioxide,[39] 5,5,10-trioxide,[39] and 5,10-tetraoxides[11, 12,50,63-65,73] have been prepared. Both hydrogen peroxide and chromic acid give excellent yields of the 5,10-tetraoxides.

The 5-dioxides can be conveniently prepared from the 5,5,10-trioxides by reduction with zinc and acetic acid,[39,52] or hydrogen bromide.[52,65] The 5,5,10-trioxides are easily prepared by the oxidation of the 5,10-dioxides with nitric acid (sp. gr., 1.4).[52]

The 5-dioxides and 5,10-tetraoxides are not reduced with zinc-acetic acid mixture, hydrogen bromide or hydriodic acid. The reported reduction of the tetraoxide with sulfur[8] may actually involve displacement rather than reduction since a similar treatment with selenium results in the formation of selenanthrene.[73b]

The oxidizing action of nitric acid depends upon the concentration, and the temperature and time of the reaction. Thus, the 5-oxides are best prepared by refluxing a solution

---

[73b] F. Krafft and A. Kaschau, *Ber.*, *29*, 443 (1896).

of the thianthrene in glacial acetic acid with nitric acid (sp. gr., 1.2) for about an hour.[40,52,63-65,69] The yields are very good. Concentrated nitric acid (sp. gr., 1.4) has been successfully used in the preparation of the 5,10-dioxides,[63,65] 5,5,10-trioxides[52,65] and 5,10-tetraoxides.[58-60,69] Fuming nitric acid (sp. gr., 1.52) oxidizes the thianthrene to the tetraoxides[40,56,65,69] although the reaction can be arrested at the stage of the 5,10-dioxide.[49]

It is interesting to note that nitration of thianthrene has not been successful. If the heterocycle is dissolved in fuming nitric acid and the solution evaporated to dryness, a quantitative yield of thianthrene-5,10-tetraoxide is obtained.[56] The action of a mixture of sulfuric and nitric acids does not proceed beyond oxidation to the tetraoxide.[47] Even where a number of activating methyl[56,58,59,64,65] or methoxy[63,65] groups are present the treatment with nitric acid proceeds in the same manner as the parent substance, thianthrene.

Sulfonation Reactions

Thianthrene has been sulfonated with sulfuric acid,[53,74] fuming sulfuric acid[49,53,74] and chlorosulfonic acid[74] to yield mono- and disubstitution products of unidentified structures. The sodium salt of a monosulfonic acid obtained by the action of sulfuric acid on dimethylthianthrene has a

---

[74] U. S. Patent 1,589,390 [*Chem. Zentr.*, *98* *I*, 360 (1927)].

strong antiphlogistic action.[74]

Thianthrene-5,10-tetraoxide, which is extremely unreactive toward electrophilic reagents, has been sulfonated by heating it with 62% fuming sulfuric acid in a sealed tube at 140° for 2 hours. The yield of the thianthrene-2-sulfonic acid 5,10-tetraoxide was 58%.[72]

Halogenation Reactions

Chlorination

Direct action of chlorine on thianthrene in benzene at room temperature forms a dithionium chloride, which, on subsequent hydrolysis gives the α-form of thianthrene-5,10-dioxide.[52] However, by using chloroform as the solvent, Fries and Vogt obtained 2-chlorothianthrene, in an excellent yield, by the action one molar equivalent of chlorine on thianthrene.[52] The same authors also obtained 2,8-dichlorothianthrene, m.p., 171°, by using two molar equivalents of chlorine in the above reaction, and also by the action of anhydrous aluminum chloride on chlorobenzene and sulfur.[52] Later workers,[39] however, failed to obtain any 2,8-dichlorothianthrene but obtained, instead, the 2,7-dichlorothianthrene, m.p., 186°, from the Friedel-Crafts type reaction. The structure of this isomer was established by its synthesis from p-chlorothiophenol and sulfuric acid.

1,6-Dichlorothianthrene has been prepared[75] by a slight modification of the method of Jacobson and Ney,[7] as a by-product in the preparation of 4-chlorothioindoxyl. The proof of the structure was not given.

Treatment of the potassium salt of 2-thianthrenesulfonic acid 5,10-tetraoxide with phosphorus pentachloride results in the displacement of the sulfonic group by chlorine. The resulting product, 2-chlorothianthrene-5,10-tetraoxide, is obtained in 78% yield.[72]

Reductive halogenation

The term reductive halogenation has been applied to the reaction in which a hydrohalic acid reacts with a heterocyclic sulfoxide to yield the halogenated heterocycle.[76] The reaction is usually very good with hydrochloric acid. 2-Chlorothianthrene has been prepared in an excellent yield by this method from thianthrene-5-oxide and hydrogen chloride using glacial acetic acid as the solvent.[52] It can be expected that thianthrene-5,10-dioxide may undergo a similar reductive chlorination to give a dichlorothianthrene, but such an attempt has not been reported. It is interesting to note that the reaction has been applied to dibrominate, reductively, 2,7-dimethoxythianthrene-5,10-

---

[75] C. E. Dalgliesh and F. G. Mann, J. Chem. Soc., 893 (1945).

[76] H. J. Page and S. Smiles, ibid., 97, 1112 (1910).

dioxide with hydrobromic acid to yield 2,7-dibromo-3,8-dimethoxythianthrene.[63]

1-Bromothianthrene has been prepared by the action of anhydrous aluminum chloride on 2-bromodiphenyl sulfide and sulfur.[10] The only reported bromination of thianthrene gave a dibromothianthrene whose structure and physical constants were not described.[77] It has been shown recently that this product is a mixture of the two isomers, 2,7- and 2,8 dibromothianthrene.[78]

Cleavage Reactions

Some of the early studies on thianthrene in this laboratory were directed with a view to cleave thianthrene-5,10-tetraoxide with sodamide in liquid ammonia. Although the tetraoxide underwent cleavage, no identifiable product was isolated from the reaction, except the small amounts of the starting material.[11,12]

The tetraoxide has been cleaved successfully with phosphorus pentachloride by heating a mixture of the two, at 240-250° for 5 hours. The products, identified as o-dichlorobenzene and benzene-o-disulfonyl chloride, again confirm the

---

[77] Swiss Patent 243,008 [C. A., 43, 5966 (1949)].

[78] H. Gilman and D. R. Swayampati, J. Am. Chem. Soc., 77, in press (1955).

ortho positions of the two sulfur atoms in thianthrene.[79]

A basic reagent which cleaves the tetraoxides to give identifiable products is alcoholic potassium hydroxide. Thianthrene-5,10-tetraoxide gives with this reagent 2-ethoxy-2'-sulfino-diphenyl sulfone using ethanol as the solvent.[52] Methanolic potassium hydroxide similarly gives the 2-methoxy-6-sulfino-4'-methoxydiphenyl sulfone from 2,7-dimethoxythianthrene-5,10-tetraoxide.[63] The cleavage has been carried a stage further by Fries, Koch and Stukenbrock who obtained 2-ethoxy-4,5-dimethoxysulfinic acid from 2,3,7,8-tetramethoxythianthrene-5,10-tetraoxide.[65]

Reactions Involving Organolithium Compounds

It has been established that the heteroatoms, oxygen and sulfur, have an ortho-directing influence in metalation reactions with n-butyllithium, and that oxygen is more reactive than sulfur in these reactions.[13] It was in a comparative study of the orientation influence of oxygen and sulfur that thianthrene was used for the first time in this laboratory. It was found then that thianthrene, like its oxygen-analog, dibenzo-p-dioxin, was metalated in the 1-position.[10] The yield of the crude 1-thianthrenecarboxylic acid, obtained upon carbonation of the reaction mixture, was 65%. The

---

[79] J. J. B. Deuss, Ber., 41, 2329 (1908).

structure of the product was established by its synthesis from 1-bromothianthrene through halogen-metal interconversion and subsequent carbonation of the reaction mixture.

1-Aminothianthrene has been prepared by the treatment of the 1-thianthrenyllithium with O-methylhydroxylamine.[10] Oxidation of 1-thianthrenyllithium with oxygen in the presence of a molar equivalent of n-butylmagnesium bromide gave 1-hydroxythianthrene in a very small yield.[14]

The use of low temperatures in metalation has been found to be interesting, and in some cases the method of choice for successful metalation. Esmay observed that the treatment of diphenyl sulfoxide with n-butyllithium at -70° followed by carbonation resulted in the cleavage of the sulfoxide to give moderate yields of benzoic acid.[13] Dibenzothiophene-5-oxide was metalated successfully only when a low temperature of -10° was used for the reaction, giving dibenzothiophene-4-carboxylic acid in a fair yield.[80] The other product of the reaction was dibenzothiophene, obtained in small yields as a result of the reduction of the sulfoxide. It has been shown that metalation preceeds reduction inthis reaction. This conclusion has been recently supported by Shirley and Lehto from the metalation studies of phenoxathiin-

---

[80] H. Gilman and D. L. Esmay, J. Am. Chem. Soc., 74, 266 (1952).

10-oxide.[81] However, no case has yet been reported in which metalation of a sulfoxide has given an unreduced carboxylic acid.

Low-temperature metalation of thianthrene-5-oxide proceeds in an even more interesting manner. Besides reduction of the sulfoxide to thianthrene, the other products of the reaction are dibenzothiophene (about 50% yield) and small amounts of 2,2'-dicarboxydiphenyl sulfide.[82]

Derivatives of Thianthrene

Tables I-VII include the known derivatives of thianthrene which have been classified according to the oxidation state of the sulfur atoms. Polynuclear heterocycles containing a thianthrene skeleton[50,61,64,82a] have not been included in the tables.

---

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

[82] H. Gilman and D. R. Swayampati, ibid., 77, in press (1955).

[82a] K. Brass and K. Heide, Ber., 57, 104 (1924).

Table I

Derivatives of Thianthrene

Name of Compound	M.P.°	Reference
<u>MONOSUBSTITUTED THIANTHRENES</u>		
2-Acetamidothianthrene	185	(36,78)
1-N^4-Acetylsulfanilamidothianthrene	154	(10)
2-N^4-Acetylsulfanylamidothianthrene	163	(10)
1-Aminothianthrene	139 121-2	(10) (83)
1-Aminothianthrene hydrochloride	231	(10)
2-Aminothianthrene*	160	(35,36,83)
1-Bromothianthrene	145	(10)
2-Bromothianthrene	89-90	(78,83)
1-Chlorothianthrene	87-8	(83)
2-Chlorothianthrene	84	(52,72,84)
Ethyl 1-Thianthreneoxyacetate	90-90.5	(83)
1-Hydroxythianthrene	117-8	(14,83)
2-Hydroxythianthrene	145	(85)
1-Iodothianthrene	187.5-8.5	(11,12)

---

[83] This Thesis.

[84] Swiss Patent 188,816 [<u>Chem</u>. <u>Zentr</u>., <u>108 II</u>, 3409 (1937)].

[85] German Patent 606,350 [<u>C</u>. <u>A</u>., <u>29</u>, 1434 (1935)].

*This product, m.p., 185°, which was reported first by Krishna as 2-aminothianthrene[68] has been shown by Keats[36] to be the 2-acetamidothianthrene.

Table I (Continued)

Name of Compound	M.P.°	Reference
2-Nitrothianthrene	128	(68)
Oxo-2-thianthrenebutyric acid	167-9	(61a)
N-Phenyl-2-thianthrenecarboxamide	200-1	(35)
1-Sulfanilamidothianthrene	120 d.	(10)
2-Sulfanilamidothianthrene	125 d.	(10)
1-Thianthreneboronic acid	147-8	(83)
1-Thianthrenecarboxylic acid	217-8 224-5	(10) (83)
2-Thianthrenecarboxamide	227	(35)
2-Thianthrenecarboxylic acid	224 227-8	(10,35) (83)
1-Thianthreneoxyacetic acid	174-5	(83)
2-Thianthrenephthaloylic acid	219-21	(61)
x-Thianthrenesulfonic acid		(74,84)
1-Thianthrenyltriphenylsilane	190.5-1.5	(83)
2-Thianthrenyltrimethylammonium iodide	190	(36)
DISUBSTITUTED THIANTHRENES		
2-Acetamido-7-methylthianthrene	180	(65)
2-Amino-7 (or 9)-carboxythianthrene hydrochloride	239	(69)
2-Amino-7-chlorothianthrene hydrochloride	272	(69)
2-Amino-7-methylthianthrene	130	(65)
2-Amino-7-methylthianthrene hydrochloride	256	(65)

Table I (Continued)

Name of Compound	M.P.°	Reference
2-Amino-8-methylthianthrene		(84)
2,7-Bis(N^4-Acetylsulfanilamido) thianthrene	180 d.	(86)
2,7-Bis(-chloroacetyl)thianthrene	177	(60)
2,7-Bis(-hydroxy- -piperidylethyl- thianthrene	141	(60)
2,7-Bis(methylmercapto)thianthrene	144.5	(66)
2,7-Bis(-piperidylacetyl)thianthrene	129	(60)
8-Chloro-2-nitrothianthrene		(84)
x,x-Diacetamidothianthrene	198-200	(58)
2,7-Diacetylthianthrene		(60)
x,x-Diacetylthianthrene	88-91	(58)
2,7-Diaminothianthrene	120	(86)
2,8-Diaminothianthrene	192	(65)
x,x-Diaminothianthrene	102-4	(58,59)
x,x-Di(4-benzamido-1-anthraquinonyl)-thianthrene		(87)
x,x-Dibenzylthianthrene	196	(58)
x,x-Dibromothianthrene		(77,87)
1,6-Dichlorothianthrene	174-5	(75)
2,7-Dichlorothianthrene	186	(39)

---

[86] P. C. Guha and V. M. Dokras, *Current Sci.*, *12*, 119 (1943).

[87] Swiss Patent 216,597 [*C. A.*, *42*, 5232 (1948)].

Table I (Continued)

Name of Compound	M.P.°	Reference
2,8-Dichlorothianthrene	171	(52,84)
x,x-Dichlorothianthrene	147	(58)
x,x-Dicyanothianthrene		(77)
2,7-Dihydroxythianthrene	233	(63)
2,7-Dimethoxythianthrene	131	(63,66)
x,x-Dimethoxythianthrene		(58,84)
2,7-Dimethylthianthrene	123	(7,60,64) (66,71,84) (88,89-91)

---

[88] H. J. Barber and S. Smiles, *J. Chem. Soc.*, 1141 (1928).

[89] A. F. Damanski and K. D. Kostic, *Bull. soc. chim. Belgrade*, *12*, 243 (1947) [Original not available for examination; abstracted in *C. A.*, *46*, 5051 (1952)].

[90] Swiss Patent 246,914 [*C. A.*, *43*, 4420 (1949)].

[91] I. N. Tits-Skvortsova, A. I. Leonova and S. Y. Levina, *Doklady Akad. Nauk. U. S. S. R.*, *80*, 377 (1951) [*C. A.*, *46*, 5009 (1952)].

Table I (Continued)

Name of Compound	M.P.°	Reference
x,x-Dimethylthianthrene	b.p. 248-50/ 15 mm.	(49,50,56) (74,92-96)
x,x-Dinitrothianthrene		(49,84)
2-Nitro-8-acetamidothianthrene	205	(65)
2-Nitro-8-aminothianthrene	198	(65)
2-Nitro-7 (or 9)-carboxythianthrene	272-3	(69)
2-Nitro-8-chlorothianthrene	215	(69)
2-Nitro-8-methylthianthrene	159-60	(65,69,84)
2-Nitrothianthrene ferrichloride	223	(68)
Thianthrene-2,7-bis(diazoaminobenzene)-4-sulfonic acid		(59)
Thianthrene-x,x-dicarbonyl chloride		(97)

---

[92] J. M. Davis, R. F. Miller and W. F. Basse, J. Am. Chem. Soc., 63, 361 (1941).

[93] E. R. Fitzgerald and J. D. Ferry, J. Colloid. Sci., 8, 1 (1953).

[94] R. M. Gordon and K. Unsworth, Ann. Trop. Med., 37, 195 (1943) [Original not available for examination; abstracted in C. A., 39, 365 (1945)] .

[95] H. Rame, Dansk Tids. Farm., 13, 21 (1939) [Original not available for examination; abstracted in C. A., 33, 5127 (1939)].

[96] Swiss Patent 241,597 [C. A., 43, 6358 (1949)].

Table I (Continued)

Name of Compound	M.P.°	Reference
Thianthrene-x,x-dicarboxylic acid	204	(58) (77,84) (97-112)
Thianthrene-2,7-diphthaloylic acid	143-60	(61)
Thianthrene-x,x-disulfonic acid		(49,53)

---

[97] U. S. Patent 2,583,448 [*C. A.*, *46*, 4243 (1952)].

