[a] s = strong; m = medium; w = weak; vw = very weak. [b] The method of preparation has been indicated in this column for those samples the synthesis of which has not been described in the preceding article[2] or where several methods were used. [c] Sample 2b was made from 12b and hydrazine, and had an identical spectrum to that of 2a. [d] A. F. Holleman, *Ber.*, **21**, 2840 (1888). [e] Sample 12b was made from dibenzoylfuroxan and fuming nitric acid in sulfuric acid, and showed an identical spectrum to that of 12a. [f] Sample 26b (prepared from *m*-nitrobenzhydroxamyl chloride and silver benzoate) and sample 26c (from *m*-nitrobenzhydroxamyl chloride and aqueous potassium hydroxide) showed an identical spectrum to 26a, and were also identified as bis-(*m*-nitrophenyl)-furoxan by mixed melting points (m.p. 184°).

ing the carbonyl frequency, increases the $\mathrm{N}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{O}\end{smallmatrix}$ frequencies.

Experimental

The infrared spectra were obtained with a Perkin–Elmer Model 21 spectrophotometer equipped with a sodium chloride prism. The samples were observed as mulls of the solid in Nujol or, when soluble, as 5% solutions in chloroform using a 0.1 mm. liquid cell. The chloroform solutions were useful in revealing the characteristic furoxan absorption in the 1475–1410 cm.$^{-1}$ region, particularly when no methyl groups were in the sample to interfere.

Table III lists the compounds investigated and the absorption frequencies found in the regions listed as characteristic of the furoxan group. A complete typical spectrum, that of dibenzoylfuroxan, is given in Fig. 1.

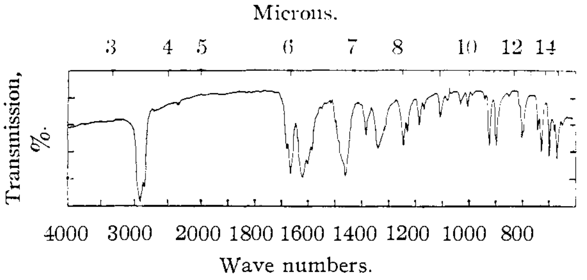


Fig. 1.—The infrared absorption spectrum of dibenzoylfuroxan, in Nujol.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF SWARTHMORE COLLEGE]

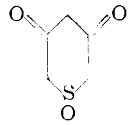
Thiapyran Derivatives. V. The Monosulfinyl and Monosulfonyl Analogs of Phloroglucinol[1]

BY EDWARD A. FEHNEL AND ALBERT P. PAUL

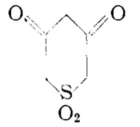
RECEIVED FEBRUARY 11, 1955

Tetrahydrothiapyran-3,5-dione 1-oxide and tetrahydrothiapyran-3,5-dione 1,1-dioxide have been synthesized to test the hypothesis that these compounds might be capable of undergoing a prototropic aromatization analogous to the rearrangement of 1,3,5-cyclohexanetrione to phloroglucinol. A study of the acidity constants and ultraviolet absorption spectra of the products shows that the monoenols and the corresponding enolate anions are the only major species present in aqueous and alcoholic solutions. It is concluded that any conjugative ability possessed by the sulfinyl and sulfonyl functions must be inoperative in these molecules.

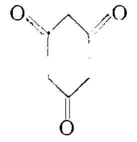
Tetrahydrothiapyran-3,5-dione 1-oxide (I) and tetrahydrothiapyran-3,5-dione 1,1-dioxide (II) may be regarded as the monosulfinyl and monosulfonyl analogs, respectively, of a tricarbonyl compound (1,3,5-cyclohexanetrione, III) which is known to exist predominantly, if not exclusively, in the trienolic form (phloroglucinol, IV). In view of recent results[2] attesting to the conjugative ability of the sulfinyl and sulfonyl groups, it seemed of interest to investigate the possibility that I and II might exist in equilibrium with tautomeric forms (V, VI) analogous to IV. The demonstration of the existence of such forms should provide conclusive evidence of the ability of the sulfinyl and sulfonyl functions to interact with adjacent groups by a resonance mechanism.



