pound with sodium hydroxide in methanol[21] (method A) or by oxidation of the corresponding azobenzene with peracetic acid[22] (method B), unless otherwise stated. They were recrystallized from ethanol to constant melting point (see Table III).

4,4-Difluoroazoxybenzene, a new compound, was prepared by peracetic acid oxidation[22] of 4,4'-difluoroazobenzene,[23] and recrystallized from alcohol as pale yellow needles, m.p. 86–87°.

Anal. Calcd. for $C_{12}H_8N_2OF_2$: C, 61.5; H, 3.4. Found: C, 61.3; H, 3.5.

Absorption Spectra.—The absorption spectra were determined in absolute ethanol, or A. R. chloroform, with a Unicam S.P. 500 spectrophotometer.

Acknowledgments.—The authors gratefully acknowledge a gift of 4,4'-difluoroazobenzene from Professor Lichtenberger (Mulhouse). One of the authors (O.H.W.) is grateful to the Rockefeller Foundation, New York, for financial assistance. Some preliminary spectroscopic measurements were carried out by Mrs. I. Boston, Spectroscopic Laboratory, Chemistry Department, Imperial College of Science and Technology, London.

ACTON, LONDON
MEXICO, D. F.

---

[21] L. Zechmeister and P. Rom, *Ber.*, **59**, 867 (1926); *Ann.*, **468**, 129 (1929).

[22] A. Angeli, *Atti. R. Accad. Lincei*, **19**, 793 (1910).

[23] J. Lichtenberger and R. Dormet, *Bull. soc. chim. France*, 318 (1951).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Oxidation of Thianthrene to Thianthrene-5-oxide by Diazonium Salts

BY HENRY GILMAN AND DHAIRYASHEEL R. SWAYAMPATI

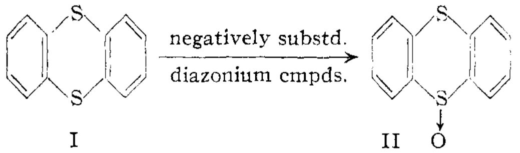
RECEIVED NOVEMBER 16, 1955

Thianthrene was oxidized to thianthrene-5-oxide in good yields by treatment with negatively substituted benzenediazonium salts in glacial acetic acid. The best results were obtained with *o*- and *p*-nitrobenzenediazonium sulfates. Thianthrene was prepared in improved yields by a modification of an earlier procedure.

Diazonium compounds react with a large number of "coupling components" such as phenols, aromatic amines, substances containing reactive methylene groups, phenolic ethers and hydrocarbons to give azo derivatives.[1] Although phenols and aromatic amines couple readily with diazotized amines, phenolic ethers and hydrocarbons require special conditions. Meyer and Tochtermann[2] were able to couple diazotized picramide with mesitylene, and Smith and Paden[3] used the same diazonium compound for successful coupling with pentamethylbenzene and with isodurene. Meyer and Lenhardt[4] were the first to couple phenolic ethers with diazonium salts. They found that phenolic ethers couple very slowly with diazonium compounds, but that the coupling reaction is greatly facilitated by the presence of more alkoxy groups in the "coupling component" and of nitro groups, particularly in the *ortho* and *para* positions, in the diazonium compound. Schoutissen[5] found that the coupling of anisole proceeds only if two nitro groups are present in the *ortho* and *para* positions in the diazonium compound, and that no coupling occurred if the two nitro groups were present in the *meta* positions.

The action of diazonium compounds on thianthrene (I), which is a thioether, was studied in the present investigation. The reaction consisted in adding a diazonium salt solution to a suspension of thianthrene in glacial acetic acid, and stirring the mixture for 12–24 hours. At the end of the reaction period the mixture was filtered, if necessary, and the solution diluted with water and the product which separated was collected and identified. It was found that thianthrene was oxidized to thianthrene-5-oxide (II) by *o*-nitro-, *p*-nitro-, 2,4-dinitro- and *p*-carboxybenzenediazonium salts. When nitrosylsulfuric acid was used for the diazotization of *o*-nitro-, *p*-nitro- and 2,4-dinitroaniline the yields of the sulfoxide were 98, 94 and 66%, respectively. With *o*-nitro- and *p*-carboxybenzenediazonium chloride only a part of the thianthrene dissolved to give the sulfoxide in 39% (90%, on the basis of unrecovered thianthrene) and 56% (93.5%, on the basis of unrecovered thianthrene), respectively.

It was found that either the nitro or the diazonium group by itself was not sufficient for the oxidation, since *m*-dinitrobenzene as well as benzenediazonium chloride failed to oxidize thianthrene.



