Ion Radicals. XI. The Reactions of Thioxanthene and Thioxanthene 10-Oxide in Sulfuric Acid[1]

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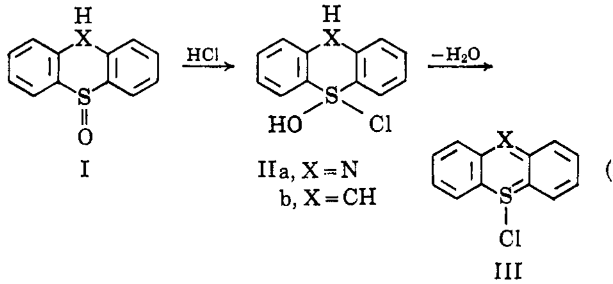
Thioxanthene in 96% sulfuric acid is converted partly into the thioxanthylium ion and partly into a sulfonated thioxanthylium ion. The products obtained from this solution were thioxanthene, thioxanthone, and a thioxanthenesulfonic acid. Solutions of thioxanthene 10-oxide in 96% sulfuric acid had the same ultraviolet, visible, and nmr spectra as solutions of thioxanthylium perchlorate in 96% sulfuric acid. The products obtained from the thioxanthene 10-oxide solution were thioxanthene and thioxanthone. These data show that the 10-oxide is converted cleanly into the thioxanthylium ion in 96% sulfuric acid. This conversion also occurs in 80% sulfuric acid and was followed by the change in the ultraviolet spectrum of the solution. Dithioxanthyl undergoes oxidative scission in 96% sulfuric acid. The thioxanthylium ion is formed. Oxidative scission occurs also under treatment with bromine in carbon tetrachloride, and thioxanthylium perbromide was isolated in almost quantitative yield. In none of our work was it possible to detect the thioxanthene cation radical.

In 1911 Hilditch and Smiles[3] commented on the similarities in the reactions of phenothiazine 5-oxide (Ia) and thioxanthene 10-oxide (Ib) with acids. The reaction of each of these sulfoxides with hydrogen chloride was formulated as in eq 1. The products (III) were



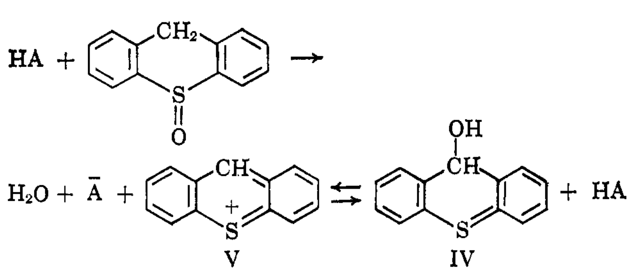
I

IIa, X = N
b, X = CH

III

(1)

called sulfonium chlorides and were regarded as being formed by the dehydration of the intermediate acid salts (II). It was reported also that the hydrolysis of the highly colored thioxanthylium chloride (IIIb) gave thioxanthene-9-ol (IV), and that the reaction of IV with hydrogen chloride gave the sulfonium chloride (IIIb). A solution of the sulfoxide Ib in concentrated sulfuric acid had the same appearance as one of IV, and when water was added to a solution of Ib in sulfuric acid, IV was precipitated. The modern formulation of these reactions would be as shown in eq 2.



V

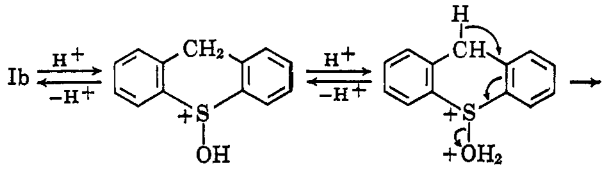
IV

A = Cl⁻ or HSO_4^- (2)

Recently[4] the reactions of phenothiazine and phenothiazine 5-oxide in acid solutions were discussed in detail. Each of these compounds can be converted to the phenothiazine cation radical and to the phenazothionium ion. Since phenothiazine and thioxanthene (VI) are isoelectronic we were interested in comparing their reactions and the reactions of their sulfoxides in strong acids. This report concerns the reactions of thioxanthene, its 10-oxide, and some related compounds.