[98] Brit. Patent 661,907 [*C. A.*, *46*, 5860 (1952)].

[99] Brit. Patent 680,168 [*C. A.*, *47*, 4622 (1953)].

[100] Swiss Patent 236,231 [*C. A.*, *43*, 8691 (1949)].

[101] Swiss Patent 238,628 [*C. A.*, *43*, 4484 (1949)].

[102] Swiss Patent 238,629 [*C. A.*, *43*, 4484 (1949)].

[103] Swiss Patent 238,630 [*C. A.*, *43*, 4484 (1949)].

[104] Swiss Patent 238,631 [*C. A.*, *43*, 4484 (1949)].

[105] Swiss Patent 238,632 [*C. A.*, *43*, 4484 (1949)].

[106] Swiss Patent 240,129 [*C. A.*, *43*, 8891 (1949)].

[107] Swiss Patent 257,938 [*C. A.*, *44*, 6645 (1950)].

[108] Swiss Patent 275,438 [*C. A.*, *46*, 6843 (1952)].

[109] Swiss Patent 279,532 [*C. A.*, *47*, 4098 (1953)].

[110] Swiss Patent 279,533 [*C. A.*, *47*, 4098 (1953)].

[111] U. S. Patent 2,453,232 [*C. A.*, *43*, 8171 (1952)].

[112] U. S. Patent 2,598,587 [*C. A.*, *46*, 8866 (1952)].

Table I (Continued)

Name of Compound	M.P.°	Reference
TRISUBSTITUTED THIANTHRENES		
2-Acetamido-7,8-dimethoxythianthrene	180	(65)
2-Amino-7,8-dimethoxythianthrene	149	(65)
2-Amino-6-methoxy-9-methylthianthrene hydrochloride	221	(69)
2-Amino-7-methylthianthrene-3-sulfonic acid	>270	(65)
x,x-Dimethylthianthrene-x-sulfonic acid		(77)
2-Nitro-6,9-dichlorothianthrene	220	(69,84)
2-Nitro-7,8-dimethoxythianthrene	194	(65)
2-Nitro-6,8-dimethylthianthrene	142-4	(69)
2-Nitro-6-methoxy-9-methylthianthrene	189-90	(69,84)
TETRASUBSTITUTED THIANTHRENES		
2,7-Diacetyloxy-3,8-dimethoxythianthrene	165	(59)
2,7-Dibromo-3,8-dimethoxythianthrene	235	(63)
4,6-Dichloro-1,9-dimethylthianthrene	195-7	(58)
2,8-Dichloro-3,7-dimethylthianthrene		(84)
x,x-Dichloro-x,x-dimethylthianthrene	145	(58)
2,7-Dihydroxy-3,8-dimethoxythianthrene	202	(59)
2,7-Dimethylthianthrene-3,8-diphthaloylic acid		(61)

Table I (Continued)

Name of Compound	M.P.°	Reference
1,3-Dinitro-7-methyl-8-aminothianthrene	203	(113)
1,3-Dinitro-7-methyl-8-diacetamidothianthrene	168	(113)
2,3,7,8-Tetraacetyloxythianthrene	224	(65)
2,3,7,8-Tetrachlorothianthrene		(84)
2,3,7,8-Tetrahydroxythianthrene	273	(65)
2,3,7,8-Tetramethoxythianthrene	175-6	(65,84,114)
1,3,6,8-Tetramethylthianthrene	118	(7,62,84)
1,4,6,9-Tetramethylthianthrene	242	(59)
2,3,7,8-Tetramethylthianthrene	125-8	(89)
1,3,8-Triamino-7-methylthianthrene		(113)
HEXASUBSTITUTED THIANTHRENES		
1,3,6,8-Tetrachloro-2,7-dihydroxythianthrene	>300	(64)

---

[113] J. Fröhlich, Ber., 40, 2489 (1907).

[114] E. Vinkler and J. Szabó, Magyar Kém. Lapja, 4, 708 (1949) Original not available for examination; abstracted in C. A., 46, 8120 (1952) .

Table II

Derivatives of Thianthrene-5-oxide

Name of Compound	M.P.°	Reference
Thianthrene-5-oxide	143.5	(40,52,82) (84,115)
MONOSUBSTITUTED THIANTHRENE-5-OXIDES		
2-Nitrothianthrene-10-oxide	166	(68)
DISUBSTITUTED THIANTHRENE-5-OXIDES		
2,7-Dichlorothianthrene-5-oxide	235-7 d.	(39)
2,7-Dihydroxythianthrene-5-oxide	300	(63)
2,7-Dimethoxythianthrene-5-oxide	154-5	(63)
2,7-Dimethylthianthrene-5-oxide	94	(64)
TETRASUBSTITUTED THIANTHRENE-5-OXIDES		
2,3,7,8-Tetraacetyloxythianthrene-5-oxide	213	(65)
2,3,7,8-Tetrahydroxythianthrene-5-oxide	200 d.	(65)
2,3,7,8-Tetramethoxythianthrene-5-oxide	196	(65)

---

[115] D. T. Gibson, H. Graham and J. Reid, _J_. _Chem_. _Soc_., 874 (1923).

Table III

Derivatives of Thianthrene-5-dioxide

Name of Compound	M.P.°	Reference
Thianthrene-5-dioxide	159 167-8	(40,52,84) (78,83)
MONOSUBSTITUTED THIANTHRENE-5-DIOXIDES		
4-Carboxythianthrene-5-dioxide	256-7	(83)
DISUBSTITUTED THIANTHRENE-5-DIOXIDES		
4,6-Dicarboxythianthrene-5-dioxide	364 d.	(83)
2,7-Dichlorothianthrene-5-dioxide	215	(39)
2,7-Dimethylthianthrene-5-dioxide	170-71	(39)
TETRASUBSTITUTED THIANTHRENE-5-DIOXIDES		
2,3,7,8-Tetraacetyloxythianthrene-5-dioxide	203	(65)
2,3,7,8-Tetrahydroxythianthrene-5-dioxide	>300 d.	(65)
2,3,7,8-Tetramethoxythianthrene-5-dioxide	253	(65)

Table IV

Derivatives of Thianthrene-5,10-dioxide

Name of Compound	M.P.°	Reference
Thianthrene-5,10-dioxide (α-form)	284	(27,39,40) (42,43)
Thianthrene-5,10-dioxide (β-form)	249	(6,8,27) (39-44,47) (49,52)
<u>MONOSUBSTITUTED THIANTHRENE-5,10-DIOXIDES</u>		
2-Nitrothianthrene-5,10-dioxide	226	(68)
<u>DISUBSTITUTED THIANTHRENE-5,10-DIOXIDES</u>		
2,7-Dichlorothianthrene-5,10-dioxide (α-form)	301	(39)
2,7-Dichlorothianthrene-5,10-dioxide (β-form)	256.5	(39)
2,7-Dimethoxythianthrene-5,10-dioxide (α-form)	266-8	(39,63)
2,7-Dimethoxythianthrene-5,10-dioxide (β-form)	198-200	(39)
2,7-Dimethylthianthrene-5,10-dioxide (α-form)	195.5	(39,64)
2,7-Dimethylthianthrene-5,10-dioxide (β-form)	168.5	(39)
<u>TETRASUBSTITUTED THIANTHRENE-5,10-DIOXIDES</u>		
2,3,7,8-Tetramethoxythianthrene-5,10-dioxide	259	(65)

Table V

Derivatives of Thianthrene-5,5,10-trioxide

Name of Compound	M.P.°	Reference
Thianthrene-5,5,10-trioxide	216 221.5-2.5	(52) (78,83)
DISUBSTITUTED THIANTHRENE-5,5,10-TRIOXIDES		
2,7-Dimethylthianthrene-5,5,10-trioxide	223	(39)
TETRASUBSTITUTED THIANTHRENE-5,5,10-TRIOXIDES		
2,3,7,8-Tetramethoxythianthrene-5,5,10-trioxide	275	(65)
x-Hydroxy-x,x,x,-trimethoxy-thianthrene-5,5,10-trioxide	270	(65)

Table VI

Derivatives of Thianthrene-5,10-tetraoxides

Name of Compound	M.P.°	Reference
Thianthrene-5,10-tetraoxide	324	(3,5,6,11) (12,40,44) (47,49,56) (72,73a-b)
MONOSUBSTITUTED THIANTHRENE-5,10-TETRAOXIDES		
2-Bromothianthrene-5,10-tetraoxide	227-8	(78,83)
1-Carboxythianthrene-5,10-tetraoxide	307-8	(83)
2-Carboxythianthrene-5,10-tetraoxide	302-3	(83)
1-Chlorothianthrene-5,10-tetraoxide	242	(83)
2-Chlorothianthrene-5,10-tetraoxide	120	(72)
2-Hydroxythianthrene-5,10-tetraoxide	189-90	(116)
2-Nitrothianthrene-5,10-tetraoxide	255	(68)
2-Sulfonamidothianthrene-5,10-tetraoxide	178	(72)
2-Thianthrenesulfonic acid 5,10-tetraoxide	321	(72)
2-Thianthrenesulfonyl chloride 5,10-tetraoxide	194	(72)

---

[116] V. V. Kozlov and N. I. Stakhovskaya, J. Gen. Chem. (U. S. S. R.), 16, 115 (1946) [C. A., 41, 2739 (1947)] .

Table VI (Continued)

Name of Compound	M.P.°	Reference
DISUBSTITUTED		
THIANTHRENE-5,0-TETRAOXIDES		
2,7-Dibromothianthrene-5,10-tetraoxide		(83)
2,8-Dibromothianthrene-5,10-tetraoxide		(83)
2,7-Dicarboxythianthrene-5,10-tetraoxide	>300	(60)
2,7-Di (β-chloroacetyl)thianthrene-5,10-tetraoxide	209-13	(73a)
2,7-Dichlorothianthrene-5,10-tetraoxide	293	(39)
x,x-Dichlorothianthrene-5,10-tetraoxide	>225	(58)
1,2-Dihydroxythianthrene-5,10-tetraoxide	197	(116)
2,7-Dimethoxythianthrene-5,10-tetraoxide	279-82	(63)
2,7-Dimethoxycarbonylthianthrene-5,10-tetraoxide	202	(60)
2,7-Dimethylthianthrene-5,10-tetraoxide	286	(64,88)
x,x-Dimethylthianthrene-5,10-tetraoxide	184	(49,56)
2-Nitro-7 (or 9)-carboxythianthrene-5,10-tetraoxide	285	(69)
2-Nitro-8-chlorothianthrene-5,10-tetraoxide	251-3	(69)
2-Nitro-8-methylthianthrene-5,10-tetraoxide	256	(69)

Table VI (Continued)

Name of Compound	M.P.°	Reference
TRISUBSTITUTED		
THIANTHRENE-5,10-TETRAOXIDES		
2-Nitro-6,9-dichlorothianthrene-5,10-tetraoxide	251-3	(69)
TETRASUBSTITUTED		
THIANTHRENE-5,10-TETRAOXIDES		
4,6-Dichloro-1,9-dimethyl-thianthrene-5,10-tetraoxide	>250	(58)
x,x-Dichloro-x,x-dimethyl-thianthrene-5,10-tetraoxide		(58)
2,3,7,8-Tetraacetyloxythianthrene-5,10-tetraoxide	245	(65)
2,3,7,8-Tetrahydroxythianthrene-5,10-tetraoxide	>310	(65)
2,3,7,8-Tetramethoxythianthrene-5,10-tetraoxide	296	(65,88)
1,4,6,9-Tetramethylthianthrene-5,10-tetraoxide	>290	(59)
HEPTASUBSTITUTED		
THIANTHRENE-5,10-TETRAOXIDES		
1,4,6-Tribromo-2,3,7,8-tetrahydroxythianthrene-5,10-tetraoxide	>340	(65)
OCTASUBSTITUTED		
THIANTHRENE-5,10-TETRAOXIDES		
1,4,6,9-Tetrabromo-2,3,7,8-tetraacetyloxythianthrene-5,10-tetraoxide	>300 d.	(65)
1,4,6,9-Tetrabromo-2,3,7,8-tetrahydroxythianthrene-5,10-tetraoxide	>350	(65)

Table VII

Thionium Salts of Thianthrenes

Name of Compound	M.P.°	Reference
Thianthrene dichloride		(48,52)
Thianthrene phenetyl chloride		(48)
2,7-Dihydroxythianthrene dichloride	118	(63)
2,7,Dihydroxythianthrene disulfate	198-202	(63)
2,3,7,8-Tetrahydroxythianthrene bromide	250 d.	(65)
2,3,7,8-Tetrahydroxythianthrene perchlorate		(65)
2,3,7,8-Tetrahydroxythianthrene sulfate	>300	(65)
2,3,7,8-Tetramethoxythianthrene chloride	164-66 d.	(65)
2,3,7,8-Tetramethoxythianthrene perbromide	220-22 d.	(65)
2,3,7,8-Tetramethoxythianthrene perchlorate	245	(65)
2,3,7,8-Tetramethoxythianthrene sulfate	230-32	(65)

Bibliography of Thianthrene

Barber, H. J., and S. Smiles, *J. Chem. Soc.*, 1141 (1928).

Berke-Meyenberg, *Dtsch. Parfüm-Ztg.*, *27*, 249 (1941) [Original not available for examination; abstracted in *Chem Zentr.*, *113 I*, 2073 (1942)].

Bost, R. W., and H. R. Baker, *J. Am. Chem. Soc.*, *55*, 1112 (1933).

Bost, R. W., and P. Borgstrom, *J. Am. Chem. Soc.*, *51*, 1922 (1929).

Baw, H., G. M. Bennett and P. Dearns, *J. Chem. Soc.*, 680 (1934).

Bennett, G. M., and S. Glasstone, *J. Chem. Soc.*, 128 (1934).

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

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

Bergmann, E., and A. Weizmann, *Chemistry & Industry*, 364 (1938).

Boeseken, I., *Rec. trav. chim.*, *24*, 209 (1905).

Böeseken, J., and A. T. H. Van der Meulen, *Rec. trav. chim.*, *55*, 925 (1936).

Brill, O., and C. B. Evans, *J. Chem. Soc.*, *93*, 1442 (1908).

Campbell, I. G. M., C. G. Le Fèvre, R. J. W. Le Fèvre and E. E. Turner, *J. Chem. Soc.*, 404 (1938).

Carrié, C., and H. Neuhaus, *Z. Haut-u. Geschlechtskrankh*, *7*, 41 (1949) [Original not available for examination; abstracted in *C. A.*, *46*, 9327 (1952)].

Cohen, J. B., and F. W. Skirrow, *J. Chem. Soc.*, 887 (1899).

Crackston, J. E., and R. G. Wood, *Nature*, *142*, 257 (1938).

Cullinane, N. M., and C. G. Davis, *Rec. trav. chim.*, *55*, 881 (1936).

Cullinane, N. M., N. M. E. Morgan and C. A. J. Plummer, *Rec. trav. chim.*, *56*, 627 (1937).

Cullinane, V. N. M., and H. J. H. Padfield, *J. Chem. Soc.*, 1131 (1935).

Cullinane, N. M., and C. A. J. Plummer, *J. Chem. Soc.*, 63 (1938).

Cullinane, N. M., and W. T. Rees, *Trans. Faraday Soc.*, *36*, 507 (1940).

Damanski, A. F., *Bull. soc. chim. Belgrade*, *No. Jubilaire*, *65-75*, (1897-1947) [Original not available for examination; abstracted in *C. A.*, *47*, 7487 (1953)].

Damanski, A. F., and K. D. Kostic, *Bull. soc. chim. Belgrade*, *13*, 209 (1948) [Original not available for examination; abstracted in *C. A.*, *46*, 8658 (1952)].

Denison, G. H., Jr., and P. C. Condit, *Ind. Eng. Chem.*, *37*, 1102 (1945).

Deuss, J. J. B., *Ber.*, *41*, 2329 (1908).

Deuss, J. J. B., *Rec. trav. chim.*, *27*, 145 (1908).

Deuss, J. J. B., *Rec. trav. chim.*, *28*, 136 (1909).

Dougherty, G., and O. Haas, *J. Am. Chem. Soc.*, *59*, 2469 (1937).

Dougherty, G., and P. Hammond, *J. Am. Chem. Soc.*, *57*, 117 (1935).

Dougherty, G., and P. D. Hammond, *J. Am. Chem. Soc.*, *61*, 81 (1939).

Esmay, D. L., Unpublished Ph. D. Thesis, Iowa State College Library, 1951.

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

French Patent 45,764 [*Chem. Zentr.*, *107 II*, 1094 (1936)].

Friedel, C., and J. M. Crafts, *Ann. chim. phys.*, *1*, 530 (1884).