I II

Since oxidation was more effective with sulfates than with chlorides it was thought that sulfuric acid may be partly responsible for the reaction. Fries and Engelbertz[6] have reported that thianthrene forms a complex with sulfuric acid, which upon hydrolysis gives a mixture of thianthrene and thianthrene-5-oxide. In an experiment in which a mixture of sulfuric acid, acetic acid and thianthrene in the usual experimental proportions was stirred at room temperature for 24 hours, no oxidation was detected. The starting material, thianthrene, was recovered in 97% yield.

It has been frequently observed that phenolic ethers couple with partial or complete elimination of the alkyl group from the ether.[7] Although

---

[1] H. A. Lubs, "The Chemistry of Synthetic Dyes and Pigments," Reinhold Publishing Corporation, New York, N. Y., 1955, p. 101; see also H. W. Grimmel in H. Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 243.

[2] K. H. Meyer and H. Tochtermann, *Ber.*, **54**, 2283 (1921).

[3] L. I. Smith and J. H. Paden, THIS JOURNAL, **56**, 2169 (1934).

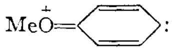
[4] K. H. Meyer and S. Lenhardt, *Ann.*, **398**, 74 (1913).

[5] H. A. J. Schoutissen, THIS JOURNAL, **55**, 4541 (1933).

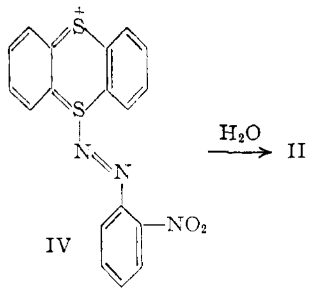
[6] K. Fries and E. Engelbertz, *Ann.*, **407**, 194 (1915).

[7] K. H. Saunders, "The Aromatic Diazo Compounds," Edward Arnold and Co., London, 1936, p. 112.

Meyer and Lenhardt[4] and Schoutissen[5] report the normal coupling of phenolic ethers with negatively substituted benzenediazonium salts, the work of the former authors could not be duplicated by Hurd and Bonner,[8] who found that *p*-nitrobenzenediazonium salt coupled with 1-methoxynaphthalene to give 4-(*p*-nitrobenzeneazo)-1-naphthol instead of the 4-(*p*-nitrobenzeneazo)-1-methoxynaphthalene, as reported by Meyer and Lenhardt. Complete elimination of the methyl group occurs when diazotized *p*-nitroaniline is coupled with 2-methoxy-3-naphthoic acid.[9] Meyer, Irschick and Schlösser[10] found that diazotized 2,4-dinitroaniline coupled with anisole and phenetole without elimination, but with partial elimination with resorcinol dimethyl ether. *m*-Nitrobenzenediazonium salt has been observed to couple with α-naphthyl ethyl ether to give the normal dye together with the dye obtained from the elimination of the ethyl group.[11] The coupling and elimination reactions may take place in two ways.[12] The aryldiazonium group may first coördinate with the oxygen atom of the ether, followed by splitting off of the alkyl group and migration of the aryldiazonium group to a carbon atom in the *o*- or *p*-position. Alternatively, coupling on a nuclear carbon atom may take place directly followed by dealkylation. The contribution by the resonance structure such as III of anisole appears to be sufficient to enable the powerful cation of 2,4-dinitrobenzenediazonium salt to attack the 4-position causing partial or complete demethylation.[12]


III

In the case of thianthrene a diazonium compound in which the terminal nitrogen atom of the diazonium group is made very positive by negative substituents in the *ortho* or *para* positions can be expected to attack the electron-rich sulfur atom to form thionium salt IV, analogous to the thionium halides[6] of thianthrene. IV would then be hydrolyzed to give II.


IV

In support of this postulation it can be said that in these oxidation reactions thianthrene dissolved to form an orange solution, comparable to that formed between chlorine or bromine and thianthrene in glacial acetic acid, although of less intense color. The orange color of the solution was changed to yellow when the reaction mixture was hydrolyzed to liberate the sulfoxide.

Evolution of nitrogen could not be observed in any of the experiments. No attempt was made to investigate the fate of the diazonium compound as the result of the oxidation of thianthrene. An attempt to oxidize the thianthrene-5-oxide to thianthrene-5,10-dioxide by this method was unsuccessful. Other sulfur-containing heterocycles such as dibenzothiophene, phenoxathiin and 10-ethylphenothiazine could not be oxidized under comparable conditions, a fact which emphasizes the great ease with which thianthrene is oxidized to thianthrene-5-oxide. Although the yields of the sulfoxide were high, the method is not as simple and rapid as the oxidation with dilute nitric acid.[13]

Among the many methods for the preparation of thianthrene is that described by Fleischer and Stemmer,[14] which is noteworthy for its inexpensiveness and simplicity. These authors report a 64% yield of thianthrene, but later workers[15,16] obtained much lower yields of the product. The yields are expressed on the basis of the reaction

$$2C_6H_6 + 2S_2Cl_2 \xrightarrow{AlCl_3} I + 4HCl + 2S$$

The modification of the above method reported here involves the dropwise addition of the sulfur monochloride to the mixture of benzene and anhydrous aluminum chloride, instead of the addition of the catalyst to the solution of benzene and sulfur monochloride. The addition of small portions of the aluminum chloride against a brisk evolution of hydrogen chloride is troublesome, and some sulfur monochloride is lost in the process. The modification makes the procedure more convenient and easier to control. Distillation of the crude product and its subsequent recrystallization from glacial acetic acid gave pure thianthrene consistently in 66–69% yield.