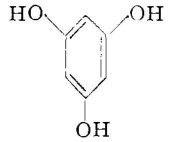
I



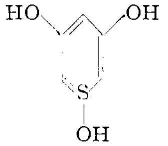
II



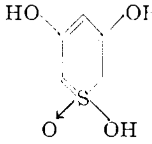
III



IV



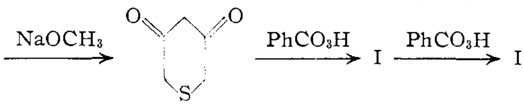
V



VI

To obtain the desired sulfoxide I and sulfone II, tetrahydrothiapyran-3,5-dione (VII) was synthesized and subjected to stepwise oxidation with perbenzoic acid, as shown in the following sequence of reactions

$$\mathrm{CH_3COCH_2Cl + NaSCH_2COOCH_3 \longrightarrow CH_3COCH_2SCH_2COOCH_3}$$



VII

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[1] Based on a thesis submitted by Albert P. Paul in partial fulfillment of the requirements for the M.A. degree, Swarthmore College, 1951. Presented before the Division of Organic Chemistry, 126th Meeting of the American Chemical Society, New York, N. Y., 1954. This investigation was supported in part by a Frederick Gardner Cottrell grant from the Research Corporation.

[2] (a) E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 231 (1949); **72**, 1292 (1950); (b) H. P. Koch, *J. Chem. Soc.*, 408 (1949); (c) D. Barnard, J. M. Fabian and H. P. Koch, *ibid.*, 2442 (1949); (d) R. H. Eastman and R. M. Wagner, THIS JOURNAL, **71**, 4089 (1949); (e) H. H. Szmant and H. J. Planinsek, *ibid.*, **72**, 4042 (1950); (f) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951); (g) E. D. Amstutz, I. M. Hunsberger and J. J. Chessick, THIS JOURNAL, **73**, 1220 (1951); (h) F. G. Bordwell and G. D. Cooper, *ibid.*, **74**, 1058 (1952); (i) H. Kloosterziel and H. J. Backer, *Rec. trav. chim.*, **71**, 295 (1952); **72**, 655 (1953); (j) E. S. Waight, *J. Chem. Soc.*, 2440 (1952); (k) F. G. Bordwell and P. J. Boutan, Abstracts of the 124th Meeting of the American Chemical Society, 1953, p. 80-O; (l) F. G. Bordwell and H. M. Andersen, THIS JOURNAL, **75**, 6019 (1953).

The products thus obtained were examined spectroscopically and acidimetrically for evidence of phenolic character.

Experimental[3]

A. **Preparation of Compounds. Tetrahydrothiapyran-3,5-dione** (VII).—Twenty-three grams (1.0 g. atom) of sodium was dissolved in 400 ml. of absolute methanol and the solution was cooled to 0° under a nitrogen atmosphere. Methyl thioglycolate[4] (106 g., 1.0 mole) was added rapidly to the mechanically stirred solution, followed by the gradual addition of 92.5 g. (1.0 mole) of freshly distilled chloroacetone. The resultant mixture was stirred at room temperature for 15 minutes and was then refluxed for another 15 minutes. The precipitate of sodium chloride was filtered off, most of the solvent was removed from the filtrate by distillation, and the residual liquid was diluted with 500 ml. of water. After separation of the layers and extraction of the aqueous phase with several small portions of ether, the combined oil layer and ether extracts were washed with dilute aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. The ether was removed and the residual oil was distilled under reduced pressure in a nitrogen atmosphere to give 115 g. (71%) of **methyl acetonylmercaptoacetate** as a colorless oil, b.p. 110–115° at 5 mm. (124–129° at 10 mm.). Redistillation of a portion of this material provided an analytically pure sample with b.p. 143° at 24 mm.

Anal. Calcd. for $C_6H_{10}O_3S$: C, 44.4; H, 6.2. Found: C, 44.5; H, 6.2.

The **semicarbazone** of this ketoester, prepared in the usual way,[5] was obtained in the form of colorless needles, m.p. 124.5–125.5°, after recrystallization from ethyl acetate.