Results and Discussion

Thioxanthene 10-Oxide (Ib) in Sulfuric Acid.—Ib dissolves rapidly in 96% sulfuric acid. The orange solution appears to be stable indefinitely. The ultraviolet and visible spectra are identical with those of thioxanthylium perchlorate (VII) in 96% sulfuric acid (Figures 1 and 2), with λ_{max} at 203, 279, and 381 mμ. Solutions of Ib and VII in 96% sulfuric acid have identical nmr spectra,[5] and the *i* factor of solutions of Ib in slightly aqueous sulfuric acid is close to 4.[5] These results leave no doubt that Ib is converted to the thioxanthylium ion (V) in 96% sulfuric acid, for which conversion we propose the reactions in eq 3.



V + H_3O^+ (3)

The ultraviolet spectrum of Ib in ethanol has λ_{max} at 206 mμ (Figure 3). Solutions of Ib in dilute sulfuric acid (*e.g.*, 15%) have a similar spectrum. Apparently, the solution is not sufficiently acidic to diprotonate Ib and convert it to V. The conversion of Ib to V takes place slowly in 80% sulfuric acid and can be followed by the change in the ultraviolet spectrum of the solution (Figure 3).

When a solution of Ib in 96% sulfuric acid is poured onto ice the color is slowly discharged. Thioxanthene (VI) and thioxanthone (VIII) are formed in amounts representing 44 and 50%, respectively, of the Ib used. These amounts are close to those expected for the disproportionation reaction shown in eq 4. The amount

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[1] Supported by the Directorate of Chemical Science, Air Force Office of Scientific Research, U. S. Air Force, under Grant No. AF-AFOSR-975-66. Presented in part at the joint meeting of the Southeast and Southwest Regions of the American Chemical Society, Memphis, Tenn., Dec. 2–4, 1965. A preliminary report of part of this work was made in *Tetrahetron Letters*, **No. 21**, 2301 (1966).

[2] Postdoctoral fellow, 1964–1966.

[3] T. P. Hilditch and S. Smiles, *J. Chem. Soc.*, **99**, 145 (1911).

[4] H. J. Shine and E. E. Mach, *J. Org. Chem.*, **30**, 2130 (1965).

[5] H. J. Shine, L. Hughes, and D. R. Thompson, *Tetrahedron Letters*, **No. 21**, 2301 (1966).

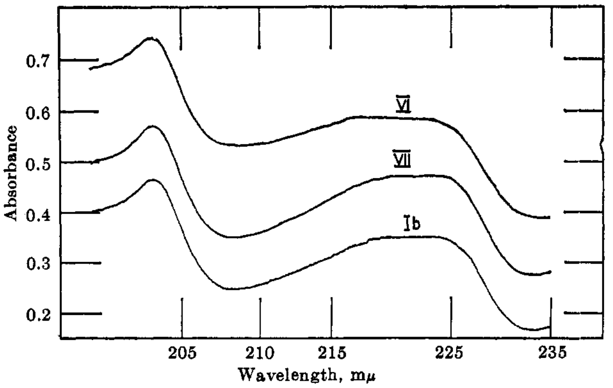
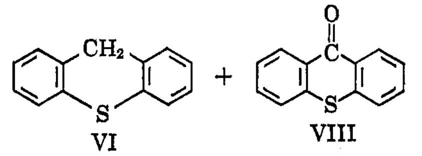


Figure 1.—The ultraviolet spectra of 2 × 10^{-5} *M* solutions of thioxanthene 10-oxide (Ib), thioxanthylium perchlorate (VII), and thioxanthene (VI) in 96% sulfuric acid. The spectrum of VII is raised 0.1 absorbance unit and the spectrum of VI 0.2 absorbance unit above the scale for the spectrum of Ib.

of VIII which was obtained was a little larger than that of VI. This may be due to the oxidation of some of the thioxanthenol (IV) by air. Our result is like that reported by Fields and Meyerson[6] for the hydrolysis of

$$\mathrm{Ib} \xrightarrow{H^+} \mathrm{V} + H_2O \xrightarrow{-H^+} \mathrm{IV} \xrightarrow{\mathrm{V}}$$



+ H^+ (4)

thioxanthylium perbromide (where, in fact, the excess of VIII over VI was larger than ours, and was attributed to the oxidation of IV by hypobromite), but differs from the report of Hilditch and Smiles that the product which precipitated from diluting a sulfuric acid solution of Ib was IV.

The ultraviolet spectrum of a solution of Ib in 80% sulfuric acid became in time like that of Ib and VII in 96% sulfuric acid. No indication of the presence of VIII was seen. It appears, therefore, that the thioxanthylium ion is stable in 80% sulfuric acid, or, as a corollary, that thioxanthenol (IV) would be readily converted to the thioxanthylium ion in 80% sulfuric acid.