Experimental

Thianthrene (I).—To a stirred suspension of 2000 ml. of thiophene-free benzene and 900 g. (6.74 moles) of granular, anhydrous aluminum chloride was added dropwise 1080 g. (8 moles) of sulfur monochloride over a period of 6 hours, at a rate so as to maintain a gentle reflux. Much sulfur distilled into the condenser during this and the subsequent reflux period of 3 hours. The dark mixture was stirred overnight and hydrolyzed cautiously with iced hydrochloric acid. When all the lumps were broken down the mixture was steam distilled for 3 hours to remove the excess benzene and steam-volatile impurities formed in the reaction. The aqueous layer was decanted off and the residue filtered. The dark oil was pressed out as much as possible. The product was warmed with 20% sodium hydroxide solution, filtered, washed successively with water and ethanol. The residue was refluxed with three liters of glacial acetic acid for 1 hour, cooled, filtered, washed with ethanol and dried to give 746 g. (86%) of crude, brown thianthrene which melted over the range 140–153°. Distillation under reduced pressure gave 691 g. (80%) of nearly colorless thianthrene melting over the range 140–153°. The product was recrystallized from glacial acetic acid to yield 575 g. (66.5%) of pure thianthrene melting at 155–156°.

---

[8] C. D. Hurd and W. A. Bonner, THIS JOURNAL, **71**, 3241 (1949).

[9] G. B. Jambuserwala and F. A. Mason, *J. Soc. Dyers Colourists*, **46**, 339 (1930).

[10] K. H. Meyer, A. Irschick and H. Schlösser, *Ber.*, **47**, 1741 (1914).

[11] J. Van Alphen and G. Drost, *Rec. trav. chim.*, **68**, 54 (1949).

[12] K. Venkataraman, "Synthetic Dyes," Vol. I, Academic Press, Inc., Publishers, New York, N. Y., 1952, p. 429.

[13] H. Gilman and D. R. Swayampati, THIS JOURNAL, **77**, 3387 (1955).

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

[15] Unpublished studies of G. A. Martin, Jr.

[16] E. Bergmann and M. Tschudnowsky, *Ber.*, **65**, 457 (1932); see also D. A. Shirley, "Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 276.

Thianthrene and Benzenediazonium Chloride.—To a stirred slurry of 2.8 g. (0.03 mole) of aniline in 15 ml. of 6 *N* hydrochloric acid was added dropwise a solution of 2.07 g. (0.03 mole) of sodium nitrite in 10 ml. of water, keeping the temperature of the reaction at 0–5°. The solution was added to a stirred suspension of 6.48 g. (0.03 mole) of thianthrene in 60 ml. of glacial acetic acid. The mixture was stirred for a period of 20 hours, subsequently filtered, and the white product washed with water and dried to give 6.40 g. (98%) of thianthrene, m.p. and mixed m.p. 154–155°.

Thianthrene and *o*-Nitrobenzenediazonium Chloride.—The solution obtained from diazotization[17] of 2.8 g. (0.02 mole) of *o*-nitroaniline was filtered into a stirred suspension of 4.32 g. (0.02 mole) of thianthrene in 50 ml. of glacial acetic acid and the mixture was stirred at room temperature for a period of 20 hours. A part of the thianthrene dissolved to form a slightly orange solution. The undissolved product was filtered off, washed and dried to give 2.41 g. (56%) of pure thianthrene (mixed m.p.).

The filtrate was diluted to 500 ml. with water, and the white product which separated was filtered, washed and dried to give 1.80 g. (39%) of nearly pure thianthrene-5-oxide, m.p. 140–142°. Recrystallization from petroleum ether (b.p. 77–115°) gave product melting at 142–143°. A mixed melting point determination with an authentic specimen of thianthrene-5-oxide[13] showed no depression. The yield of the sulfoxide, on the basis of unrecovered thianthrene, was 90%.