Friedel, C., and J. M. Crafts, *Ann. chim. phys.*, *14*, 438 (1888).

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

Fries, K., and W. Volk, *Ber.*, *42*, 1170 (1909).

Fries, K., and W. Vogt, Ber., 44, 756 (1911).

Genvresse, P., Bull. soc. chim. France, 15, 409 (1896).

Genvresse, P., Bull. soc. chim. France, 15, 1038 (1896).

German Patent 330,834 [Chem. Zentr., 92 II, 265 (1921)].

Gibson, D. T., H. Graham and J. Reid, J. Chem. Soc., 874 (1923).

Gilman, H., and D. L. Esmay, J. Am. Chem. Soc., 76, 5787 (1954).

Gilman, H., and C. G. Stuckwisch, J. Am. Chem. Soc., 65, 1461 (1943).

Glass, H. B., and E. E. Reid, J. Am. Chem. Soc., 51, 3428 (1929).

Graebe, C., Ann., 179, 180 (1875).

Graebe, C., Ber., 7, 50 (1874).

Hartman, W. W., L. A. Smith and J. B. Dickey, Ind. Eng. Chem., 24, 1317 (1932).

Hinsberg, O., Ber., 70, 936 (1937).

Hinsberg, O., J. prakt. Chem., 93, 302 (1916).

Jacobson, P., and H. Janssen, Ann., 277, 218 (1893).

Jacobson, P., and E. Ney, Ber., 22, 904 (1889).

Japan. Patent 2,799 [C. A., 47, 6613 (1953)].

Kambara, S., K. Okita and C. Muto, J. Soc. Rubber Ind. Japan, 21, 158 (1948) [Original not available for examination; abstracted in C. A., 43, 5622 (1949)].

Keats, G. H., J. Chem. Soc., 1592 (1937).

Kozlov, V. V., E. P. Fruktova and O. M. Shemyakina, J. Gen. Chem. (U. S. S. R.), 10, 1077 (1940) [Original not available for examination; abstracted in C. A., 35, 4028 (1941)].

Krafft, F., and A. Kaschau, Ber., 29, 443 (1896).

Krafft, F., and R. E. Lyons, Ber., 29, 435 (1896).

Krishna, S., *J. Chem. Soc.*, *123*, 156 (1923).

Macallum, A. D., *J. Org. Chem.*, *13*, 154 (1948).

Martin, G. A., Jr., Unpublished Ph. D. Thesis, Iowa State College Library, 1945.

Martin, G. A., Jr., *Iowa State Coll. J. Sci.*, *21*, 38 (1946).

Meulen, H., *Bull. soc. chim. France*, *2*, 1692 (1935).

Mukerji, S. K., and B. Lal, *Indian J. Phy.*, *25*, 309 (1951).

Mukerji, S. K., and B. Lal, *Indian J. Phy.*, *26*, 276 (1952).

Mukerji, S. K., and B. Lal, *Nuovo Cimento*, *9*, 699 (1952) [*C. A.*, *46*, 9424 (1952)].

Murphy, C.M., H. Ravner and N. S. Smith, *Ind. Eng. Chem.* *42*, 2479 (1950).

Prasad, M., J. Shanker and B . H. Peermohamed, *J. Indian Chem. Soc.*, *14*, 177 (1937).

Rame, H., *Dansk. Tids. Farm.*, *13*, 21 (1939) [Original not available for examination; abstracted in *C. A.*, *33*, 5127 (1939)].

Ray, J. N., *J. Chem. Soc.*, 1335 (1920).

Ray, J. N., *J. Chem. Soc.*, 1966 (1921).

Schmidt, E. B., *Ber.*, *11*, 1173 (1878).

Scholl, R., and Chr. Seer, *Ber.*, *44*, 1233 (1911).

Schönberg, A., and A. Mustafa, *J. Chem. Soc.*, 889 (1949).

Schönberg, A., A. Mustafa and W. Askar, *Science*, *109*, 522 (1949).

Shirley, D. A., and P. A. Roussel, *Science*, *113*, 208 (1951).

Singh, L., *Nuovo Cimento*, *10*, 89 (1953) [*C. A.*, *47*, 3699 (1953)].

Smith, L. E., and R. Melvin, *J. Econ. Entomol.*, *36*, 475 (1943).

Stenhouse, J., *Ann.*, *149*, 252 (1869).

Sutton, L. E., and G. C. Hampson, *Trans. Faraday Soc.*, *31*, 945 (1935).

Swiss Patent 188,816 [*Chem. Zentr.*, *108 II*, 3409 (1937)].

Swiss Patent 241,597 [*C. A.*, *43*, 6358 (1949)].

Swiss Patent 243,008 [*C. A.*, *43*, 5966 (1949)].

Taylor, T. W., *J. Chem. Soc.*, 625 (1945).

Tits-Skvotsova, I. N., A. I. Leonova, S. Ya. Levina and E. A. Karaseva, *J. Gen. Chem.* (*U. S. S. R.*), *23*, 317 (1953) [Cited in *Current Chemical Papers*, *9*, 462 (1954)].

Tomita, M., *J. Pharm. Soc. Japan*, *58*, 517 (in German, 139) (1938) [*C. A.*, *32*, 7463 (1938)].

Tomita, M., and T. Ikeda, *J. Pharm. Soc. Japan*, *58*, 780 (in German, 231) (1938) [*C. A.*, *33*, 2526 (1939)].

Turner, E. E., and A. B. Sheppard, *J. Chem. Soc.*, 544 (1925).

U. S. Patent 1,589,390 [*Chem. Zentr.*, *98 I*, 360 (1927)].

U. S. Patent 2,480,220 [*C. A.*, *44*, 1142 (1950)].

U. S. Patent 2,538,941 [*C. A.*, *45*, 5193 (1951)].

Walls, W. S., and C. P. Smyth, *J. Chem. Physics*, *1*, 337 (1933).

Wood, R. G., and J. E. Crackston, *Phil. Mag.*, *31*, 62 (1941).

EXPERIMENTAL[117,118]

Reactions Involving Organometallic Compounds

Preparation of 1-thianthrenecarboxylic acid

To a stirred suspension of 43.2 g. (0.2 mole) of thianthrene[50] in 400 ml. of anhydrous ether was added, over a period of 30 minutes, 300 ml. (0.3 mole) of *n*-butyllithium,[118a] and the resulting mixture was stirred at room temperature for 20 hours. Color Test II[119] was positive after this period, but was found to be negative after a total reaction period of 40 hours. Color Test I[120] was positive throughout.

The organolithium intermediate was carbonated by adding it jet wise to a stirred slurry of Dry Ice and anhydrous

---

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

[118] The infrared spectra of the compounds described were obtained by use of the Baird double beam infrared spectrophotometer of the Institute for Atomic Research, Iowa State College. The writer wishes to thank Messrs. Richard Hedges, Robert Kross and Robert McCord for the actual determination of the spectra.

Unless otherwise indicated, the spectra were determined on Nujol mulls of the compounds.

[118a] In the preparation of *n*-butyllithium by the method of H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, *ibid.*, *71*, 1499 (1949), it has been found by Dr. K. Oita of this laboratory that an 85-92% yield can be consistently obtained by using a temperature of -30° for the reaction.

[119] H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, *62*, 1847 (1940).

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

ether. When all carbon dioxide had evaporated, water was added to the mixture and the two layers were separated. The ethereal layer was dried over anhydrous sodium sulfate and filtered. Removal of the solvent left 8.0 g. of a soft, yellow solid from which was obtained, after several recrystallizations from chloroform, 3.0 g. (7% recovery) of pure thianthrene identified by its mixed melting point.

The aqueous layer was warmed to expel the dissolved ether, treated with Norit-A, filtered and acidified with 10% hydrochloric acid. The yellow product which separated was filtered, washed and dried to give 43.0 g. (83%) of the 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 more from the same solvent to yield 14.5 g. (28%) of the pure 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 compound has been prepared by Gilman and Stuckwisch in 65% crude yield by the same reaction and shown to be 1-thianthrenecarboxylic acid. However, they report its melting point as 217-218°, and the yield of the pure product was not reported.[10]

<u>Preparation of 1-carboxythianthrene-5,10-tetraoxide</u>

This derivative of the above acid was prepared for later use in the structural proof of another carboxylic acid of thianthrene.

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 18.1 g. (0.16 mole, 100% excess) of hydrogen peroxide (30%) 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 give 4.13 g. of the pure acid melting at 306-7° with decomposition. The mother liquor upon dilution gave another 1.4 g. of the slightly impure acid melting at 302-304°. The total yield of the acid 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.

Preparation of 1-hydroxythianthrene

To a stirred suspension of 108 g. (0.5 mole) of thianthrene in 250 ml. of anhydrous ether was added 500 ml. (0.625 mole, 25% excess) of *n*-butyllithium and the mixture was refluxed for 24 hours. To the stirred suspension was added slowly an ethereal solution of 0.5 mole of *n*-butylmagnesium bromide. The mixture was stirred vigorously while oxygen was allowed to sweep over its surface at a gentle rate. Color Test I was negative in 14 hours. Cold 10% hydrochloric acid was added until the aqueous layer was acidic. The layers were separated, and the ethereal layer was extracted with 5% sodium hydroxide solution several times and the extracts combined.

The ethereal layer was evaporated to dryness and the residue crystallized from chloroform to give 40.0 g. (37% recovery) of thianthrene (mixed m.p.).

The aqueous layer was treated with Norit-A, filtered and acidified with 10% hydrochloric acid. The syrupy, dark liquid which separated was extracted with ether. Evaporation of the solvent left a dark, gummy mass which did not become hard on standing. Distillation under reduced pressure gave 24.0 g. of the crude phenol melting over the range 110-115°. Recrystallization of the product from petroleum ether (b.p. 77-115°) gave 21.3 g. (18.3%) of the pure 1-hydroxythianthrene melting at 117-118°.

The yield of the pure product, based on the unrecovered thianthrene, was 29%.

Preparation of 1-aminothianthrene

To the 1-thianthrenyllithium solution prepared, as described before, 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 O-methylhydroxylamine[121] 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 the Color Test I was 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 after which no more crystals separated. The cream-colored product was filtered and dried to yield 23 g. of the 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. It was recrystallized from 70% ethanol to give 12.0 g. of the pure 1-aminothianthrene melting at 120-121°.

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

---

[121] The free base was obtained by the drop-wise 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.

55%, respectively.

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

The reported melting point of this compound is 139°,[10] however, a close examination of the experimental part of the reference showed that the reported analysis of the product was far from satisfactory, and the purity of the product was not, therefore, dependable.

Preparation of 1-thianthrenyltriphenylsilane

To the 1-thianthrenyllithium solution prepared, as described before, from 43.2 g. (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 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 190.5-191.5°.

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

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

Preparation of 1-thianthreneboronic acid

To a stirred suspension of 54.0 g. (0.25 mole) of thianthrene in 300 ml. of anhydrous ether was added 220 ml. (0.25 mole) of an ethereal solution of n-butyllithium, and the mixture was stirred at room temperature for 30 hours. Color Test II was negative after this period.

The above suspension 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[122] in 200 ml. of anhydrous ether which was maintained at -70° during the addition. The low temperature was maintained for an additional 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 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.

---

[122] The reagent was kindly supplied by Mr. Ralph Ranck of this laboratory.

Recrystallization from benzene gave 17.5 g. of nearly pure product melting at 146-148°. Another recrystallization from benzene gave 14.4 g. (22.2%) of the pure 1-thianthreneboronic acid melting at 147-148°.

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.

Cleavage of thianthrene-5-oxide with n-butyllithium

Run I. To a stirred suspension of 18.6 g. (0.08 mole) of thianthrene-5-oxide[82] in 200 ml. of anhydrous ether at -40° was added slowly 215 ml. (o.24 mole, 3 equivalents) of an ethereal solution of n-butyllithium. The resulting mixture was stirred at -40 to -45° for 5 hours. Subsequently Color Test II was negative.

The olive-green solution was poured jet-wise into a stirred slurry of Dry Ice and anhydrous ether. When all the carbon dioxide had evaporated the mixture was warmed to expel the ether, and the dried residue was extracted with benzene in a Soxhlet extractor. The yellow extract was evaporated to dryness and the residue was filtered to remove most of a yellow oily material. The impure solid was recrystallized from 90% acetic acid to give 9.2 g. (50%) of crude dibenzothiophene melting over the range 88-94°. Recrystallization of the product from ethanol, methanol, acetic acid and petroleum ether (b.p. 77-115°) did not raise the melting point. This was probably due to the formation of a mixed crystal system of dibenzothiophene and the reduction-product, thianthrene. The mixture was sublimed under reduced pressure keeping the oil bath at 45-50°. The sublimate was recrystallized from methanol to give 5.0 g. (34%) of pure dibenzothiophene melting at 98-99°. The identity was established by the method of mixed melting point and the comparison of the infrared spectra.

The residue from the sublimation was recrystallized from methanol to yield 0.7 g. (4%) of thianthrene melting at 156-157°. Its admixture with an authentic specimen melted undepressed.

Run II. To a stirred suspension of 23.2 g. (0.1 mole) of thianthrene-5-oxide in 200 ml. of anhydrous ether at -70° was added slowly 195 ml. (0.3 mole, 3 equivalents) of an ethereal solution of n-butyllithium over a period of 30 minutes, and the reaction mixture was stirred at this temperature for 7 hours. Subsequently, Color Test I was positive and Color Test II was negative. The olive-green solution was poured jet-wise into a stirred slurry of Dry Ice and ether. When all carbon dioxide had evaporated water was added to the mixture. The ethereal layer was dried over anhydrous sodium sulfate. Evaporation of the solvent left a white crystalline product contaminated with a small amount of a yellow oil. The mixture was filtered and most of the oily material was pressed out. The residue was washed once with a small amount of petroleum ether (b.p. 60-70) to yield 10.1 g. (55%) of crude dibenzothiophene melting at 96-98°. Recrystallization of the crude product from methanol gave 9.55 g. (52%) of pure dibenzothiophene melting at 99°.

The aqueous layer was warmed to expel the dissolved ether. A small amount of a white product separated as the ether was removed. The mixture was filtered and the residue was recrystallized from methanol to yield 0.7 g. (3.2%) of thianthrene (mixed m.p.)

The filtrate from above was treated with Norit-A, filtered, cooled and acidified with 10% hydrochloric acid. The resulting solid was filtered, washed and dried to yield 0.7 g. of a yellow acid. The crude material was recrystallized twice from aqueous acetone to yield slightly yellow crystals melting over the range 220-226°. Another recrystallization from glacial acetic acid gave 0.28 g. of the acid melting at 229-230°. The values obtained for the neutral equivalent, 140 and 141, were in a fair agreement with the calculated value of 137 for 2,2'-dicarboxydiphenyl sulfide. The melting point of an authentic specimen of this acid was not depressed by the product obtained from the above reaction. The identity of the two was further established by the comparison of their infrared spectra. The yield of the pure acid was 1%.

Run III. This run differed from run II in that 1.1 equivalents of *n*-butyllithium were used for the reaction. From the ether layer was obtained 9.2 g. (50%) of pure dibenzothiophene. The aqueous layer gave a small amount of acidic material which was discarded.

Run IV. This run differed from run II in that the reaction was carried out at 5-10° with 2 equivalents of n-butyllithium. The reaction mixture was worked up in the same way to yield 1.91 g. (10.4%) of pure dibenzothiophene and 2.85 g. (13.2%) of thianthrene. The aqueous layer gave a yellow acid which was dissolved in 10% potassium hydroxide solution, treated with Norit-A, filtered and acidified with 10% hydrochloric acid. The yellow product which separated was filtered, washed and dried to yield 3.38 g. (13%) of 1-thianthrenecarboxylic acid melting over the range 205-216°. The crude acid was recrystallized twice from 90% acetic acid to give 2.1 g. (8.1%) of the pure product melting at 225-226°. An admixture of the product with an authentic specimen of 1-thianthrenecarboxylic acid was not depressed.

Run V. To a stirred suspension of 11.6 g. (0.05 mole) of thianthrene-5-oxide in 100 ml. of anhydrous ether at -70° was added, over a period of 10 minutes, 36 ml. (0.055 mole, 1.1 equivalents) of n-butyllithium. Color Test II was negative immediately after the addition of the n-butyllithium was complete. The pale green suspension was filtered through glass wool into a stirred slurry of Dry Ice and anhydrous ether. When all the carbon dioxide had evaporated, water was added, and the layers were separated. The ethereal layer was evaporated to dryness to give a white residue which was crystallized from methanol to yield 4.22 g. (46%) of pure dibenzothiophene (mixed m.p.).