Thioxanthene (VI) in Sulfuric Acid.—Solutions of VI in 96% sulfuric acid had ultraviolet and visible spectra which were similar to but not identical with those of the thioxanthylium ion (Figures 1 and 2). Thioxanthene, thioxanthone, and a thioxanthenesulfonic acid (IX) were isolated after a solution of VI in 96% sulfuric acid had been poured onto ice. Apparently, some of the thioxanthene was oxidized and some was sulfonated by 96% sulfuric acid. We believe that the sulfonated thioxanthene was also oxidized to give the sulfonated thioxanthylium ion (X), because peaks characteristic of the methylene group (*i.e.*, in an unoxidized molecule) were not present in the nmr spectrum of VI in 96% sulfuric acid. If VI in 96% sulfuric acid was converted to two thioxanthylium ions (V and X), we would expect that the pouring of the solution onto ice would give four products: VI, VIII, IX, and a thioxanthonesulfonic acid (XI, eq 5 and 6). The fact is that no compound like XI was isolated, although we

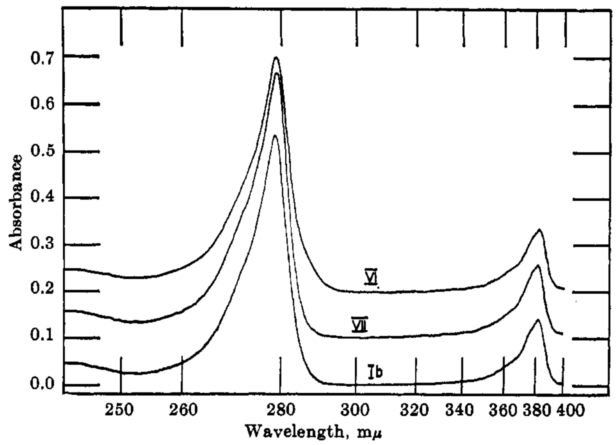


Figure 2.—Parts of the ultraviolet and visible spectra of 0.5 × 10^{-5} *M* solutions of thioxanthene 10-oxide (Ib), thioxanthylium perchlorate (VII), and thioxanthene (VI) in 96% sulfuric acid. The spectrum of VII is raised 0.1 absorbance unit and of VI 0.2 absorbance unit above the scale for the spectrum of Ib.

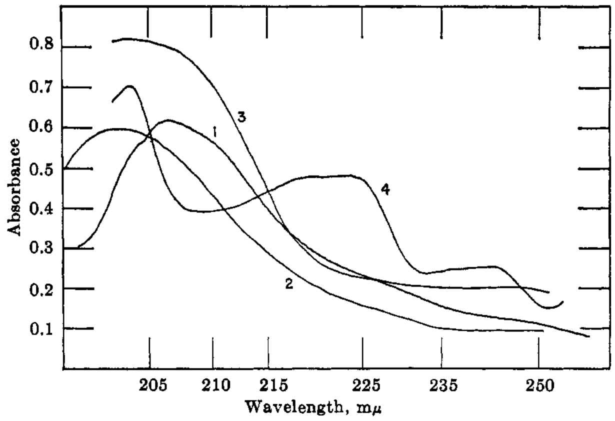
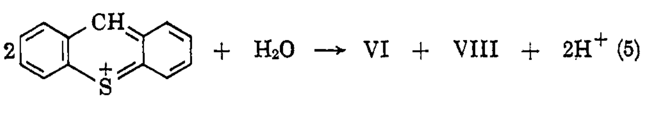
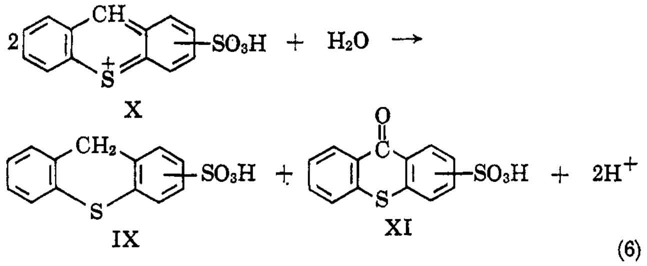


Figure 3.—The ultraviolet spectra of solutions of thioxanthene 10-oxide: 1, 1 × 10^{-5} *M* in absolute ethanol; 2, 1 × 10^{-5} *M* in 15% sulfuric acid; 3, 2 × 10^{-5} *M* in 80% sulfuric acid 5 min after being made; 4, 2 × 10^{-5} *M* in 80% sulfuric acid 26 hr after being made.

believe that one may have been formed (see the Experimental Section). The amount of VIII isolated was always greater than that of VI. There are several possible reasons for this. The initial product of hydrolysis of the thioxanthylium ion is thioxanthenol.