Anal. Calcd. for $C_7H_{13}O_3N_3S$: C, 38.3; H, 6.0. Found: C, 38.7; H, 5.9.

Five-hundred ml. of anhydrous benzene was placed in a one-liter four-necked flask fitted with a mechanical stirrer, a thermometer, a dropping funnel and an attachment for the addition of solid material,[6] and the flask was cooled in an ice-bath. The benzene was stirred vigorously and as soon as the temperature had dropped to 6° the simultaneous addition of 48.6 g. (0.30 mole) of methyl acetonylmercaptoacetate and 0.60 mole of finely powdered sodium methoxide (freshly prepared from 13.8 g. of sodium) was begun and continued at such a rate that the addition of both reagents was completed in 30 minutes. Stirring and cooling were continued for another 30 minutes, and the pasty yellow reaction mixture was then poured into an ice-cold solution of 60 ml. of concd. hydrochloric acid in 400 ml. of water. After vigorous agitation, the layers were separated and the aqueous phase was extracted with fifteen 25-ml. portions of chloroform. The combined benzene and chloroform solutions were dried over anhydrous magnesium sulfate and evaporated to dryness at room temperature under reduced pressure in a nitrogen atmosphere. The yellow-orange crystalline residue was washed several times with small portions of absolute ether and dried *in vacuo* to yield 23.5 g. (60%) of almost colorless crystals which melted at 77–79°. Recrystallization from benzene afforded pure VII in the form of colorless crystals with m.p. 80–81°. This product dissolved in aqueous sodium bicarbonate with effervescence and gave a blood-red color with aqueous ferric chloride.

Anal. Calcd. for $C_5H_6O_2S$: C, 46.1; H, 4.7. Found: C, 45.8; H, 4.4.

Treatment of a solution of 1.30 g. of VII in 12 ml. of 50% ethanol with 0.32 g. of benzaldehyde and 3 drops of piperidine according to the directions given by Horning and Horning[7] for the preparation of methone derivatives of aldehydes yielded 0.95 g. of **4,4′-benzylidenebis-(tetrahydrothiapyran-3,5-dione)** in the form of colorless crystals melting at 205–207° with decomposition.[8] Recrystallization from methanol raised the melting point to 212–213° with decomposition.[8]

Anal. Calcd. for $C_{17}H_{16}O_4S_2$: C, 58.6; H, 4.6. Found: C, 58.9; H, 4.6.

The **enol methyl ether of VII** was prepared by the gradual addition of 50 ml. of an anhydrous ether solution containing *ca.* 1.5 g. (0.035 mole) of diazomethane[9] to a suspension of 3.90 g. (0.030 mole) of VII in 25 ml. of absolute ether at 0–5°. After the evolution of nitrogen had subsided, the clear yellow solution was decanted from a small amount of gummy residue and evaporated to dryness under reduced pressure at room temperature. The greasy yellow crystals thus obtained were recrystallized directly from ligroin (b.p. 60–90°) to yield 2.93 g. (68%) of pale yellow crystals which melted at 63.5–65°. A second recrystallization from ligroin afforded colorless crystals with m.p. 64–65°, $\lambda_{\max}^{EtOH}$ 251 mμ (log ε 4.06). This material gave no color with ferric chloride and was insoluble in aqueous sodium bicarbonate.

Anal. Calcd. for $C_6H_8O_2S$: C, 50.0; H, 5.6. Found: C, 50.3; H, 5.8.

Tetrahydrothiapyran-3,5-dione 1-Oxide (I).—A solution of 18.2 g. (0.14 mole) of VII in 200 ml. of chloroform was cooled to 0° in an ice–salt bath, and 288 ml. of an anhydrous chloroform solution containing 20.7 g. (0.15 mole) of perbenzoic acid[10] was added in small portions with stirring and cooling to keep the temperature at 0–5°. The reaction mixture was allowed to remain in the freezing bath for another 30 minutes, and the precipitated product was then collected, washed with chloroform, and dried *in vacuo* to yield 18.9 g. (93%) of almost colorless microcrystalline powder, which became dark red on heating above 100° and melted with decomposition at 114–116°. Recrystallization from an ethanol–petroleum ether mixture afforded colorless crystals melting at 118–118.5° with decomposition. This product dissolved in aqueous sodium bicarbonate with effervescence and gave a blood-red color with aqueous ferric chloride.