The aqueous layer was warmed to expel the dissolved ether and the white product which separated was filtered, dissolved in methanol, treated with Norit-A and filtered. The filtrate was cooled, and the white crystalline product was filtered and dried to yield 0.51 g. (4.7%) of thianthrene (mixed m.p.).

The aqueous filtrate was cooled and acidified with 10% hydrochloric acid to give a cream-colored product which was too small to work up.

Run VI. To a stirred suspension of 11.6 g. (0.05 mole) of thianthrene-5-oxide in 100 ml. of anhydrous ether at -70° was added, over a period of 3 minutes, 42 ml. (0.055 mole) of *n*-butyllithium which had been previously cooled to -70°. A sample of the solution was withdrawn for Color Test II which was found to be negative, and the remaining solution was carbonated as before.

The residue in the flask was recrystallized from methanol to give 2.04 g. (17.6% recovery) of thianthrene-5-oxide, identified by the method of mixed melting point.

The remaining procedure for working up the reaction was identical with that in run V. The ethereal layer gave 2.50 g. (27.1% of pure dibenzothiophene. The aqueous layer, upon warming, gave 1.0 g. (9.3%) of pure thianthrene. Acidification of the aqueous layer, after filtration, gave a small amount of a gummy material which did not solidify upon long standing, and was discarded.

Run VII. This run differed from run V in that 3 equivalents of n-butyllithium were added, over a period of 30 minutes, for the reaction. Color Test II taken at 0, 15, and 25 minutes after the addition of the n-butyllithium was found to be positive. At the end of a total reaction period of 1 hour, Color Test II became negative.

The reaction mixture was carbonated and worked up in the same manner. The ethereal layer gave 4.9 g. (53.2%) of pure dibenzothiophene. The aqueous layer was warmed and filtered to yield 0.86 g. (8%) of pure thianthrene. Acidification of the aqueous layer gave a small amount of a colorless oil, which did not solidify upon standing and was discarded.

Preparation of methyllithium

Methyl bromide (Dow Chemical) vapor was bubbled through a stirred suspension of 8.1 g. (1.17 g. atom) of lithium wire cut into about 5-mm. pieces. All lithium had dissolved during a period of 4 hours. After stirring for an additional period of 30 minutes the solution was transferred to a graduated separatory funnel. The yield, as determined by titration against standard hydrochloric acid, was 80%.

Metalation of thianthrene-5-oxide with methyllithium

Run I. To a stirred suspension of 23.2 g. (0.1 mole) of thianthrene-5-oxide in 150 ml. of anhydrous ether at -70° was added, over a period of 10 minutes, 93 ml. (0.11 mole) of the methyllithium solution. After an additional period of 5 minutes the mixture was carbonated by adding it to a stirred slurry of Dry Ice and anhydrous ether. When all the carbon dioxide had evaporated the mixture was filtered. The ethereal layer was concentrated and cooled. The white product which separated was filtered and dried to yield a total of 7.7 g. of crude thianthrene-5-oxide melting over the range 124-127°. Two recrystallization from methanol gave 4.9 g. (21.1%) of pure thianthrene-5-oxide (mixed m.p.).

The aqueous layer was warmed to expel the dissolved ether. A white product which separated was filtered and recrystallized from methanol to yield 1.50 g. (7%) of thianthrene, identified by its mixed melting point.

The mother liquor from the recrystallization of the crude thianthrene-5-oxide gave an additional 1.1 g. of thianthrene. The total yield of thianthrene obtained from the reaction was 2.71 g. (12.5%).

The aqueous filtrate was cooled and acidified with 10% hydrochloric acid. No acidic material was obtained.

Run II. This run was identical with run I except that a period of 16 hours was allowed for the reaction. The mixture was carbonated and worked up as before. The yield of the recovered thianthrene-5-oxide was 10.6 g. (46%) and that of thianthrene was 4.5 g. (21%). No acidic product was obtained by the acidification of the aqueous layer.

Run III. To a stirred suspension of 11.6 g. (0.05 mole) of thianthrene-5-oxide in 100 ml. of anhydrous ether was added, over a period of 30 minutes, 180 ml. (0.15 mole, 3 equivalents) of methyllithium solution. The addition was carried out at room temperature and the mixture was subsequently stirred for a period of 16 hours. The sulfoxide had not dissolved after two equivalents of methyllithium had been added, and a partial solution was effected only after the addition of the third equivalent was completed. An orange-brown color developed slowly.

The reaction mixture was carbonated and worked up as before. No thianthrene-5-oxide was recovered in this run. The total yield of pure thianthrene obtained from the recrystallization of the residue in the flask, the product from the evaporation of the ethereal layer, and the material which had separated upon warming the aqueous layer, was 6.5 g. (60%).

The aqueous filtrate was cooled and acidified with 10% hydrochloric acid to yield 0.19 g. of a brown powder melting over the range 205-215°. Recrystallization from glacial acetic acid gave 0.14 g. (1%) of pure 1-thianthrenecarboxylic acid, identified by its mixed melting point.

Cleavage of thianthrene-5-oxide with methylmagnesium iodide (attempted)

To a stirred suspension of 11.6 g. (0.05 mole) of thianthrene-5-oxide in 100 ml. of anhydrous ether at -70° was added, over a period of 15 minutes, 90 ml. (0.1 mole) of methylmagnesium iodide. The mixture was stirred at the low temperature for 20 hours.

The suspension was carbonated and worked up as usual. The ethereal layer gave 7.32 g. (63% recovery) of thianthrene-5-oxide (mixed m.p.). The aqueous layer failed to yield any product upon acidification.

Cleavage of thianthrene-5-oxide with ethylmagnesium bromide

Run I. To a stirred suspension of 23.2 g. (0.1 mole) of thianthrene-5-oxide in 200 ml. of anhydrous ether at -70° was added 120 ml. (0.11 mole) of an ethereal solution of ethylmagnesium bromide, and the mixture was stirred at the low temperature for a period of 20 hours. Carbonation was carried out as usual by adding the suspension jet-wise to a stirred slurry of Dry Ice and anhydrous ether. When all the carbon dioxide had evaporated water was added, and the layers were separated. The ethereal layer was evaporated to dryness. The white crystalline residue weighed 19.4 g. and melted over the range 140-143°. Recrystallization of the crude material from methanol gave 17.2 g. of white crystals melting at 143.5-144°. An admixture of this product with an authentic specimen of thianthrene-5-oxide melted undepressed. The yields of the crude, and pure thianthrene-5-oxide recovered were 88%, and 74%, respectively.

The aqueous layer was warmed to expel the dissolved ether, treated with Norit-A and filtered. The filtrate was cooled and acidified with 10% hydrochloric acid. The white product which separated was filtered, washed and dried to give 2.9 g. of an acidic material which melted with decomposition over the range 150-154°. Recrystallization from a mixture of ethanol and petroleum ether (b.p. 60-70°) gave 2.32 g. of white crystals melting at 158-159° with decomposition.

The infrared spectra showed absorption bands at 5.95 μ, 9.84 μ and 13.76 μ, indicative of the carbonyl group, the sulfoxide group and 1,2-disubstitution. The acid has been tentatively established as 2-ethylsulfinyl-2'-carboxydiphenyl sulfide.

Anal. Calcd. for $C_{15}H_{14}O_3S_2$: neut. equiv., 306;S, 20.91. Found: neut. equiv., 310, 310; S, 20.85.

The yields of the crude and pure acid, based on the unrecovered thianthrene-5-oxide, were 36% and 29%, respectively.

Run II. This run differed from run I only in that 3 equivalents of ethylmagnesium bromide were used for the reaction. The reaction mixture was carbonated and worked up in the same manner. The ethereal layer gave a total of 17.83 g. (76.8% recovery) of thianthrene-5-oxide. The aqueous layer gave 0.8 g. of the pure acid melting at 157-158° with decomposition. The yield of the pure acid, based on unrecovered thianthrene-5-oxide, was 11.2%.

Preparation of 2-ethylmercapto-2'-carboxydiphenyl sulfide

A mixture of 0.8 g. (0.0026 mole) of the 2-ethylsulfinyl-2'-carboxydiphenyl sulfide, 15 ml. of 90% acetic acid and 2 g. of zinc dust was refluxed for 4 hours. The supernatant, colorless solution was filtered into an excess of water, and dilute hydrochloric acid was added until the mixture was distinctly acidic (Congo Red). The product which separated was filtered, washed and dried to yield 0.48 g. (64%) of white crystals melting at 195-196°. Further recrystallization of the product from benzene failed to raise its melting point.

Anal. Calcd. for $C_{15}H_{14}O_2S_2$: neut. equiv., 290; S, 22.2. Found: neut. equiv., 294, 295; S, 22.1.

Cleavage of thianthrene-5-oxide with n-butylmagnesium bromide

Run I. To a stirred suspension of 23.2 g. (0.1 mole) of thianthrene-5-oxide in 100 ml. of anhydrous ether at -70° was added 85 ml. (0.1 mole) of an ethereal solution of *n*-butylmagnesium bromide. The resulting mixture was stirred at the low temperature for 16 hours. At the end of this period, the cooling bath was removed and stirring was continued for 15 more minutes. Powdered Dry Ice was added slowly to the mixture. When all the carbon dioxide had evaporated water was added, and the layers were separated. The residue in the reaction flask and the ethereal layer together gave 5.4 g. (23% recovery) of thianthrene-5-oxide (mixed m.p.).

The aqueous layer was warmed, treated with Norit-A, filtered and acidified with 10% hydrochloric acid. A sticky, white material which separated, solidified in a short time. The product was filtered, washed with water and dried to give 11.3 g. of white crystals melting over the range 141-144°

with decomposition. Recrystallization from aqueous methanol gave 6.25 g. (25.4%) of the product, tentatively established as 2-n-butylsulfinyl-2'-carboxydiphenyl sulfide, melting at 149-149.5° with decomposition.

The infrared spectrum showed absorption bands at 5.9 μ, 9.5 μ and 13.2 μ, indicative of the carbonyl group, the sulfoxide group and 1,2-substitution, respectively.

Anal. Calcd. for $C_{17}H_{18}O_3S_2$: neut. equiv., 334; S, 19.1. Found: neut. equiv., 336, 336; S, 18.9.

Run II. This run differed from run I in that 2 equivalents of n-butylmagnesium bromide were used for the reaction. At the end of 16 hours the reaction mixture was carbonated and worked up as before. Recrystallization of the residue in the reaction flask and the solid obtained from the ethereal layer gave a total of 12.55 g. (54.1% recovery) of thianthrene-5-oxide (mixed m.p.).

The aqueous layer gave, after the customary treatment and acidification with 10% hydrochloric acid, 6.1 g. of the crude 2-n-butylsulfinyl-2'-carboxydiphenyl sulfide. Recrystallization from benzene gave 5.4 g. of the pure product melting at 149-149.5° with decomposition. The yields of the crude and pure acid, based on the unrecovered thianthrene-5-oxide, were 40% and 35.3%, respectively.

Run III. This run differed from run I in that 3 equivalents of n-butylmagnesium bromide were used for the reaction, and that the reaction period was 6 hours only. The mixture was carbonated and worked up as before. The residue in the reaction flask, and the solid obtained from the ethereal layer together gave, after recrystallization from methanol, a total of 15.03 g. (64.8% recovery) of thianthrene-5-oxide. The aqueous layer yielded, after the usual treatment and acidification with 10% hydrochloric acid, 1.2 g. (10.3%, based on the unrecovered thianthrene-5-oxide) of the pure 2-n-butylsulfinyl-2'-carboxydiphenyl sulfide melting at 149-149.5°.

Run IV. To a stirred suspension of 46.4 g. (0.2 mole) of thianthrene-5-oxide in 300 ml. of anhydrous ether at -70° was added, over a period of 15 minutes, 99 ml. (0.22 mole) of n-butylmagnesium bromide. The resulting mixture was stirred at the low temperature for a period of 48 hours. Carbonation was carried out by the jet-wise addition of the cold 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 two layers were worked up as before. Recrystallization of the residue in the reaction flask and the solid obtained from the ethereal layer gave a total of 31.64 g. (68.2% recovery) of pure thianthrene-5-oxide.

The aqueous layer yielded 9.0 g. (42.4%) of the crude and 7.4 g. (34.8%) of pure 2-n-butylsulfinyl-2'-carboxydiphenyl sulfide melting at 149-149.5°. The yields are based on the unrecovered thianthrene-5-oxide.

Run V. To a stirred suspension of 34.8 g. (0.15 mole) of thianthrene-5-oxide in 150 ml. of anhydrous ether at -70° was added, over a period of 15 minutes, 108 ml. (0.15 mole) of an ethereal solution of *n*-butylmagnesium bromide. The reaction mixture was stirred at the low temperature for a period of 16 hours. The cooling bath was subsequently removed, and olive-green suspension was allowed to warm up during a period of 1 hour.

Powdered Dry Ice was added carefully to the reaction flask. When all the carbon dioxide had evaporated, water was added and the mixture was worked up as before. The recovered thianthrene-5-oxide weighed 20.8 g. (59.8%). The aqueous layer gave 11.0 g. of the crude acid melting over the range 142-148°. Recrystallization from 90% acetic acid gave 10.01 g. of the pure acid. The yields of the crude and pure 2-*n*-butylsulfinyl-2'-carboxydiphenyl sulfide, based on the unrecovered thianthrene-5-oxide, were 54.7% and 50%, respectively.

Preparation of 2-n-butylmercapto-2'-carboxydiphenyl sulfide

To a hot solution of 10.01 g. (0.0302 mole) of 2-*n*-butylsulfinyl-2'-carboxydiphenyl sulfide in 90 ml. of 90% acetic acid was added 6 g. of zinc dust, and the resulting mixture was refluxed for a period of 4 hours. The clear, colorless solution was decanted into an excess of water. The zinc lumps in the reaction flask were washed with acetic acid, and the washings were added to the above solution, which was subsequently made distinctly acidic (Congo Red) with hydrochloric acid. The mixture was filtered and the residue was washed with water and dried to give 8.6 g. (91.3%) of the pure product melting at 137-138°. If the melting point was determined at a very small rate of rise of the bath-temperature, the product melted at 142. If the melt obtained at 137-138° was allowed to cool and its melting point determined again, it melted at 142°.

The infrared spectrum of the acid showed absorption bands at 6.05 μ and 13.4 μ, indicative of the carbonyl group and 1,2-substitution, respectively.

Anal. Calcd. for $C_{17}H_{18}O_2S_2$: neut. equiv., 318; S, 20.1. Found: neut. equiv., 321, 322; S, 20.1, 20.4.

Preparation of 2-n-butylsulfonyl-2'-carboxydiphenyl sulfone

To a hot solution of 3.34 g. (0.01 mole) of 2-n-butylsulinyl-2'-carboxydiphenyl sulfide in 15 ml. of glacial acetic acid was added a solution of 18 g. of hydrogen peroxide (30%) in 10 ml. of glacial acetic acid. The resulting solution was refluxed for 2 hours. No crystals separated after it was kept in the refrigerator for 48 hours. The solution was diluted to approximately 100 ml. with water. A white, sticky product separated which hardened in a short time. The product was filtered and dried to give 3.48 g. (91%) of the pure 2-n-butylsulfonyl-2'-carboxydiphenyl sulfone melting at 159.5-160.5° with decomposition.

The infrared spectrum showed absorption bands at 5.9 μ, 8.7 μ and 13.1 μ, indicative of the carbonyl group, the sulfone group and 1,2-substitution, respectively. The band indicative of the sulfoxide group had disappeared.

Anal. Calcd. for $C_{17}H_{18}O_6S_2$: neut. equiv., 382; S, 16.75. Found: neut. equiv., 380, 379; S, 16.58, 16.62.

Metalation of thianthrene-5-dioxide with n-butyllithium

Run I. To a stirred suspension of 9.92 g. (0.04 mole) of thianthrene-5-dioxide[78] 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. The reaction flask was immersed in an ice-bath during the addition of the n-butyllithium 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 residue was washed and dried to give 3.7 g. (37%) of the crude thianthrene-5-dioxide melting over the range 150-170°. Recrystallization from acetic acid gave 2.1 g. (21% recovery) of the pure product, m.p., and mixed m.p. 167-168°.

The filtrate from above was treated with Norit-A, filtered and acidified with 10% hydrochloric acid. A grey, sticky product separated which hardened on standing. The material was filtered, washed and dried to yield 7.8 g. of a white product. Part of it melted over the range 230-235°, and the remainder melted between 290 and 300°. Separation of the mono- and the dicarboxylic acid 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 pure acid, identified as 4-carboxythianthrene-5-dioxide, melting at 255-256°. The yield is based on unrecovered thianthrene-5-dioxide.