(6)

Coincidental oxidation of this instead of disproportionation would lead to VIII without the simultaneous formation of VI (as mentioned earlier). If the sulfonated thioxanthylium ion were to suffer reduction by hydride transfer from thioxanthenol in competition with hydration, the formation of VIII would occur without

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(6) E. K. Fields and S. Meyerson, *J. Org. Chem.*, **30**, 937 (1965).

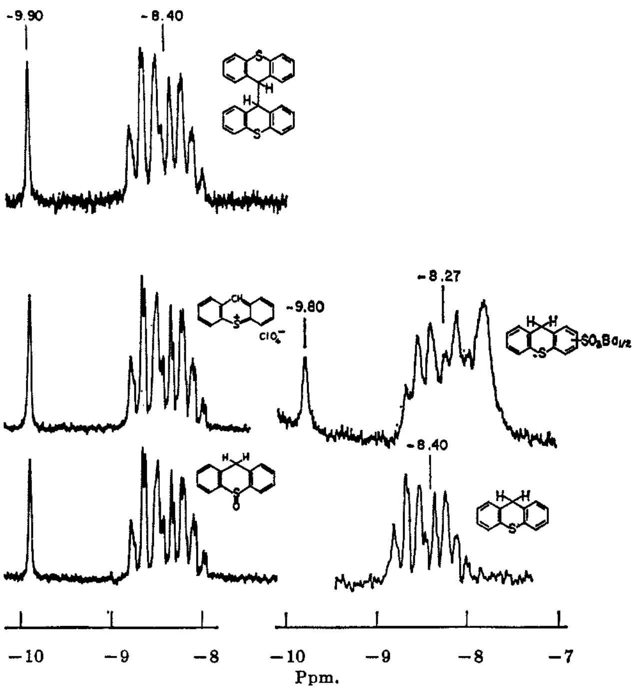


Figure 4.—The nmr spectra of solutions of thioxanthene, thioxanthene 10-oxide, thioxanthylium perchlorate, dithioxanthyl, and a thioxanthenesulfonic acid salt in 96% sulfuric acid. The ppm scale is based on tetramethylsilane as 0. The spectrum of the thioxanthene solution was obtained with the aid of a computer of average transients which caused the covering of the singlet at 9.90 ppm by summed sulfuric acid peaks. Each solution contained 200 mg of solute per milliliter of sulfuric acid, except that of thioxanthene which contained only 10 mg/ml.

the formation of VI. This is a speculative reason for obtaining an excess of VIII. It is attractive because it would also account for the apparent formation of only a small amount of XI. Finally, we found that, when thioxanthene was suspended in dilute (0.9 *N*) sulfuric acid, a small amount underwent oxidation to thioxanthone. Since the suspensions obtained by pouring the solutions of thioxanthene in 96% sulfuric acid onto ice were allowed to coagulate by standing for several days some of the thioxanthene therein could have become oxidized to thioxanthone.

The reactions of thioxanthene in 96% sulfuric acid are dependent on the concentration of the thioxanthene. When the concentration of thioxanthene was high enough (20 g/100 ml) for recording the nmr spectrum, several strong peaks were present (in addition to the thioxanthylium ion spectrum) which were not present in the nmr spectrum of either the thioxanthylium ion (obtained from thioxanthylium perchlorate in 96% sulfuric acid) or the sulfonated thioxanthylium ion (obtained by dissolving the barium salt of the thioxanthenesulfonic acid in 96% sulfuric acid). These peaks appeared at −9.41, −9.05, −8.90, and −8.84 ppm. When the concentration of thioxanthene was 1 g/100 ml (*i.e.*, that used for product determinations) it was necessary to record the nmr spectrum with the aid of a computer of average transients (a Varian Associates Model C-1024 "CAT" was used). The nmr spectrum then lacked the additional peaks mentioned above, and corresponded well with the spectrum of the thioxanthylium ion (Figure 4). Unfortunately, the use of the CAT resulted in the loss of some of the hyperfine structure of the spectrum. Also, the low-field, benzylic proton peak became merged with sulfuric acid peaks in the computer's summation of signals. Nevertheless, the absence of the peaks between −9.41 and −8.84 ppm was definite, and their presence in the spectrum of concentrated solutions (20 g/100 ml) is attributable to reactions which do not occur in dilute solutions and whose nature we have not pursued.