Anal. Calcd. for $C_5H_6O_3S$: C, 41.1; H, 4.1; neut. equiv., 146. Found: C, 41.2; H, 4.4; neut. equiv., 148.

The **enol methyl ether of I** was obtained when a suspension of 4.38 g. (0.030 mole) of I in 25 ml. of absolute ether was treated with 90 ml. of an anhydrous ether solution containing *ca.* 2.8 g. (0.067 mole) of diazomethane[9] and the mixture allowed to stand for 30 minutes with occasional agitation. The solid was then collected, washed with ether, and dried *in vacuo* to give 3.90 g. (81%) of peach-colored powder, which darkened on heating above 90° and melted with decomposition at 120–123°. Treatment of this material with Nuchar and recrystallization from benzene provided almost colorless crystals, m.p. 128–129° with decomposition, $\lambda_{\max}^{EtOH}$ 253 mμ (log ε 4.06). This product gave no color with ferric chloride, failed to evolve carbon dioxide from aqueous sodium bicarbonate, and dissolved in dilute aqueous sodium hydroxide with the appearance of an intense violet color.

Anal. Calcd. for $C_6H_8O_3S$: C, 45.0; H, 5.0. Found: C, 45.4; H, 5.2.

Tetrahydrothiapyran-3,5-dione 1,1-Dioxide (II).—A solution of 2.1 g. (0.015 mole) of freshly prepared perbenzoic acid[10] in 25 ml. of acetone was added to a suspension of 2.19 g. (0.015 mole) of I in 25 ml. of acetone, and the mixture was warmed cautiously in such a manner that the temperature rose gradually to the boiling point over a 15-minute period. Boiling continued spontaneously for several minutes, after which the resultant amber-colored solution was allowed to cool slowly to room temperature over a 30-minute period. Removal of the solvent by distillation under reduced pressure in a nitrogen atmosphere left a brown crystalline residue, which was ground to a powder, washed several times with small portions of absolute ether, and dried *in vacuo* to provide 1.95 g. (80%) of light brown powder, m.p. 172–176° with decomposition (charring begins *ca.* 150°). None of the usual solvents appeared to be suitable for re-

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[3] Microanalyses by the Clark Microanalytical Laboratory, Urbana, Illinois.

[4] Prepared from freshly distilled thioglycolic acid in 74% yield (b.p. 143–146°) according to the directions of B. R. Baker, M. V. Querry, S. R. Safir and S. Bernstein, *J. Org. Chem.*, **12**, 144 (1947).

[5] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 170.

[6] L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, 1941, p. 311.

[7] E. C. Horning and M. G. Horning, *J. Org. Chem.*, **11**, 95 (1946).

[8] When immersed in the m.p. bath at 200°.

[9] F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 166, note 3.

[10] G. Braun, ref. 9, Coll. Vol. I, 2nd ed., p. 431.

crystallization of this product, and further purification was achieved only with some difficulty by careful reprecipitation from hot solutions in anhydrous ethyl acetate by the addition of petroleum ether. An almost colorless product was finally obtained which melted at 184–186° with decomposition, dissolved in aqueous sodium bicarbonate with effervescence, and gave a blood-red color with aqueous ferric chloride.

Anal. Calcd. for $C_5H_6O_4S$: C, 37.0; H, 3.7; neut. equiv., 162. Found: C, 37.3; H, 3.9; neut. equiv., 163.