The infrared spectrum showed absorption bands at 5.9 μ, 8.7 μ 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 other pure product, later identified as thianthrene-4,6-dicarboxylic acid, weighed 0.25 g. (2% based on the unrecovered thianthrene-5-dioxide).

Run II. To a stirred suspension of 24.8 g. (0.1 mole) of thianthrene-5-dioxide in 200 ml. of anhydrous ether at -40 to -45° was added 261 ml. (0.3 mole, 3 equivalents) of an ethereal solution of n-butyllithium. The mixture was stirred at the low temperature for a period of 5 hours. Color Tests I and II were positive. Carbonation was effected by the jet-wise addition of the suspension to a stirred slurry of Dry Ice and ether. From the reaction mixture and the ethereal layer was isolated 7.7 g. (31%) of pure thianthrene-5-dioxide (mixed m.p.).

The aqueous layer was treated with Norit-A, filtered and acidified with 10% hydrochloric acid. The grey, sticky product which separated hardened on standing to give 15.3 g. of the dried product. Fractional crystallization from ethanol gave 3.1 g. of the 4,6-dicarboxythianthrene-5-dioxide which melted at 364° with decomposition. The yield of the pure product, based on unrecovered thianthrene-5-dioxide, was 12%.

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

Anal. Calcd. for $C_{13}H_8O_6S_2$: neut. equiv., 168; S, 19.03. Found: neut. equiv., 167, 167; S, 19.02, 18.98.

Run III. To a stirred suspension of 22.3 g. (0.09 mole) of thianthrene-5-oxide 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 mixture was carbonated and worked up as in run II. The ethereal layer gave only a small amount of an oil which had an odor of n-butyl mercaptan. The unreacted thianthrene-5-dioxide left in the reaction flask was recrystallized from ethanol to give 13 g. (58.3% recovery) of the pure product, m.p., and mixed m.p. 167-168°. The aqueous layer was treated with Norit-A, filtered and acidified with 10% hydrochloric acid to give 4.0 g. (36.5%) of the crude 4-carboxythianthrene-5-dioxide melting over the range 235-240°. Recrystallization from aqueous acetone gave 2.5 g. (22.7%) of the pure acid melting at 255-256°.

Run IV. To a stirred suspension of 24.8 g. (0.1 mole) of thianthrene-5-dioxide in 200 ml. of anhydrous ether at -70° was added, over a period of 30 minutes, 225 ml. (0.3 mole, 3 equivalents) of an ethereal solution of n-butyllithium. The brown suspension was stirred at the low temperature for 16 hours.

At the end of the reaction period, the mixture was carbonated and worked up as in run II. Recrystallization of the residue left in the reaction flask and the product obtained from the evaporation of the ether layer gave a total of 11.95 g. (48.2% recovery) of pure thianthrene-5-dioxide (mixed m.p.). The aqueous layer gave 8.2 g. of the crude 4-carboxythianthrene-5-dioxide melting over the range 230-246°. Recrystallization of the product from ethanol gave 6.15 g. of the pure acid melting at 255-256°. The yields of the crude and pure acid, based on unrecovered thianthrene-

5-dioxide, were 54% and 41%, respectively.

Metalation of thianthrene-5,10-dioxide (α-form) (attempted)

Run I. To a stirred suspension of 24.8 g. (0.1 mole) of thianthrene-5,10-dioxide[41] in 200 ml. of anhydrous ether at -70° was added 80 ml. (0.1 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. Carbonation was effected as usual by the jet-wise addition of the suspension to a stirred slurry of Dry Ice and ether.

From the residue left in the reaction flask was recovered a total of 19.8 g. (80%) of thianthrene-5,10-dioxide (mixed m.p.). The reaction mixture was treated with water and the layers were separated. The ethereal layer left a very small amount of a yellow oil which did not solidify on long standing. The aqueous layer was treated with Norit-A, filtered and acidified with 10% hydrochloric acid. A small amount of an unidentified yellow oil separated which did not solidify on long standing.

Run II. This run differed from run I in that 3 equivalents of n-butyllithium were used and the reaction period was 12 hours. The mixture was carbonated and worked up as before. The only identified product was the starting material thianthrene-5,10-dioxide obtained in 65% yield. The yellow, oily, acidic product from the aqueous layer did not solidify on long standing.

Metalation of thianthrene-5,10-dioxide (β-form) (attempted)

To a stirred suspension of 9.92 g. (0.04 mole) of thianthrene-5,10-dioxide in 100 ml. of anhydrous ether at -70° was added 110 ml. (0.1 mole, 2.5 equivalents) of an ethereal solution of n-butyllithium, and the resulting mixture was stirred for 16 hours. Carbonation was effected by the jet-wise addition of the suspension to a stirred slurry of Dry Ice and anhydrous ether, and the reaction mixture was worked up as usual.

The starting material, thianthrene-5,10-dioxide, was recovered in 87% yield. The aqueous layer gave only traces of oily, acidic material.

Cleavage of thianthrene-5,5,10-trioxide

To a stirred suspension of 26.4 g. (0.1 mole) of thianthrene-5,5,10-trioxide 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 was negative. The brown solution was added jet-wise to a stirred slurry of Dry Ice and anhydrous ether. When all the carbon dioxide had evaporated water, was added to the mixture, 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 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 pure dibenzothiophene-5-dioxide, identified by its mixed melting point. The total yield of dibenzothiophene-5-dioxide 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. After standing for 7 days it became a white, soft, sticky mass. The small amount of an oily material was removed from it by distillation under reduced pressure, keeping the heating bath at 100°. The residue was washed with hot benzene and dried to yield 8.0 g. of a white powder melting between 213 and 217°. The product was recrystallized from water to yield 5.1 g. of the pure acid melting at 218-219°.

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

The product did not depress the melting point of the authentic specimen of 2,2'-dicarboxydiphenyl sulfone prepared by Gilman and Esmay.[123] The infrared spectra of the two products were identical. The yields of the crude and pure products were 26% and 16.6%, respectively.

<u>Metalation of thianthrene-5,10-tetraoxide (attempted)</u>

<u>Run I</u>. To a stirred suspension of 56.0 g. (0.2 mole) of thianthrene-5,10-tetraoxide in 400 ml. of anhydrous ether was added, over a period of 30 minutes, 187 ml (0.22 mole) of an ethereal solution of *n*-butyllithium. The reaction flask was immersed in an ice-bath during the addition of the *n*-butyllithium. After an additional reaction period of 30 minutes, Color Test II was negative. The dark red solution was added jet-wise to a stirred slurry of Dry Ice and anhydrous ether. When all the carbon dioxide had evaporated water was added, and the layers were separated. The ethereal layer was dried over anhydrous sodium sulfate, and the solvent was subsequently evaporated to dryness to leave a mixture of a white solid and a yellow oil. The mixture was filtered and the oil was pressed out. The residue was crystallized from methanol to give 3.6 g. of an unidentified, sulfur-containing product melting over the range 66-69°. Repeated recrystallization from methanol failed to yield a sharp-melting product.

From residue left in the reaction flask was recovered

---

[123] H. Gilman and D. L. Esmay, *J. Am. Chem. Soc.*, *75*, 278 (1953).

20.0 g. (36%) of thianthrene-5,10-tetraoxide melting at 322-324°. A mixed melting point with an authentic specimen was not depressed.

The aqueous layer was treated with Norit-A, filtered and acidified. The gummy, yellowish product which separated did not solidify on long standing.

Run II. To a stirred suspension of 28.0 (0.1 mole) of thianthrene-5,10-tetraoxide in 200 ml. of anhydrous ether at -70° was added, over a period of 10 minutes, 71 ml. (0.11 mole) of an ethereal solution of *n*-butyllithium. The resulting mixture was stirred at the low temperature for 2 hours. At the end of this period Color Test I was positive and Color Test II was negative.

The dark green solution was added jet-wise to a stirred slurry of Dry Ice and anhydrous ether. The reaction mixture was worked up in the same manner as in run I. The ethereal layer upon evaporation left a small amount of an oily material. The aqueous layer was treated with Norit-A, filtered and acidified with 10% hydrochloric acid, to yield 0.9 g. of an acidic product melting over the range 100-105°. Two recrystallizations from benzene gave 0.2 g. of a yellowish product melting at 109-110°. The amount of material was too small to identify. Its low melting point indicates that it is a product of cleavage rather than metalation.

From the residue in the flask was recovered 24.0 g. (86%) of thianthrene-5,10-tetraoxide, identified by its melting point and mixed melting point.

Preparation of 2-thianthrenecarboxylic acid

To a solution of 5.90 g. (0.02 mole) of 2-bromothianthrene[78] 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 after this period. Carbonation was effected by the jet-wise addition of the mixture to a stirred slurry of Dry Ice and anhydrous ether. Water was added after all the carbon dioxide had evaporated, and the layers were separated. The ethereal layer was dried over anhydrous sodium sulfate, and the solvent was removed by evaporation. Only a very small amount of white residue was left.

The aqueous layer was warmed to expel the dissolved ether, and subsequently treated with Norit-A, filtered and acidified with 10% hydrochloric acid. The white product which separated was filtered, washed and dried to yield 3.58 g. (70%) of nearly pure acid melting at 226-228°. Recrystallization from glacial acetic acid gave 2.68 g. (51%) of the pure product melting at 227-228°.

The acid fluoresces under ultraviolet rays, and is white. The other isomer, 1-thianthrenecarboxylic acid is yellow.

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.

Preparation of 2-aminothianthrene

To a stirred solution of 4.4 g. (0.015 mole) of 2-bromothianthrene in 50 ml. of anhydrous ether was added, over a period of 5 minutes, 13 ml. (0.015 mole) of an ethereal solution of *n*-butyllithium. The mixture was maintained at 0-5° during the addition of the *n*-butyllithium solution, and was subsequently allowed to warm up to room temperature. After a total reaction period of 20 minutes Color Test II was found to be negative.

To the above stirred mixture was added a solution of 0.24 g. (0.005 mole) of O-methylhydroxylamine[121] in 20 ml. of anhydrous ether. After a stirring period of 15 minutes Color Test I was found to be negative. The mixture was hydrolyzed with cold water, the layers were separated and the aqueous layer was extracted with ether. The combined ether extract was dried over anhydrous sodium sulfate. Hydrogen chloride was bubbled through the ethereal solution until no more crystals separated. The product was filtered and dried to give 1.91 g. of the hydrochloride, which was subsequently warmed with 5% sodium hydroxide solution. The liberated free base was filtered, washed with water and recrystallized from 95% ethanol to give 0.72 g. (63%) of white crystals melting at 160°. The melting point of the product was not depressed when it was mixed with 2-aminothianthrene obtained by the method of Keats.[36] The identity was established further by the identical infrared spectra,[118] which showed absorption bands at 12.3 μ and 13.3 μ, characteristic of 1,2,4- and 1,2-substitution, respectively.

Anal. Calcd. for $C_{12}H_9NS_2$: S, 27.7. Found: 27.5, 27.3.

The mother liquor from the precipitation of the hydrochloride was evaporated in a current of dry air, and the yellowish residue was recrystallized from methanol to yield 1.64 g. (76%) of thianthrene, identified by its mixed melting point. The yields of the two products are based on the following equation:

$$3\ RLi + CH_3ONH_2 \longrightarrow RNH_2 + 2RH + LiOCH_3$$

Halogen Derivatives

Preparation of 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 copper (I) chloride in hydrochloric acid was added to the mixture. The copper (I) chloride solution was freshly prepared from 62.5 g. of copper (II) sulfate pentahydrate in accordance with the procedure described by Vogel.[124] A vigorous reaction followed the addition of the catalyst, and the red diazotized mixture became 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, after treatment with Norit-A from the same solvent, gave 1.4 g. (18.6%) of the nearly pure product melting at 79.5-81.5°. The analytical sample melted at 85-85.5°.

The infrared spectrum showed absorption bands at 13.0 μ 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: 25.4, 24.9.

Preparation of 2-bromothianthrene

Method I. A solution of 23.2 g. (0.1 mole) of thianthrene-5-oxide in 250 ml. of glacial acetic acid at room temperature was saturated with hydrogen bromide. The orange crystals which separated dissolved, upon heating, to give a red solution. A slight yellow color persisted at the end of

---

[124] A. I. Vogel, "A Textbook of Practical Organic Chemistry", Longmans, Green and Company, New York, N. Y., 1948, p. 186.

a reflux period of 24 hours. The reaction mixture was allowed to cool and diluted with 2 liters of cold water. A white product which separated was filtered and recrystallized from methanol to give 17.6 g. of a white solid melting over the range 80-96°. Two recrystallizations of the product from methanol gave 3.2 g. (11%) of 2-bromothianthrene, m.p., 88-89°. The analytical sample melted at 89-90°. The product gave a qualitative test for bromine.

The infrared spectrum showed absorption bands at 12.4 μ and 13.4 μ, characteristic of 1,2,4- and 1,2-substitution, respectively, and the spectrum was similar to that of 2-chlorothianthrene.[52]

Anal. Calcd. for $C_{12}H_7BrS_2$: S, 21.69. Found: 21.89, 21.66.

Method II. A mixture of 11.6 g. (0.05 mole) of thianthrene-5-oxide and 100 ml. of 48% hydrobromic acid was refluxed for 10 hours. Bromine was liberated as soon as the mixture became warm, and a red oil separated. At the end of the reaction period the contents of the flask were cooled, and the mixture was extracted with ether. The ether extract was washed successively with dilute sodium hydroxide and water, and dried over anhydrous sodium sulfate. The solvent was removed in a current of dry air, and the oily residue was crystallized from glacial acetic acid to give 2.9 g. (20%) of white crystals, melting over the range 84-87°. Recrystallization from the same solvent gave 2.5 g. (17%) of the pure 2-bromothianthrene, m.p., 89-90°.

The use of a 32% solution of hydrobromic acid in the above method gave a better yield (35.8%) of 2-bromothianthrene. More dilute (16%) solution of the acid gave only traces of 2-bromothianthrene, the main product of the reaction being thianthrene.

Method III. To a hot solution of 21.6 g. (0.1 mole) of thianthrene in 200 ml. of glacial acetic acid was added a solution of 17.6 g. (0.11 mole) of bromine in 50 ml. of glacial acetic acid, and the resulting red solution was refluxed for 7 hours, after which only a slight yellow color persisted. The mixture was allowed to cool and kept at room temperature for 24 hours, but no product separated during this period. Seeding was effected by the addition of a few crystals of 2-bromothianthrene. In a few minutes a white, crystalline product separated, which was filtered and dried to give 13.75 g. (47%) of crude 2-bromothianthrene melting over the range 80-84°. Recrystallization from glacial acetic acid gave 9.65 g. (33%) of the pure product melting at 88-89°. A mixed melting point with the 2-bromothianthrene, obtained from the method I was not depressed.

The mother liquor from the reaction mixture was concentrated and allowed to cool. A white product separated, which after several recrystallizations from glacial acetic acid gave 0.9 g. (4.2%) of thianthrene (mixed m.p.).

Preparation of 2,7- and 2,8-dibromothianthrene

Method I. A mixture of 10.8 g. (0.05 mole) of thianthrene, 17.6 g. (0.11 mole) of bromine and 60 ml. of glacial acetic acid was refluxed for 16 hours after which a slight yellow color persisted in the solution. The mixture was allowed to cool, and the white product which separated was filtered and dried. The product, later shown to be a mixture of 2,7- and 2,8-dibromothianthrene, weighed 15.44 g. (82.6%), and melted over the range 115-130°. Attempts to obtain a sharp-melting product from this mixture were unsuccessful. Four recrystallizations from glacial acetic acid gave 7.3 g. of the white amorphous product melting over the range 140-149°.

Anal. Calcd. for $C_{12}H_6Br_2S_2$: S, 17.11; Br, 42.78. Found: S, 17.20, 16.74; Br, 42.71, 42.60.

The infrared spectrum showed an absorption band at 12.4 μ, characteristic of 1,2,4-substitution, but the band at 13.3 μ, characteristic of 1,2-substitution, which was present in the spectrum of 2-bromothianthrene, had disappeared, indicating that substitution had taken place in both rings. The spectrum did not show a band indicative of 1,2,3-substitution. It is considered from these data that the disubstitution had taken place in the 2,7 and/or 2,8 positions. Since neither the product itself, nor its tetraoxide could be obtained in sharp-melting forms, it is inferred that both of the 2,7- and 2,8-dibromothianthrene are present in the product.

The reported dibromothianthrene of unknown structure and physical constants[77] was prepared in essential accordance with the procedure described in the reference. The product, after several recrystallizations from glacial acetic acid, melted over the range 140-150°. Its infrared spectrum was identical with that of the dibromothianthrene obtained by Method I.