The Failure to Detect the Thioxanthene Cation Radical.—In none of the work with thioxanthene and thioxanthene 10-oxide were we able to detect the presence of radicals by esr spectroscopy. The thioxanthene cation radical appears to be too unstable to oxidation to be formed under the conditions we have used. This is in contrast with the isoelectronic phenothiazine cation radical. A scheme of reactions for aryl sulfides and sulfoxides has been proposed,[7] showing their stepwise conversion to cation radicals and dications (eq 7 and 8). At the present time it seems that the reac-

$$R_2S \xrightarrow{-\bar{e}} R_2S\cdot^+ \xrightarrow{-\bar{e}} R_2S^{2+} \qquad (7)$$

$$\begin{tikzcd} R_2S{=}O \arrow[r, "H^+"] & R_2\overset{+}{S}{-}OH \arrow[r, "H^+"] \arrow[d, "-(\dot{O}H)"] & R_2S^{2+} + H_2O \qquad (8) \\ & R_2S\cdot^+ & \end{tikzcd}$$

tions of thioxanthene and its 10-oxide correspond only with the dication–formation steps. The loss of a proton from the dication completes the over-all reaction with the formation of the very stable thioxanthylium ion. The thioxanthylium ion is isoelectronic with the phenazothionium ion. In the discussion[4] of the chemistry of phenothiazine it was proposed that the phenazothionium ion became protonated in 96% sulfuric acid; that is that the ion present was, in fact, the dication, and that the phenazothionium ion was formed only in solutions of lower acidity. Evidence has been obtained with freezing point measurements[8] which support this proposal, and show, as would be anticipated, that the phenazothionium ion is a stronger base than the thioxanthylium ion.

Xanthene in 96% Sulfuric Acid.—It is interesting to note the difference between the reactions of xanthene and thioxanthene with sulfuric acid. Xanthene is converted quantitatively to the xanthylium ion in 55 to 85% sulfuric acid.[9] Leisten and Walton[10] concluded from *i*-factor determinations that in slightly aqueous sulfuric acid xanthene was disulfonated but not oxidized, and commented that somewhere between 85 and 100% acid concentration the action of sulfuric acid on xanthene changes in character. We have found that xanthene is disulfonated in 96% sulfuric acid. The odor of sulfur dioxide was not detected. Furthermore, the nmr spectrum of a solution of xanthene in 96% sulfuric acid did not have a low-field singlet which we would associate with the xanthylium ion, but did have a broad peak near −4 ppm, which we attribute to the methylene protons of a xanthenedisulfonic acid. In contrast with xanthene, at least 60% of the thioxanthene was oxidized by 96% sulfuric acid and the re-

(7) H. J. Shine and D. R. Thompson, *Tetrahedron Letters*, **No. 15**, 1591 (1966).

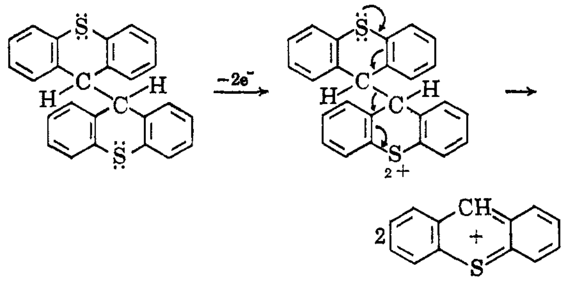
(8) Unpublished work of Mr. D. R. Thompson.

(9) N. Deno, G. Saines, and M. Spangler, *J. Am. Chem. Soc.*, **84**, 3295 (1962).

(10) J. A. Leisten and P. R. Walton, *J. Chem. Soc.*, 3180 (1964).

mainder appeared to undergo monosulfonation and oxidation.

The Reactions of Dithioxanthyl (XII).—This dimer dissolved slowly in 96% sulfuric acid. The nmr spectrum (Figure 4) appeared to be identical with that of thioxanthylium perchlorate in 96% sulfuric acid. On the other hand, although the ultraviolet and visible spectra of dithioxanthyl in 96% sulfuric acid were very similar to those of solutions of thioxanthylium perchlorate, they were not identical with them. Small differences were present whose origin we do not know. It appears to us that dithioxanthyl is oxidized to the thioxanthylium ion in 96% sulfuric acid and that some other reactions may occur but on a minor scale. Dithioxanthyl reacted with bromine in carbon tetrachloride solution to give almost a quantitative yield of thioxanthylium perbromide.[5,6] A plausible explanation of these oxidation reactions is given in eq 9.