B. **Acidity Constants.**—Dilute aqueous solutions of the compounds listed in Table I were titrated potentiometrically with 0.1 *N* carbonate-free sodium hydroxide, using a Beckman *p*H meter, model N, equipped with a glass electrode. Titration curves characteristic of moderately strong monobasic acids were obtained with I, II, VII and 5,5-dimethyl-1,3-cyclohexanedione. Phloroglucinol consumed two equivalents of base before an inflection point was reached in its titration curve, indicating the presence of two nearly equally dissociable hydrogen atoms. The apparent dissociation constants of VII, 5,5-dimethyl-1,3-cyclohexanedione, and phloroglucinol were calculated by application of the Henderson equation, $pH = pK_a + \log [c_b/(c - c_b)]$, in which c is the initial concentration of the acid and c_b is the concentration of added base in the half-neutralization region. In order to correct for the appreciable hydrogen ion concentration in partially neutralized solutions of I and II, the more exact equation

$$pH = pK_a + \log [(c_b + c_{H^+})/(c - c_b - c_{H^+})]$$

was employed for the calculation of the dissociation constants of these two compounds. The data and results are summarized in Table I.

TABLE I

ACID DISSOCIATION CONSTANTS

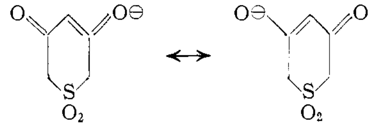
Compound	c (moles/ l.)	c_b (moles/ l.)	pH (obs.)	pK_a (calcd.)
VII	0.0508	0.0229	4.25	4.34
I	.0493	.0279	3.26	3.12
II	.0509	.0250	2.76	2.72
5,5-Dimethyl-1,3-cyclohexanedione[a]	.0485	.0239	5.25	5.26
Phloroglucinol[b]	.0306	.0144	8.49	8.54

[a] G. Schwarzenbach and K. Lutz [*Helv. Chim. Acta*, **23**, 1162 (1940)] give $pK_a = 5.253$. [b] C. T. Abichandani and S. K. K. Jatkar [*J. Indian Inst. Sci.*, **21A**, 417 (1938); *C. A.*, **33**, 3662 (1939)] give $K_1 = 3.56 \times 10^{-9}$ and $K_2 = 1.32 \times 10^{-9}$.

C. **Ultraviolet Absorption Spectra.**—The absorption spectra were determined with a Beckman quartz spectrophotometer, model DU, readings being made at intervals of 5 mμ or less (1 mμ in the vicinity of absorption maxima) with a nominal band width of approximately 1 mμ.

Discussion

From an examination of the pK_a data (Table I) it is apparent that neither the sulfoxide I nor the sulfone II resembles phloroglucinol in acidimetric behavior. Unlike this weakly ionized polyhydric phenol, all three of the heterocyclic β-diketones (I II, VII) obtained in the present investigation are relatively strong monobasic acids, resembling in this respect the alicyclic β-diketones (*e.g.*, 5,5-dimethyl-1,3-cyclohexanedione). Since an endocyclic β-dicarbonyl system appears to be a much more strongly acidic grouping than an endocyclic β-ketosulfonyl system,[11] the dissociable hydrogen atom in the sulfone II is doubtless derived from the β-dicarbonyl portion of the molecule, and the conjugate base may therefore be formulated as a resonating enolate anion (VIII) analogous to the anions formed by alicyclic β-diketones


VIIIa VIIIb

The 400-fold increase in acid strength which occurs when the methylenic function at the 5-position of the alicyclic β-diketone is replaced by a sulfonyl group must then be attributed either to the inductive electron-withdrawing effect of the hetero group, acting through the α-carbon atoms at both ends of the mesomeric keto–enolate system, or to the field effect of the hetero group operating across the ring, or to a combination of both these effects.[12]

Similar structures may be assigned to the anions derived from the sulfoxide I and the sulfide VII. As would be expected on the basis of this interpretation, the observed order of acid strengths in this series of cyclic β-diketones (II > I > VII > 5,5-dimethyl-1,3-cyclohexanedione) parallels the variation in the inductive electron-attracting powers of the thio, sulfinyl, sulfonyl and methylene groups ($SO_2 > SO > S > CR_2$).