<u>Method II</u>. A mixture of 9.92 g. (0.04 mole) of thianthrene-5,10-dioxide (α-form) and 100 ml. of 32% hydrobromic acid was refluxed for 16 hours. Bromine was liberated as soon as the mixture became warm, and a red oil separated as a heavier layer. At the end of the reflux period the aqueous layer retained a slight yellow color. The mixture was cooled and extracted with ether. The ether extract was washed successively with dilute sodium hydroxide and water, treated with Norit-A, filtered and dried over anhydrous sodium sulfate. Upon evaporation of the solvent a colorless oil was left as the residue which soon solidified. The dried product melted over the range 110-125°. Four recrystallizations from glacial acetic acid raised the melting range to 142-151°. The infrared spectrum of this product was identical with that of the isomeric mixture obtained by Method I.

<u>Method III</u>. To a suspension of 11.6 g. (0.05 mole) of thianthrene-5-oxide in 60 ml. of glacial acetic acid was added 8.8 g. (0.055 mole) of bromine. The sulfoxide dissolved

immediately to give a red solution. The mixture was subsequently refluxed for 16 hours after which a supernatnat, yellow acetic acid solution, and a heavier, yellow oil remained in the reaction flask. A white product which separated upon cooling was filtered and dried to give an amorphous powder melting over the range 110-125°. Four recrystallizations from glacial acetic acid raised the melting range to 139-149°. The infrared spectrum of this product was identical with that of the isomeric mixture obtained by Method I. The yield of the crude product was 15.0 g. (80.2%).

Bromination of thianthrene-5-dioxide (attempted)

A solution of 2.48 g. (0.01 mole) of thianthrene-5-dioxide and 1.6 g. (0.01 mole) of bromine in 10 ml. of glacial acetic acid was refluxed for 16 hours. A slight yellow color of the solution persisted. The mixture was cooled, filtered, washed and dried to give 2.28 g. (92%) of the unreacted thianthrene-5-dioxide (mixed m.p.).

Oxidation Reactions

Preparation of 2-bromothianthrene-5,10-tetraoxide

To a hot solution of 2.06 g. (0.007 mole) of 2-bromothianthrene in 10 ml. of glacial acetic acid was added a solution of 6.3 g. (0.056 mole) of hydrogen peroxide (30%) in 10 ml. of glacial acetic acid. Another 10 ml. of the solvent was added to effect a complete solution which was subsequently refluxed for 2 hours. A white, crystalline product which separated upon cooling was filtered and dried to give 2.20 g. (88%) of 2-bromothianthrene-5,10-tetraoxide, m.p., 226-227°. Recrystallization of the product from glacial acetic acid did not raise the melting point.

The mother liquor, upon dilution, gave another 0.23 g. of the impure product melting over the range 200-213°. Two recrystallizations from glacial acetic acid gave 0.12 g. of the pure product melting at 226-227°. The total yield of the pure product was 2.32 g. (92.1%).

The infrared spectrum showed bands at 11.9 μ, 13.1 μ and 8.65 μ, indicative of 1,2,4- and 1,2-substitution, and the sulfone group, respectively.

Anal. Calcd. for $C_{12}H_7BrO_4S_2$: S, 17.83. Found: S, 17.63.

Preparation of 2,7- and 2,8-dibromothianthrene-5,10-tetraoxide

To a hot solution of 3.74 g. (0.01 mole) of the isomeric mixture of dibromothianthrene in 40 ml. of glacial acetic acid was added a solution of 9.0 g. (0.08 mole) of hydrogen peroxide (30%) in 10 ml. of glacial acetic acid, and the resulting solution was refluxed for 2 hours. The mixture was cooled, and the white product which separated was filtered and dried to give 3.08 g. of the tetraoxide melting over the range 237-264°. From the mother liquor was obtained, upon dilution, another 1.17 g. of white product melting over the range 210-240°. Attempts to separate the mixture into sharp-melting products were unsuccessful. After several recrystallizations from glacial acetic acid the product melted over the range 246-280°. The total yield of the tetraoxide was 4.25 g. (96%).

Anal. Calcd. for $C_{12}H_6Br_2O_4S_2$: S, 14.61; Br, 36.53. Found: S, 14.64, 14.43; Br, 36.59, 36.44.

Preparation of 1-chlorothianthrene-5,10-tetraoxide

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 hydrogen peroxide (30%) 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 (84%) of 1-chlorothianthrene-5,10-tetraoxide 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.

Preparation of 2-carboxythianthrene-5,10-tetraoxide

To a hot solution of 0.9 g. (0.0035 mole) of 2-thianthrenecarboxylic acid in 20 ml. of glacial acetic acid was added 5 ml. of hydrogen peroxide (30%). The solution became colorless in a few minutes. The mixture was refluxed for 2 hours. A white product which separated upon cooling was filtered, and dried to yield 0.95 g. (87%) of 2-carboxythianthrene-5,10-tetraoxide 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.

Oxidation of 4-carboxythianthrene-5-dioxide

To a hot solution of 1.46 g. (0.005 mole) of 4-carboxythianthrene-5-dioxide, obtained from the metalation of thianthrene-5-dioxide, in 20 ml. of glacial acetic acid was added 9.0 of hydrogen peroxide (30%) 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. (83%) of the pure product melting at 306-307°.

The mother liquor was concentrated to a volume of 25 ml. and allowed to cool. The white product which crystallized out was filtered and dried to give 0.25 g. of the acid melting at 307-308°. The total yield of the pure product was 1.60 g. (99%).

An admixture of the product with 1-carboxythianthrene-5,10-tetraoxide, obtained from the oxidation of 1-thianthrenecarboxylic acid, was not depressed. The identity was established further by the comparison of the infrared spectra.

Preparation of thianthrene-5,5,10-trioxide

Chlorine was bubbled at a rapid rate through a suspension of 129.6 g. (0.6 mole) of thianthrene in 1500 ml. of boiling 90% acetic acid. In a few minutes all of the thianthrene dissolved to give a pink solution. At this stage the solution was allowed to cool, while the addition of chlorine was continued. Heating was resumed as soon as white crystals began to separate. The pink color of the solution disappeared, and a clear, yellow solution resulted during a period of 1 hour. The solution was allowed to cool, and a small sample of the white needles which separated was taken out. It did not melt below 230°. This indicated that the product was thianthrene-5,10-dioxide, since both the α-and the β-form of the disulfoxide melt above the melting point of the trioxide (221.5-222.5°). The mixture was cooled to room temperature, and more chlorine was added for approximately 15 minutes. Upon heating a clear, yellow solution resulted. A white product separated in the form of small prisms as the solution cooled. Addition of chlorine was discontinued at this stage, and the mixture was diluted to 3 liters with cold water. The product which separated was filtered, washed successively with dilute sodium sulfite solution and water, and dried to yield 145 g. (91.5%) of the crude product melting over the range 215-220°. Recrystallization from 90% acetic acid gave 132 g. (83.3%) of the pure product melting at 221.5-222.5°. Fries and Vogt[52] have reported the melting point of this compound as 216°.

The infrared spectrum showed bands at 8.63 μ, 9.8 μ and 13.1 μ, characteristic of the sulfone group, the sulfoxide group and 1,2-substitution, respectively.

Anal. Calcd. for $C_{12}H_8O_3S_2$: S, 24.24. Found: S, 24.18, 24.15.

Preparation of thianthrene-5-oxide

Fries and Vogt obtained thianthrene-5-oxide in 83% yield by the oxidation of thianthrene with nitric acid (sp. gr. 1.2).[52] A slight modification of the method gave excellent yields of the product.

To a stirred refluxing solution of 86.4 g. (0.4 mole) of distilled thianthrene in 1400 ml. of glacial acetic acid was added drop-wise 150 ml. of the dilute nitric acid over a period of 1.5 hours, and the mixture was refluxed for an additional period of 15 minutes. The yellow solution was diluted with 5 liters of ice-water. The product which separated in the form of very fine needles was filtered, washed with water and dried to yield 90.5 g. (98%) of the pure 5-oxide melting at 143-143.5°.

Reduction Reactions

Preparation of thianthrene-5-dioxide

Reduction with zinc and acetic acid. To a solution of 105.6 g. (0.4 mole) of thianthrene-5,5,10-trioxide in 500 ml. of hot 90% acetic acid was added 60 g. of zinc dust, and the mixture was refluxed for 3 hours. The hot solution was decanted into 1.5 liters of cold water. The white product which separated was filtered, washed and dried to yield 94.0 g. (95%) of thianthrene-5-dioxide melting at 167-168°. Recrystallization from glacial acetic acid raised its melting point to 168-169°.

The infrared spectrum showed bands at 8.65 μ and 13.2 μ, characteristic of the sulfone group and 1,2-substitution, respectively.

Anal. Calcd. for $C_{12}H_8O_2S_2$: S, 25.80. Found: S, 25.50, 25.52.

Fries and Vogt[52] have reported the melting point of this product as 159°.

Reduction with hydrobromic acid. A mixture of 7.92 g. (0.03 mole) of thianthrene-5,5,10-trioxide and 60 ml. of 32% hydrobromic acid was refluxed for 16 hours. Free bromine was liberated as soon as the mixture became warm, and the color of bromine slowly disappeared leaving a slight yellow color in the suspension at the end of the reaction period.

The mixture was cooled, filtered, washed and dried to yield 7.41 g. (99.6%) of thianthrene-5-dioxide melting over the range 162-165°. Recrystallization of the crude product from 90% acetic acid gave 6.87 g. (92%) of the pure product (mixed m.p.).

Reduction of 2-ethylsulfinyl-2'-carboxydiphenyl sulfide

A solution of 0.8 g. (0.0026 mole) of 2-ethylsulfinyl-2'-carboxydiphenyl sulfide in 30 ml. of glacial acetic acid at room temperature was saturated with hydrogen bromide. A yellow solution resulted after which yellow crystals began to separate. The mixture was left at room temperature for 4 days and subsequently diluted with water. The white product was filtered, washed with water and dried to yield

0.7 g. (93%) of crude 2-ethylmercapto-2'-carboxydiphenyl sulfide melting over the range 165-190°. Successive recrystallizations from benzene, aqueous acetone and 90% acetic acid gave product melting at 191-193°. It did not depress the melting point of the product obtained from the reduction of the same starting material with zinc and acetic acid.

Reduction of 2-*n*-butylsulfinyl-2'-carboxydiphenyl sulfide

A solution of 0.9 g. (0.0027 mole) of 2-*n*-butylsulfinyl-2'-carboxydiphenyl sulfide in 10 ml. of glacial acetic acid at room temperature was saturated with hydrogen bromide. After allowing the mixture to stand for 1 hour it was diluted with water, and the product which separated was filtered and recrystallized from 90% acetic acid to give 0.4 g. (46%) of white crystals melting over the range 128-132°. Two additional recrystallizations from the same solvent failed to raise the melting point. The product did not depress the melting point of the pure 2-*n*-butylmercapto-2'-carboxydiphenyl sulfide, obtained from the reduction of the same starting material with zinc and acetic acid.

Reduction of 2-nitrothianthrene with tin and hydrochloric acid

A mixture of 1.03 g. (0.005 mole) of 2-nitrothianthrene,[68] 10 ml. of hydrochloric acid, 7.0 g. of tin and 3 ml. of ethanol was refluxed for 4 hours. The yellow color of the 2-nitrothianthrene disappeared in a few minutes and a white solid remained in the reaction flask. The mixture was cooled and filtered. The residue was warmed with 10% sodium hydroxide solution, filtered, washed and recrystallized from ethanol to yield 0.6 g. (52%) of 2-aminothianthrene melting at 160°. A mixed melting point with an authentic specimen[36] was not depressed.

Condensation Reactions

Preparation of 2-acetamidothianthrene

A solution of 0.23 g. (0.001 mole) of 2-aminothianthrene in 3 ml. of acetic anhydride was boiled for 5 minutes, diluted with water, cooled and filtered. The white residue was recrystallized from dilute ethanol to give 0.20 g. (73%) of white flakes melting at 182-183°. A mixed melting point with the product obtained by reducing 2-nitrothianthrene according to Krishna's method[68] was not depressed, and the infrared spectra of the two products were identical.

Preparation of ethyl 1-thianthreneoxyacetate

To a solution of 0.92 g. (0.04 g. atom) of sodium in 50 ml. of absolute ethanol were added 9.28 g. (0.04 mole) of 1-hydroxythianthrene and 6.68 g. (0.04 mole) of ethyl bromoacetate. The mixture was refluxed for 2 hours, and the resulting red solution was diluted with excess of water. The mixture was extracted with ether, and the extract was dried over sodium sulfate. The solvent was evaporated to leave an oil which solidified on standing. The crude product weighed 11.05 g. (87%). Several recrystallizations from methanol gave 3.0 g. (23.6%) of the pure ester melting at 90-90.5°.

Anal. Calcd. for $C_{16}H_{14}O_3S_2$: S, 20.1. Found: S, 20.2, 19.8.

Preparation of 1-thianthreneoxyacetic acid

To a solution of 4.53 g. (0.113 mole) of sodium hydroxide in 60 ml. of water were added 11.6 g. (0.05 mole) of 1-hydroxythianthrene and 5.92 g. (0.063 mole) of chloroacetic acid. The mixture was refluxed for 13 hours, after which it was diluted with water and filtered. The filtrate was acidified with 10% hydrochloric acid. The cream-colored product was filtered and washed. The crude, dried product weighed 13.3 g. (92%) and melted over the range 145-155°. After several recrystallizations from 90% acetic acid was obtained 4.3 g. (30%) of the 1-thianthreneoxyacetic acid melting at 174-175°.

Anal. Calcd. for $C_{14}H_{10}O_3S_2$: neut. equiv., 290; S, 20.07. Found: neut. equiv., 288, 287; S, 22.57, 22.61.

DISCUSSION

Reactions Involving Organometallic Compounds

Metalation of heterocycles such as dibenzofuran and dibenzothiophene usually proceeds satisfactorily with n-butyllithium. In each case the substitution takes place in the position ortho to the hetero atom. Although dimetalation has been observed in a few cases, the reaction usually results in monometalation.[13] It has been found that oxygen has a greater orientation influence than sulfur. This conclusion has been based upon several facts.[125] First, metalation of a mixture of dibenzofuran and dibenzothiophene with insufficient amount of n-butyllithium resulted in the metalation of dibenzofuran only. Second, dibenzofuran metalated more readily than dibenzothiophene. Third, dibenzothienyllithium metalated dibenzofuran, but dibenzofuryllithium did not metalate dibenzothiophene. Fourth, phenoxathiin metalated in the 4-position (ortho to oxygen atom).

In agreement with these findings thianthrene metalated less readily than dibenzo-p-dioxin.[10] The acid obtained from thianthrene upon carbonation melted at 217-218°, and was shown to be 1-thianthrenecarboxylic acid.

---

[125] H. Gilman, M. W. Van Ess, H. B. Willis and C. G. Stuckwisch, J. Am. Chem. Soc., 62, 2606 (1940).

The above work was checked experimentally. The yellow acid melted at 224-225°. Its neutral equivalent showed it to be a monocarboxylic acid, which was confirmed as the 1-isomer since the only other isomer, 2-thianthrenecarboxylic acid, is white and melts at 227-228°. The 2-thianthrenecarboxylic acid was prepared from 2-bromothianthrene[78] through halogen-metal interconversion with n-butyllithium and subsequent carbonation of the reaction mixture.

The reported melting point of 1-aminothianthrene, prepared by the action of O-methylhydroxylamine on 1-thianthrenyllithium, is 139°.[10] A close examination of the experimental part of the reference revealed that the analysis for nitrogen did not show a satsifactory agreement. The amine prepared in the course of this investigation melted at 120-121°, and the theoretical and experimental values for the percent of nitrogen agreed very well. The reported product was, therefore, impure.

The oxidation of an organolithium compound by oxygen in the presence of n-butylmagnesium bromide results in the formation of the corresponding phenol. 4-Hydroxydibenzofuran has been prepared by this reaction in 45-52% yield.[126] The corresponding dibenzothiophene derivative was obtained in

---

[126] H. Gilman, L. C. Cheney and H. B. Willis, ibid., 61, 951 (1939).

33%[127] and 21%[128]. The reaction gave poor yields of 4-hydroxyphenoxathiin (15%) and 1-hydroxythianthrene (2.5%).[14] The reported method of the preparation of 1-hydroxythianthrene was slightly modified. The oxidation of the 1-thianthrenyllithium was carried out at room temperature instead of at -2°. The crude product was distilled under reduced pressure to give the pure 1-hydroxythianthrene in 29% yield.