(9)

Nmr Spectra.—The nmr spectra of thioxanthene 10-oxide, thioxanthylium perchlorate, dithioxanthyl, barium thioxanthenesulfonate, and thioxanthene in 96% sulfuric acid are given in Figure 4. Each spectrum has a single peak (except that of thioxanthene, for the reason given earlier) at −9.80 or −9.90 ppm (downfield from tetramethylsilane) and a number of aromatic hydrogen peaks centered at −8.30 or −8.40 ppm. No other peaks are observed, particularly at higher fields where the methylenic proton signals of unoxidized molecules would appear. The spectra of the solutions of thioxanthene 10-oxide, thioxanthylium perchlorate, and dithioxanthyl appear to be identical; these solutions contained the thioxanthylium ion. The spectrum of thioxanthene, obtained with the aid of a computer of average transients, shows only the aromatic hydrogen signals and these are probably due mostly to the thioxanthylium ion. In view of our having isolated a thioxanthenesulfonic acid from solutions of thioxanthene in 96% sulfuric acid, we had anticipated that the nmr spectrum of the thioxanthene solution would consist of the overlapping spectra of the thioxanthylium and sulfonated thioxanthylium ions. The spectrum of the latter ion has strong lines at the high-field side of the aromatic hydrogen group. Since the character of the aromatic portion of the spectrum of the thioxanthene solution is closely like that of the spectrum of the thioxanthylium ion, it appears that not enough of the sulfonated thioxanthylium ion was present in the thioxanthene solution to be detected by a qualitative examination of the nmr spectrum of the solution.

The positions of peaks in the nmr spectra were dependent on the concentration of the solute and also of the acid. Thus the single peak in the spectrum of the thioxanthylium ion shifted 18 cps upfield in 80% sulfuric acid and 3.5 cps downfield in 100% sulfuric acid, compared with the position obtained with 96% sulfuric acid. Also the total width of the spectrum increased from 107 to 115 cps in going from 80 to 96% sulfuric acid. When the concentration of the thioxanthylium ion was increased the spectrum shifted upfield. The effects of changing solute concentration and acidity were additive.

Experimental Section[11]

Thioxanthene (VI), Aldrich Chemical Co., was purified by chromatography on silica gel (Davison, Grade 950, 60–200 mesh) using benzene as the eluent. Crystallization from ethanol containing 3 ml of benzene per 100 ml gave mp 128.5–129°.

Thioxanthene 10-Oxide (Ib).—Four grams of 29% hydrogen peroxide was diluted with 50 ml of water and added over a period of 10 min to a stirred solution of 6.0 g of thioxanthene in 400 ml of acetic anhydride. The temperature was kept at 10° during the addition. Stirring was continued for 2 hr at 10–15°, and 500 ml of water was added. Stirring was continued until the mixture was homogeneous and 250 g of potassium hydroxide in 500 ml of water was added slowly, with cooling. Thioxanthene 10-oxide, 5.3 g (82%), mp 113–114°, precipitated. Crystallization from carbon tetrachloride gave mp 119° cor (lit.[3] mp 109°).

Anal. Calcd for $C_{13}H_{10}OS$: C, 72.88; H, 4.70; S, 14.96. Found: C, 72.99; H, 4.80; S, 14.69.

Thioxanthone (VIII) was prepared from the condensation of thiosalicylic acid with benzene by the method of Davies and Smiles.[12] Crystallization from acetic acid gave mp 211–212° (lit.[12] mp 209°).

Thioxanthen-9-ol (IV) was prepared from thioxanthone by the method of Oehlschlaeger and McGregor.[13] The product had mp 103–104° (lit.[13] mp 104–105°). Occasionally a product was obtained with a lower melting point, *e.g.*, 93–94° after crystallizing from a mixture of carbon tetrachloride and ligroin (bp 30–60°). Attempts to raise the melting point by recrystallization were not successful, and the product was discarded.

Dithioxanthyl (XII) was prepared by illuminating a benzene solution of thioxanthene with a tungsten lamp. The light was directed onto the surface of the solution in an open beaker for 24 hr. The benzene was then evaporated and the residue was crystallized from xylene, giving mp 325° cor (lit.[14] mp 325°).