Thianthrene and *p*-Carboxybenzenediazonium Chloride.—To a stirred suspension of 2.74 g. (0.02 mole) of *p*-aminobenzoic acid in 30 ml. of glacial acetic acid containing 5 ml. of hydrochloric acid was added dropwise a solution of 1.38 g. (0.02 mole) of sodium nitrite in 15 ml. of water. The temperature of the mixture was maintained at 0–5° during the addition of the sodium nitrite solution and for a subsequent stirring period of 30 minutes. The diazonium solution was filtered into a stirred suspension of 4.32 g. (0.02 mole) of thianthrene in 50 ml. of glacial acetic acid. After stirring the mixture for 16 hours the undissolved material was filtered, washed and dried to yield 1.74 g. (40%) of thianthrene (mixed m.p.). The filtrate was diluted to 500 ml. with water and filtered to give 2.60 g. (56%) of nearly pure thianthrene-5-oxide, melting at 140–141°. The product did not depress the melting point of an authentic sample of the sulfoxide. The yield of the thianthrene-5-oxide, on the basis of unrecovered thianthrene, was 93.5%.

Thianthrene and *o*-Nitrobenzenediazonium Sulfate.—A solution of 0.022 mole of nitrosylsulfuric acid[18] was added to 3.04 g. (0.022 mole) of *o*-nitroaniline in 40 ml. of glacial acetic acid. The temperature was maintained at 10–15° during the addition of the nitrosylsulfuric acid. The lumps were broken to give a clear solution in 30 minutes. The diazonium solution was filtered into a stirred suspension of 4.32 g. (0.02 mole) of thianthrene and stirred at room temperature for 12 hours. The resulting clear, orange solution was diluted to 500 ml. with water, and the white product which separated was filtered, washed with water and dried to yield 4.54 g. (97.8%) of nearly pure thianthrene-5-oxide (mixed m.p.).

Thianthrene and *p*-Nitrobenzenediazonium Sulfate.—An identical procedure was employed for this reaction as in the preceding experiment, except that the *o*-nitroaniline was substituted by the *p*-nitroaniline. The resulting orange solution was worked up in the same manner to give 4.35 g. (93.7%) of nearly pure thianthrene-5-oxide (mixed m.p.).

Thianthrene and 2,4-Dinitrobenzenediazonium Sulfate.—The solution obtained from the diazotization[18] of 0.022 mole of 2,4-dinitroaniline in 40 ml. of glacial acetic acid was filtered into a stirred suspension of 4.32 g. (0.02 mole) of thianthrene in 50 ml. of glacial acetic acid. The mixture was stirred at room temperature for 16 hours, and the clear, orange solution was diluted to 500 ml. with water. The yellowish product which separated was filtered, dried and recrystallized (Norit-A) from petroleum ether (b.p. 77–115°) to yield 3.05 g. (65.7%) of nearly pure thianthrene-5-oxide, melting at 141–143°. A mixed melting point with the authentic sulfoxide was not depressed.

Thianthrene and *m*-Dinitrobenzene.—A powdered mixture of 4.32 g. (0.02 mole) of thianthrene and 1.68 g. (0.01 mole) of *m*-dinitrobenzene was suspended in 50 ml. of glacial acetic acid, and the suspension was stirred at room temperature for a period of 24 hours. No sign of a reaction could be noticed. The mixture was filtered and the white residue was recrystallized from petroleum ether (b.p. 77–115°) to yield 3.6 g. (83%) of thianthrene, m.p. and mixed m.p. 154–155°.

The filtrate was diluted to 500 ml. with water, and the white product which separated was filtered, dried and recrystallized from petroleum ether (b.p. 77–115°) to yield 0.9 g. (53%) of *m*-dinitrobenzene (mixed m.p.).

Thianthrene and Sulfuric Acid.—To a stirred suspension of 4.32 g. (0.02 mole) of thianthrene in 50 ml. of glacial acetic acid was added a solution of 11 ml. of sulfuric acid in 40 ml. of glacial acetic acid. The slightly pink suspension was stirred at room temperature for 24 hours. The mixture was diluted with water to approximately 250 ml. and the white product was filtered, washed with water and dried to yield 4.20 g. (97%) of thianthrene, m.p. and mixed m.p. 153–155°.

Thianthrene-5-oxide and 2,4-Dinitrobenzenediazonium Sulfate.—The solution obtained from the diazotization[18] of 0.022 mole of 2,4-dinitroaniline in 40 ml. of glacial acetic acid was filtered into a stirred solution of 4.64 g. (0.02 mole) of thianthrene-5-oxide[13] in 50 ml. of glacial acetic acid. The solution acquired a slight orange color during a stirring period of 16 hours. The mixture was diluted to approximately 400 ml. with water, and the white product which separated was filtered, washed with water and dried. Recrystallization from petroleum ether (b.p. 77–115°) gave 3.7 g. (80%) of thianthrene-5-oxide (mixed m.p.).

AMES, IOWA

---

[17] R. S. Schreiber, *Org. Syntheses*, **31**, 14 (1951).

[18] S. V. Sunthankar and H. Gilman, *J. Org. Chem.*, **15**, 1200 (1950).