The other two derivatives, 1-thianthrenyltriphenylsilane and 1-thianthreneboronic acid, prepared by the action of 1-thianthrenyllithium on triphenylchlorosilane and tri-n-butyl borate, respectively, are the first reported thianthrene compounds containing silicon or boron atom, and may prove to be of interest for other studies.

Although the orientation influence of the sulfur atom in metalation reactions is less than that of oxygen, the oxidation products, sulfoxides and sulfones, have much greater influence than either sulfur or oxygen. Thus, it has been found that dibenzothiophene-5-oxide can be metalated at -10° at which temperature dibenzothiophene does not,[80] and dibenzothiophene-5-dioxide can be metalated at -30° to yield, upon carbonation, 4-carboxydibenzothiophene-5-dioxide and 4,6-dicarboxydibenzothiophene-5-dioxide.[123] Thianthrene-5-

---

[127] H. Gilman and A. L. Jacoby, J. Org. Chem., 3, 108 (1938).

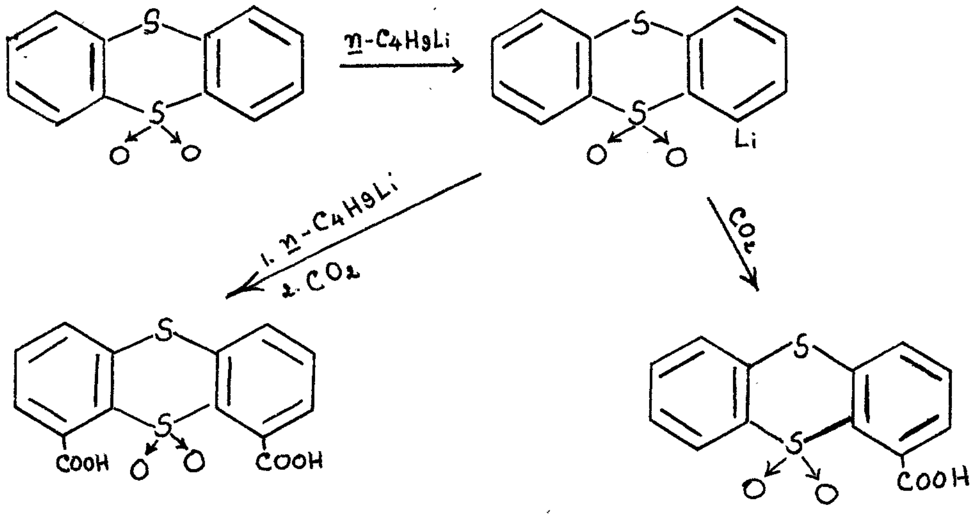
[128] K. E. Lentz, Unpublished M. S. Thesis, Iowa State College Library, 1949.

dioxide could be metalated with n-butyllithium even at a lower temperature to give, upon carbonation, both the mono- and dicarboxylic acids. The monocarboxylic acid upon oxidation yielded a product which gave analysis corresponding to monocarboxythianthrene-5, 10-tetraoxide. The product did not depress the melting point of authentic 1-carboxythianthrene-5,10-tetraoxide obtained from 1-thianthrenecarboxylic acid by oxidation with hydrogen peroxide (30%). The comparison of the infrared spectra established further the identity of the two products. This proved that the metalation of thianthrene-5-dioxide took place in either the 1- or the 4-position. The 1-position is ruled out from consideration in view of the fact that the sulfone group is much more reactive than the sulfide group as shown before. Thianthrene itself, which contains two sulfide groups, could not be metalated at -70° under the conditions under which thianthrene-5-dioxide was. Phenoxathiin metalates in the 4-position,[125] but phenoxathiin-10-dioxide metalates in the 1-position.[81,128a] The monocarboxylic acid is therefore established as 4-carboxythianthrene-5-dioxide. By using a low temperature of -70°, the reaction could be restricted to monometalation. At higher temperatures a mixture of the mono- and a dicarboxylic acid was obtained. The infrared spectrum of the dicarboxylic acid indicated that substitution

---

[128a] Unpublished studies of Mr. S. Eidt of this laboratory.

had taken place in both of the benzene rings. One of the two carboxylic groups must be in the 4-position since the reaction would be expected to proceed in stages. The other group must be in the 6-position since the dimetalation, followed by carbonation, of diphenyl sulfone, dibenzothiophene-5-dioxide and phenoxathiin-10-dioxide results in the formation of 2, 2'-dicarboxydiphenyl sulfone,[123] 4,6-dicarboxydibenzothiophene-5-dioxide[123] and 1,9-dicarboxyphenoxathiin-10-dioxide,[128a] respectively. The best conditions for monometalation required stirring thianthrene-5-dioxide with 3 equivalents of n-butyllithium for 16 hours at -70°. The 4-carboxythianthrene-5-dioxide was obtained in 41% yield upon carbonation of the reaction mixture. The dicarboxylic acid was obtained in 12% yield when the metalation was carried out at -40 to -45° for 5 hours and the mixture subsequently carbonated. The reaction obviously proceeds in stages.



The study of the reactions of thianthrene-5-oxide with organometallic compounds proved to be most interesting. The first successful metalation of a sulfoxide was that of dibenzothiophene-5-oxide.[80] Gilman and Esmay found that metalation of this sulfoxide with *n*-butyllithium followed by carbonation gave 4-dibenzothiophenecarboxylic acid in 35.7% yield. The other product of the reaction was dibenzothiophene, formed as a result of reduction. It was shown that metalation preceeded reduction in the reaction. Esmay observed that treatment of diphenyl sulfoxide with *n*-butyllithium at low temperatures resulted in cleavage, and benzoic acid was formed as a result in fair yields upon carbonation of the reaction mixture.[13] Schönberg observed that the action of sodamide on diphenyl sulfoxide in boiling toluene resulted in the formation of dibenzothiophene in 25% yield as a result of cyclization and reduction.[129] Substitution of toluene by benzene in the above reaction improved the yield of dibenzothiophene to 30-32%.[130]

In the present investigation it was found that treatment of thianthrene-5-oxide with *n*-butyllithium at low temperatures resulted in cleavage, reduction and metalation. The main product of the reaction was dibenzothiophene obtained

---

[129] A. Schönberg, *Ber.*, *56*, 2275 (1923).

[130] C. Courtot, M. Chaix and L. Nicolas, *Compt. rend.*, *194*, 1660 (1932).

in about 50% yield. The other products of the reaction were thianthrene, 2,2'-dicarboxydiphenyl sulfide and 1-thianthrenecarboxylic acid. The products of the reaction with n-butyllithium and with methyllithium are summarized in table VIII.

Table VIII

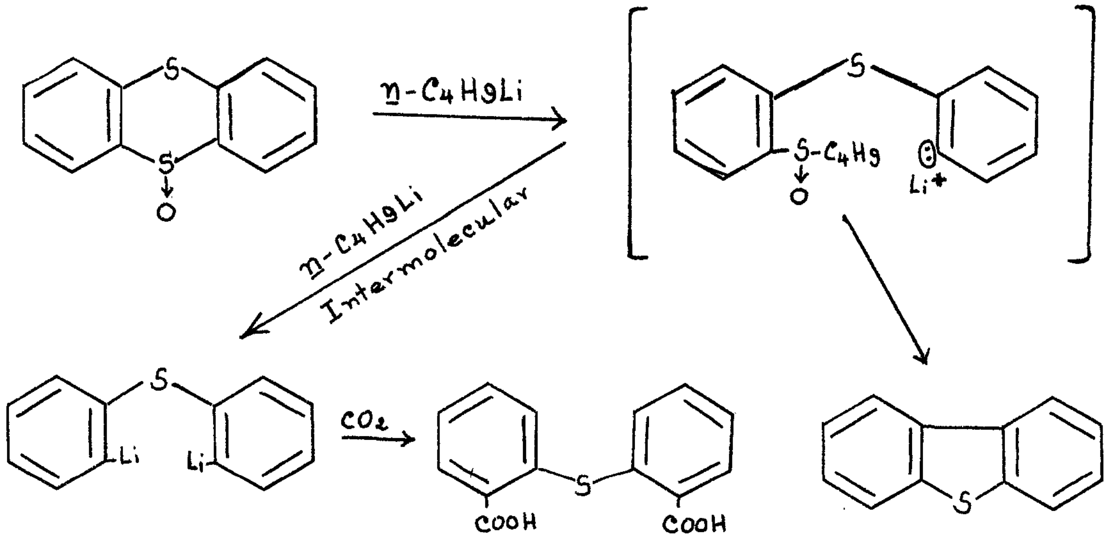
Reaction Products of Thianthrene-5-oxide with *n*-Butyllithium and with Methyllithium

Equivalents of alkyllithium	Time of reaction	Temperature	Yield of dibenzothiophene	Yield of thianthrene	Yield of acid	Recovery of starting material
REACTION WITH *n*-BUTYLLITHIUM						
1.1	3 minutes	-70	27.1%	9.3%		17.6%
1.1	10 minutes	-70	46%	4.7%		
1.1	7 hours	-70	50%			
3	30 minutes	-70	53.2%	8%		
3	7 hours	-70	52%	3.2%	1%[*]	
3	5 hours	-40	34%	4%		
2	7 hours	5-10	10.4%	13.2%	8.1%[**]	
REACTION WITH METHYLLITHIUM						
1.1	15 minutes	-70		12.5%		21.1%
1.1	16 hours	-70		21%		46%
3	16 hours	20-25		60%	1%[**]	

[*] The acid was 2,2'-dicarboxydiphenyl sulfide.

[**] The acid was 1-thianthrenecarboxylic acid.

The starting material, thianthrene-5-oxide, could be partly recovered only when the reaction time was limited to 3 minutes at -70°. The conversion of the sulfoxide to dibenzothiophene is nearly completed in about 10 minutes. The reaction thus resembles a typical halogen-metal interconversion and may be termed "sulfoxide-metal interconversion". Metalation is favored at higher temperature, while cleavage is preferred at low temperatures. The cleavage reaction apparently proceeds in stages. The intermediate could undergo a "sulfoxide-metal interconversion" in an intermolecular, and a ring closure in an intramolecular manner. The latter would explain the formation of dibenzothiophene, and the former, that of 2,2'-dicarboxydiphenyl sulfide.



The expected by-products, di-n-butyl sulfoxide, di-n-butyl sulfide or n-butanesulfenic acid, were not isolated. The intramolecular reaction is apparently favored since dibenzothiophene is formed in about 50% yield irrespective of the excess of n-butyllithium. If the intermolecular reaction was preferred, more of 2,2'-dicarboxydiphenyl sulfide should be formed.

The formation of 1-thianthrenecarboxylic acid at higher temperature shows that metalation is accompanied by reduction. Whether metalation precedes reduction in this reaction is not established. It may be that the two processes take place simultaneously.

The reaction took a different course when methyllithium was used. The amount of reduction was much greater. Thianthrene was obtained in 60% yield by stirring thianthrene-5-oxide at room temperature with 3 equivalents of methyllithium for 16 hours. This fact indicates that methyllithium could be profitably employed as a reducing agent for sulfoxides. The extent of metalation at best was small. No dibenzothiophene was isolated. No acidic product indicating cleavage was obtained.

Ethylmagnesium bromide has been found to effectively reduce dibenzothiophene-5-oxide, but phenylmagnesium bromide showed no reaction.[130a] Thianthrene-5-oxide was cleaved by

---

[130a] C. Courtot and C. Pomonis, Compt. rend., 182, 893 (1926).

ethylmagnesium bromide to yield a white acid which is assigned the structure 2-ethylsulfinyl-2'-carboxydiphenyl sulfide. n-Butylmagnesium bromide similarly cleaved the sulfoxide to give the corresponding product, 2-n-butylsulfinyl-2'-carboxydiphenyl sulfide in good yields. The reactions were carried out at -70°.

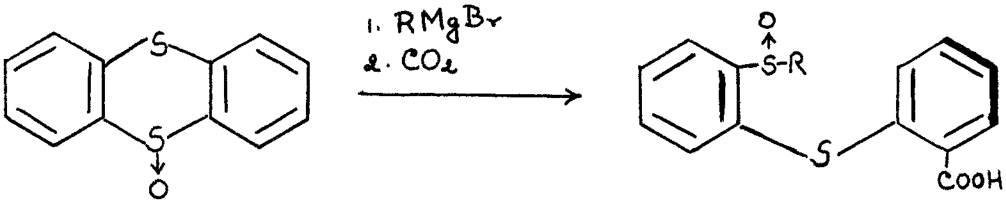


Table IX

Reactions of Thianthrene-5-oxide with Alkylmagnesium Halides

Equivalents of alkylmagnesium halide	Time of reaction	Temperature	Yield of acid	Recovery of starting material
	METHYLMAGNESIUM IODIDE			
2	20 hours	-70		63%
	ETHYLMAGNESIUM BROMIDE			
1.1	20 hours	-70	29.0%*	74%
3	20 hours	-70	11.2%	77%
	n-BUTYLMAGNESIUM BROMIDE			
1	16 hours	-70	25.4%**	23%
1	16 hours***	-70	50.0%	60%
2	16 hours	-70	35.3%	54%
3	6 hours	-70	10.3%	65%
1.1	48 hours	-70	34.8%	68%

---

*The acid obtained with ethylmagnesium bromide was 2-ethylsulfinyl-2'-carboxydiphenyl sulfide.

**The acid obtained with *n*-butylmagnesium bromide was 2-*n*-butylsulfinyl-2'-carboxydiphenyl sulfide.

***This was followed by a stirring period of 1 hour during which the cooling bath was removed and the reaction mixture allowed to warm up.

Attempts to synthesize 2-n-butylsulfinyl-2'-carboxydiphenyl sulfide were unsuccessful. The correctness of the assigned structures to the two acids rests upon several facts. First, the analytical and spectral data show satisfactory agreement. Second, the acids could be reduced to the sulfides, while 2-n-butylsulfinyl-2'-carboxydiphenyl sulfide could be oxidized to the corresponding tetraoxide. Third, no thianthrene was isolated in any run with the alkylmagnesium bromides, indicating that reduction of the sulfoxide group during the formation of the organomagnesium compounds was unlikely. Fourth, cleavage is the main reaction of n-butyllithium with diphenyl sulfoxide[13] and thianthrene-5-oxide[83] at -70°, with the formation of benzoic acid and dibenzothiophene, respectively. It can be imagined that with n-butylmagnesium bromide which is less reactive than n-butyllithium the reaction does not proceed beyond the stage of the intermediate postulated in the cleavage of thianthrene-5-oxide with n-butyllithium.

From the preceeding results it was anticipated that thianthrene-5,10-dioxide would give cyclobutadibenzene when treated with n-butyllithium at -70°. No such product was isolated with either of the two forms of the disulfoxide, probably due to the extreme insolubility of the product in ether particularly at low temperatures. The starting material was recovered in 65-87% yield.

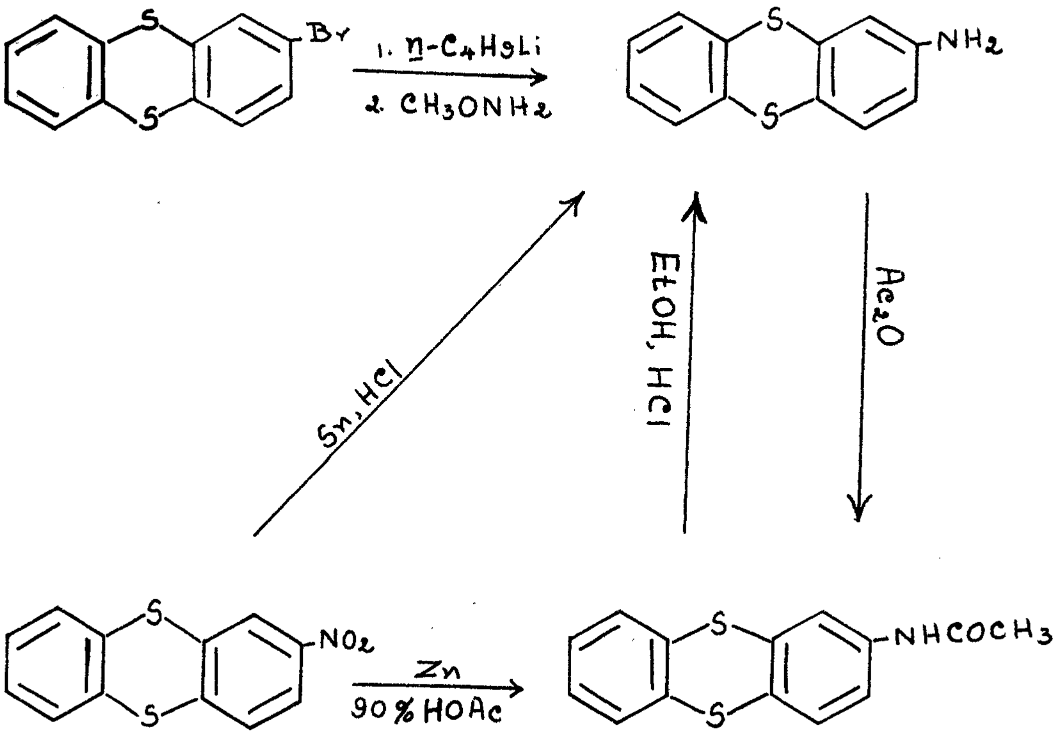
The cleavage reaction, however, was successfully applied to thianthrene-5,5,10-trioxide. The action of 3 equivalents of n-butyllithium at -70° for 3 hours resulted in the formation of dibenzothiophene-5-dioxide in 5% yield, and of 2,2'-dicarboxydiphenyl sulfone in 16.6% yield.