Thioxanthylium perchlorate (VII) was prepared from thioxanthen-9-ol by the method of Price and had mp 229° (lit.[15] mp 229°).

The Reaction of Bromine with Dithioxanthyl.—A solution of 0.57 g (3.56 mmoles) of bromine in 10 ml of carbon tetrachloride was added to a solution of 0.47 g (1.19 mmoles) of dithioxanthyl in 50 ml of carbon tetrachloride. Hydrogen bromide was not evolved. A red precipitate was filtered off after 3 hr, weighing 0.98 g (94%), mp 169°. The melting point was not depressed by mixture with thioxanthylium perbromide made by the reaction of thioxanthene with bromine.[6]

Products from Thioxanthene in 96% Sulfuric Acid. 1. Thioxanthene and Thioxanthone.—Several experiments were carried out in which 1.0 g of thioxanthene was dissolved in 100 ml of sulfuric acid and the solution was poured onto crushed ice after about 8 hr. The precipitated material was filtered off, washed and dried, dissolved in benzene, and chromatographed on a column of silica gel using benzene for elution. The products were thioxanthene and thioxanthone, the former coming off the column first, and separated by a large gap from the latter. The amount of thioxanthone was always larger than that of thioxanthene. The efficiency of the chromatographic separations was high since the melting points of the separated thioxanthene and thioxanthone were good. Some results given as the time the precipitate was kept under aqueous acid, the amount of thioxanthene and thioxanthone, and the per cent of the original thioxanthene which each represents follow: 6 days, 0.27 g (27%), 0.41 g (38%); 7

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[11] Analyses were by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[12] E. G. Davies and S. Smiles, *J. Chem. Soc.*, 1290 (1910).

[13] H. F. Oehlschlaeger and I. R. McGregor, *J. Am. Chem. Soc.*, **72**, 5332 (1950).

[14] A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 657 (1945).

[15] C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Am. Chem. Soc.*, **85**, 2278 (1963).

days, 0.26 g (26%), 0.43 g (40%); 9 days, 0.17 g (17%), 0.46 g (43%).

2. **A Thioxanthenesulfonic Acid (IX).**—A solution of 2.0 g of thioxanthene in 250 ml of 96% sulfuric acid was made. After several experiments with aliquots of this solution the best method of isolating a sulfonic acid was found to be the following. An aliquot (50 ml) was poured onto ice and the volume of the solution was diluted to about 2 l. with water. The suspension of thioxanthene and thioxanthone was filtered off, and the filtrate was neutralized with solid barium carbonate. The precipitated barium sulfate was removed and the filtrate was evaporated to dryness. The solid residue was extracted with benzene, dried, and shaken with 150 ml of water to extract the barium salt of the sulfonic acid from barium carbonate. A solution of the barium sulfonate was passed through a Dowex 50W-X4 50–100 mesh cation-exchange column, and the effluent was neutralized with standard sodium hydroxide solution.

The neutral solution was evaporated to dryness. The residue was dissolved in water and a solution of S-benzylisothiouronium chloride was added. A solid precipitated, having mp 217° before and after crystallization from acetic acid.

Anal. Calcd for $C_{21}H_{20}N_2O_3S_3$: C, 56.73; H, 4.53; N, 6.30; S, 21.63. Found: C, 55.98; H, 4.56; N, 6.11; S, 21.55, 21.63.

3. **A Thioxanthonesulfonic Acid (XI).**—The barium sulfate which was precipitated and filtered off in the isolation of the thioxanthenesulfonic acid gave a yellow-green solution when treated with 96% sulfuric acid. Although this is only slender, circumstantial evidence, we believe that it indicates the presence of the barium salt of a thioxanthonesulfonic acid. Attempts to extract the sulfonic acid were unsuccessful.

Thioxanthone was sulfonated by heating 1.5 g of the ketone with 6 g of 30% fuming sulfuric acid for 5.5 hr at 150° (similar to the method of Kurihara and Niwa[16]). We were able to isolate 1.84 g of a mixture of barium salts of thioxanthonesulfonic acids. This mixture was yellow. We were unable to separate the monosulfonic acid[16] from this mixture. The barium salts dissolved in 96% sulfuric acid and the solution was yellow-green.