The only identifiable product from the attempted metalation of thianthrene-5,10-tetraoxide was the starting material obtained in 36-86% yield.

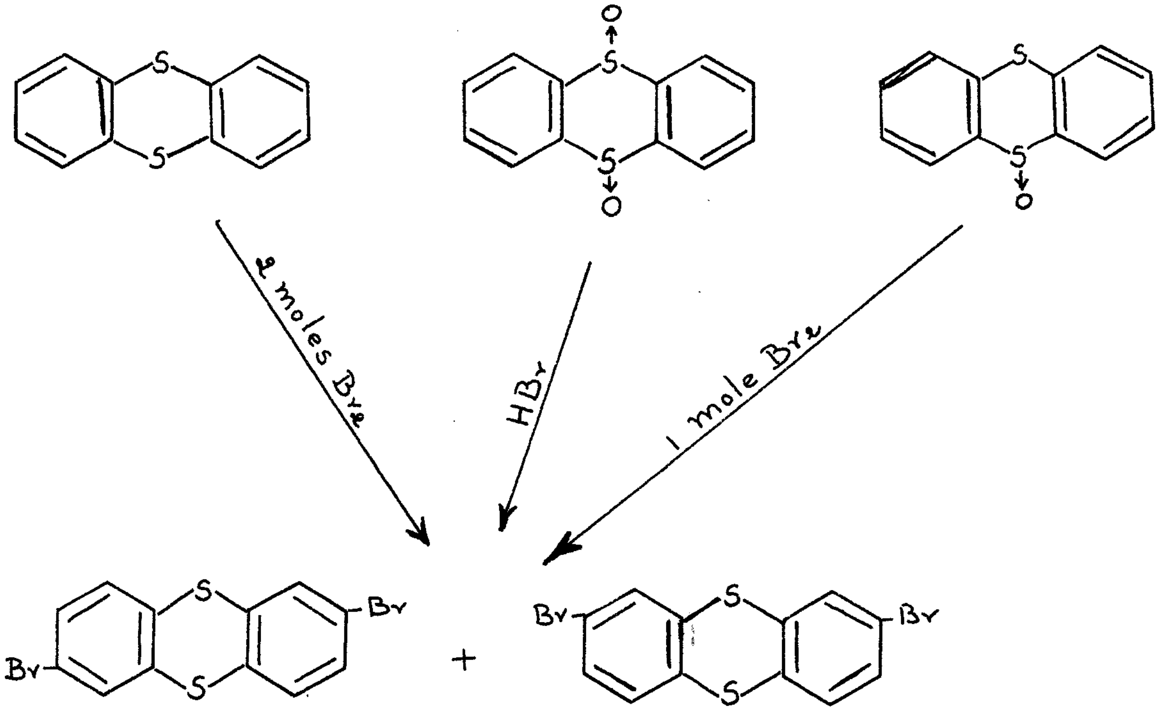
Halogenation Reactions

1-Bromothianthrene has been synthesized from 2-bromodiphenyl sulfide by condensation with sulfur in the presence of anhydrous aluminum chloride.[10] No successful monobromination of thianthrene has been reported. A dibromothianthrene has been prepared from thianthrene and bromine, but its physical characteristics and structure were not reported.[77] In the course of the present investigation 2-bromothianthrene was prepared in fair yields by the action of one molar equivalent of bromine on thianthrene and of 32% hydrobromic acid on thianthrene-5-oxide.

The structure of 2-bromothianthrene was established by its conversion to the aminothianthrene which was identical with the authentic 2-aminothianthrene obtained by Keats' method.[36] Krishna reduced 2-nitrothianthrene with zinc and 90% acetic acid, and reported the product he obtained as 2-aminothianthrene.[68] Keats showed that Krishna's product was actually 2-acetamidothianthrene which could be hydrolyzed to 2-aminothianthrene with ethanol and hydrochloric acid.[36] The structural proof of 2-bromothianthrene incidentally substantiated the finding of Keats. It was further found that acylation of the 2-aminothianthrene gave a compound which was identical with Krishna's product.



The action of two molar equivalents of bromine on thianthrene gave a product which was identical with the product obtained by the action of hydrobromic acid on thianthrene-5, 10-dioxide. The same product was also obtained by refluxing a solution of thianthrene-5-oxide and one molar equivalent of bromine in glacial acetic acid. Attempts to obtain a sharp-melting substance from it were unsuccessful. From its analysis, the examination of its infrared spectrum, and the comparison with the dibromination of dibenzothiophene,[131,132] it is considered to be a mixture of 2,7-and 2,8-dibromothianthrene.

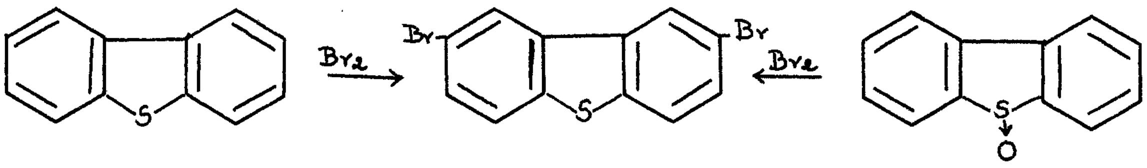


In the case of dibenzothiophene the sulfur atom has only one pair of *para* positions, therefore dibromination gives only one product, 2,8-dibromodibenzothiophene. In the thianthrene molecule, on the other hand, positions 2 and 8 are *para* to the sulfur atom 5. At the same time positions 2 and 7 are

---

[131] C. R. Neumoyer and E. D. Amstutz, *J. Am. Chem. Soc.*, *69*, 1920 (1947).

[132] H. Gilman and R. K. Ingham, *ibid.*, *73*, 4982 (1951).



para to the sulfur atoms 5 and 10, respectively. Thus, two products of dibromination, 2,7- and 2,8-dibromothianthrene, are possible with thianthrene. Attempts to separate the mixture into the two isomers through oxidation to the tetraoxides and subsequent recrystallizations were unsuccessful.

The reductive chlorination of 10-methylphenothiazine-5-oxide with hydrochloric acid to give 3-chloro-10-methylphenothiazine[76] has been recently investigated further by Schmalz and Burger.[133] These authors have suggested two mechanisms for this reaction. According to one mechanism, the chloride ion attacks the positively charged intermediate phenazothionium ion. The other mechanism involves the initial reduction of the sulfoxide to the sulfide. A mole of the free halogen, liberated in the process, subsequently attacks the heterocycle.

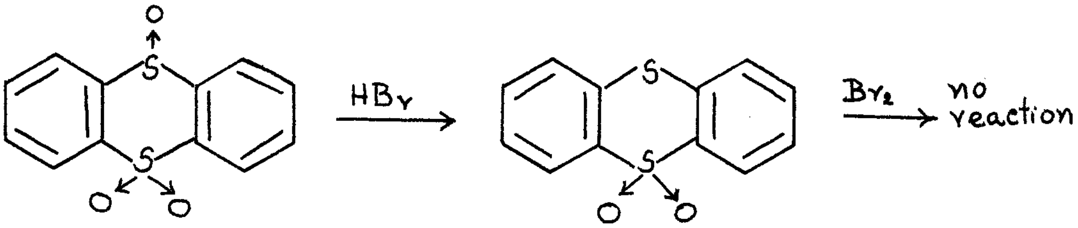
Other experimental studies from these laboratories favor the second mechanism.[134] The present investigation in the thianthrene system also indicates that the second mech-

---

[133] A. C. Schmalz and A. Burger, ibid., 76, 5455 (1954).

[134] H. Gilman and J. Eisch, ibid., 77, in press (1955).

anism is more probable. With all the three sulfoxides, thianthrene-5-oxide, thianthrene-5,10-dioxide and thianthrene-5,5,10-trioxide, hydrobromic acid first gave free bromine as evidenced by the color of the solution and of the vapor above the solution. The presence of a sulfone group, which would deactivate the benzene rings toward electrophilic attack, was expected to hinder bromination. Thianthrene-5-dioxide was not brominated with bromine under the experimental conditions, while hydrobromic acid reduced thianthrene-5,5,10-trioxide quantitatively to thianthrene-5-dioxide, but no bromination product was obtained from the reaction.



Oxidation Reactions

The tetraoxides are convenient derivatives of substituted thianthrenes. Accordingly, 1-carboxythianthrene, 2-carboxythianthrene, 4-carboxythianthrene-5-dioxide, 1-chlorothianthrene, 2-bromothianthrene, 2,7- and 2,8-dibromothianthrene and 2-n-butyl sulfinyl-2'-carboxydiphenyl sulfide were oxidized with hydrogon peroxide (30%) to the corresponding tetraoxides. The identity of the tetraoxides obtained from 1-thianthrenecarboxylic acid and 4-carboxythianthrene-5-dioxide established the fact that metalation of thianthrene-5-dioxide took place either in the 1- or in the 4-position.

Thianthrene-5,5,10-trioxide was prepared in excellent yields by the action of chlorine on thianthrene in boiling 90% acetic acid. Thianthrene-5-oxide was prepared by a modification of the method of Fries and Vogt[52] in improved yields.

Reduction Reactions

The reagents used for reduction during the course of this investigation were zinc and 90% acetic acid, tin and hydrochloric acid, hydrobromic acid and sodium sulfite. The reduction of a sulfoxide was better carried out with zinc and 90% acetic acid. 2-Alkylsulfinyl-2'-carboxydiphenyl sulfides gave impure products when reduced with hydrobromic acid probably due to accompanied bromination, but reduction of these products with zinc and 90% acetic acid gave very pure 2-alkylmercapto-2'-carboxydiphenyl sulfides.

Reduction of thianthrene-5,5,10-trioxide gave excellent yields of thianthrene-5-dioxide both with zinc and 90% acetic acid and with hydrobromic acid.

Reduction of 2-nitrothianthrene with zinc and 90% acetic acid has been shown to result in the formation of 2-acetamidothianthrene.[36] Direct reduction of the nitro compound to the 2-aminothianthrene was accomplished with tin and hydrochloric acid.

Condensation Reactions

Treatment of 2-aminothianthrene with acetic anhydride gave a product which was identical with Krishna's[68] product. This again confirms the finding of Keats that reduction of 2-nitrothianthrene with zinc and 90% acetic acid results in the formation of 2-acetamidothianthrene instead of 2-aminothianthrene.

1-Thianthreneoxyacetic acid and its ethyl ester were prepared from 1-hydroxythianthrene. These products may have interesting possibilities as plant hormones.

Suggestions for Further Research

The cleavage of thianthrene-5-oxide with organometallic compounds has been an interesting study. The use of solvents other than ether, such as petroleum ether (b.p. 28-36°) should be attempted.

The cleavage reactions were carried out usually at -70°. Lower temperatures may have interesting possibilities.

It was found that methyllithium gave a 60% yield of thianthrene when thianthrene-5-oxide was stirred at room temperature with the organolithium compound for 16 hours. This establishes the importance of methyllithium as a reducing agent for sulfoxides, and should be attempted for the reduction of diphenyl sulfoxide, phenoxathiin-10-oxide, and dibenzothiophene-5-oxide.

The cleavage of thianthrene-5-oxide with n-butyllithium gives dibenzothiophene in about 50% yield. The reaction probably could be carried a step further to obtain cyclobutadibenzene from dibenzothiophene-5-oxide. The possibility of obtaining this interesting hydrocarbon from thianthrene-5,10-dioxide is not ruled out, although the few attempts in that direction were unsuccessful.

Bromination of thianthrene-5-oxide with bromine gave an isomeric mixture of 2,7-and 2,8-dibromothianthrene. The bromination of thianthrene-5,10-dioxide may result in the tetrabromination of thianthrene.

The preparation of 2-bromothianthrene from thianthrene and thianthrene-5-oxide opens a field for research. A number of substituted thianthrenes could be prepared through halogen-metal interconversion and subsequent treatment of the intermediate organometallic compound with suitable reagents. One such product would be 2-hydroxythianthrene, which could be converted to the 2-thianthreneoxyacetic acid. This derivative, like the 1-isomer, may have interesting possibilities as a plant hormone. Both of the products should be chlorinated. The chlorination products again must be examined for activity as plant hormones.

Substituted thianthrenes should be oxidized to the monosulfoxides, which upon treatment with n-butyllithium at -70° may give the corresponding dibenzothiophene derivatives. For example, 1-hydroxythianthrene upon oxidation would give a sulfoxide which may be the 5-oxide or the 10-oxide. The 5-oxide would result in the formation of 4-hydroxydibenzothiophene, while the 10-oxide would give 1-hydroxydibenzothiophene. This reaction would enable one to determine the position of the oxygen atom in a monosulfoxide of thianthrene, which would be otherwise very difficult, if not impossible.

The cleavage of thianthrene-5-oxide with other alkylmagnesium bromides should be investigated with a view to obtain the corresponding 2-alkylsulfinyl-2'-carboxydiphenyl sulfides.

SUMMARY

A survey of the literature was made for the purpose of collecting and systematizing the available knowledge about thianthrene. The known derivatives of the heterocycle were classified according to the oxidation state of the sulfur atoms and grouped in the tables I-VII.

1-Thianthrenecarboxylic acid and 1-aminothianthrene were obtained from 1-thianthrenyllithium in greater purity. A modification of the method of preparation of 1-hydroxythianthrene gave the product in an improved yield. 1-Thianthrenyltriphenylsilane and 1-thianthreneboronic acid were prepared by the action of triphenylchlorosilane and tri-n-butyl borate, respectively, on 1-thianthrenyllithium.

The reaction of some organometallic compounds on thianthrene-5-oxide at low temperatures was investigated. With n-butyllithium the sulfoxide was cleaved to give dibenzothiophene as the main product of the reaction. Methyllithium gave a 60% yield of the reduced product thianthrene when the reaction was carried out at the reflux temperature of ether. The sulfoxide was cleaved by ethylmagnesium bromide at -70° to give a fair yield of 2-ethylsulfinyl-2'-carboxydiphenyl sulfide, while n-butylmagnesium bromide gave the corresponding product, 2-n-butylsulfinyl-2'-carboxydiphenyl sulfide in a good yield. Methylmagnesium iodide failed to give any acidic product. With all the three Grignard reagents the starting

material was recovered in good yields, while none of them gave any reduction of the sulfoxide.

Thianthrene-5-dioxide was successfully metalated with *n*-butyllithium to yield 4-carboxythianthrene-5-dioxide and 4,6-dicarboxythianthrene-5-dioxide.

Thianthrene-5,5,10-trioxide was cleaved with *n*-butyllithium at -70° to yield 2,2'-dicarboxydiphenyl sulfone.

2-Bromothianthrene was prepared in fair yields from thianthrene by the action of a molar equivalent of bromine, and from thianthrene-5-oxide by the action of hydrobromic acid. An isomeric mixture of 2,7- and 2,8-dibromothianthrene was obtained by the action of 2 molar equivalents of bromine on thianthrene, of hydrobromic acid on thianthrene-5,10-dioxide, and of a molar equivalent of bromine on thianthrene-5-oxide. Attempts to separate the isomers or their tetraoxides were unsuccessful. 1-Chlorothianthrene was prepared from 1-aminothianthrene through diazotization and Sandmeyer reactions.

2-Aminothianthrene was prepared from 2-bromothianthrene and also from 2-nitrothianthrene by direct reduction with tin and hydrochloric acid.

Oxidation to the tetraoxides of a number of thianthrene derivatives was carried out with hydrogen peroxide (30%).

Reduction of sulfoxides with zinc and 90% acetic acid gave purer products than with hydrobromic acid.

1-Thianthreneoxyacetic acid and its ethyl ester were prepared in fair yields.

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Henry Gilman for helpful advice, constructive criticism and encouragement given during the course of this investigation.