4. **Sulfur Dioxide.**—The sulfur dioxide obtained from the oxidation of weighed amounts of thioxanthene by 96% sulfuric acid was carried through Ascarite-filled tubes by a current of nitrogen. Two experiments were performed and gave 81 and 82% of the theoretical amount of sulfur dioxide based on a two-electron oxidation per molecule of thioxanthene.

Thioxanthene in Aqueous Acid.—Finely ground thioxanthene (0.200 g), mp 129–130°, was placed in 400 ml of 0.9 *N* sulfuric acid for 8 days with occasional shaking. Filtration gave 0.184 g, mp 128–130°. Thin layer chromatography showed the presence of thioxanthone.

Products from Thioxanthene 10-Oxide in 96% Sulfuric Acid.—A solution of 1.00 g of the oxide in 100 ml of 96% sulfuric acid was kept for 24 hr and poured onto crushed ice. The orange color of the aqueous solution slowly disappeared. A precipitate formed and was filtered off after standing 1 day. After being washed with water and dried, the solid weighed 0.944 g, mp 150–175°. Column chromatography with silica gel and benzene elution gave 409 mg of thioxanthene, mp 127–128°, and 496 mg of thioxanthone, mp 210°. The amounts anticipated on the basis of the reaction of the thioxanthylium ion with its hydration product (thioxanthenol) were 462 and 495 mg, respectively.

Recovery of Thioxanthone from Its Solution in 96% Sulfuric Acid.—A solution of 1.00 g of thioxanthone in 100 ml of acid was made. After 15 min, 20 ml of this solution was poured onto ice. A solid precipitated immediately. Its weight after washing and drying was 199 mg, mp 213–214°. After being kept for 48 hr, 50 ml of the acid solution was similarly treated giving 470 mg, mp 212°. Each experiment represents almost quantitative recovery of thioxanthone.

Anodic Oxidation of Thioxanthene.—A solution of thioxanthene (10^{-2} *M*) and tetrabutylammonium perchlorate (10^{-1} *M*) in nitromethane was used. Electrolysis was carried out in a Varian Associates electrolysis cell, using a platinum grid anode and changing the voltage periodically while searching continuously for an esr signal, but none was detected. The solution near the anode was colored orange, and the color did not disappear on standing after the current was stopped.

Sulfonation of Xanthene.—A solution of 1.0 g of xanthene in 100 ml of 96% sulfuric acid was kept for 2 hr and poured onto ice. The golden solution was neutalized with solid barium hydroxide. The barium sulfate was removed and the filtrate was concentrated to 100 ml. Filtration was repeated and the filtrate was converted to a solution of the acid with a cation-exchange column. The acid solution was neutralized with sodium hydroxide and evaporated to dryness. A portion (0.200 g) of the sodium salt was converted to the free acid by ion exchange and the acid was found by titration to have the equivalent weight of a xanthenedisulfonic acid.

Spectra.—Nmr spectra were obtained with a Varian Associate's A-60 instrument. The internal reference used for the sulfuric acid solutions was tetramethylammonium chloride (TMA). When the instrument had been "zeroed" for tetramethylsilane (TMS) in deuteriochloroform the single peak of TMA in 96% sulfuric acid came at −3.11 ppm. Calibration of TMA against TMS was not made in any other way. The minor changes in the displacement of a TMA signal with respect to TMS which occur when solvents are varied have been discussed by Deno.[17] The temperature of the samples in the probe was about 35°.

Ultraviolet and visible spectra were obtained with a Beckman DK-2 Instrument, using ground-glass stoppered cells.

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Reactions of Phosphorus Compounds. XI. A General Synthesis of Substituted 1,2-Dihydroquinolines

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A series of acyl- and arylsulfonyl-1,2-dihydroquinolines has been prepared from substituted *o*-formyl- and *o*-ketoanilines employing vinyltriphenylphosphonium bromide as the cyclization reagent.

The use of vinyltriphenylphosphonium bromide (**3**) as a general reagent for the synthesis of heterocyclic and carbocyclic compounds has been demonstrated.[1-3] This reagent has also been used in preparing olefinic compounds *via* a chain-extension reaction.[4] We now wish to report the further use of salt **3** in a general synthesis of 1,2-dihydroquinolines, as shown in Scheme I.

The sodium salts **2a–g** were prepared by reaction with sodium hydride in ether or benzene and were not isolated. Addition of the vinylphosphonium salt **3** and dimethylformamide to the salt **2** resulted in the formation of the highly colored ylide **4**. Stirring at room temperature and, in some cases, with heating

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