The spectroscopic results confirm these conclusions regarding the structure of the anions and, in addition, justify extending the structural analogy between I, II, VII and the alicyclic β-diketones to include their undissociated forms. Thus the ultraviolet absorption spectra (Figs. 1–3) exhibited by I, II and VII in neutral, acidic and basic media do not differ significantly from those exhibited by typical 1,3-cyclohexanediones[13] under similar conditions. In both classes of compounds the most prominent features of the spectra are: (1) in acidic media, a broad absorption band with a maximum between 255 and 265 mμ; (2) in basic media, a broad absorption band with a maximum between 280 and 295 mμ; (3) in neutral media, a concentration-dependent combination of these two limiting bands; and (4) a well-defined isosbestic point in the 265–275 mμ region. As has been pointed out in connection with a spectroscopic study of alicyclic β-diketones,[13] these spectral characteristics indicate the existence of a reversible equilibrium between two chromophoric species, which in the case of the 1,3-cyclohexanediones have been identified as the undissociated monoenol (IX, X = CR_2) and the corresponding enolate anion (X, X = CR_2). It is reasonable to conclude, therefore, that analogous species (IX and X, X = SO, SO_2 and S, respectively)

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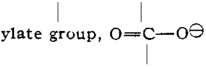
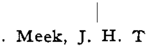
[11] Compare, for example, the relative acid strengths of 5,5-dimethyl-1,3-cyclohexanedione, for which $pK_a = 5.3$, and tetrahydrothiapyran-3-one 1,1-dioxide, the pK_a of which must be greater than 6.5 since it does not liberate carbon dioxide from sodium bicarbonate solution [E. A. Fehnel, THIS JOURNAL, **74**, 1569 (1952)]. NOTE ADDED IN PROOF.—The pK_a of tetrahydrothiapyran-3-one 1,1-dioxide has been determined recently in this Laboratory and found to be 9.03.

[12] Compare the 300-fold increase in acid strength observed when the β-methylene group of butyric acid (pK_a 4.82) is replaced by a sulfonyl group (methylsulfonylacetic acid, pK_a 2.36) [A. Mellander, *Svensk Kem. Tid.*, **46**, 99 (1934); *C. A.*, **28**, 5408 (1934)]. It is interesting to note in this connection that the keto-enolate system,  $O{=}\underset{|}{C}{-}CH{=}\underset{|}{C}{-}O^{\ominus}$, may be regarded as a vinylog of the carboxylate group,  $O{=}\underset{|}{C}{-}O^{\ominus}$.

[13] E. G. Meek, J. H. Turnbull and W. Wilson, *J. Chem. Soc.*, 2891 (1953); E. R. Blout, V. W. Eager and D. G. Silverman, THIS JOURNAL, **68**, 566 (1946).

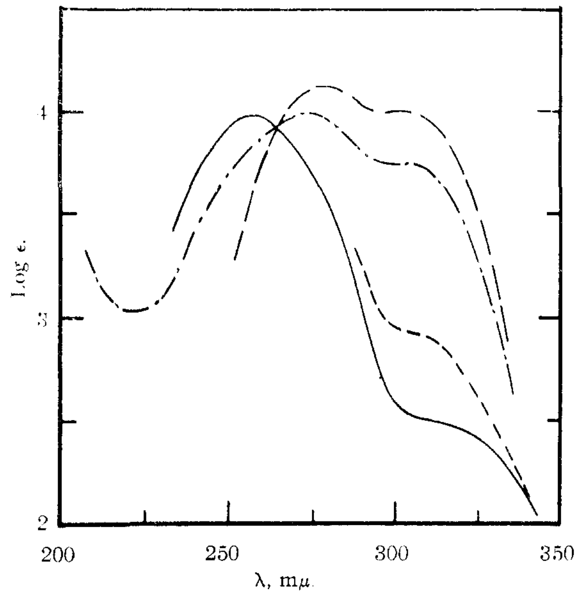


Fig. 1.—Ultraviolet absorption spectra of tetrahydrothiapyran-3,5-dione: in 0.01 *N* ethanolic hydrogen chloride, —; in absolute ethanol ($C = 10^{-3}$ *M*), - - - - -; in absolute ethanol ($C = 10^{-4}$ *M*), —·—; in absolute ethanol ($C = 10^{-5}$ *M*) and in 0.01 *N* ethanolic sodium ethoxide, — — —.

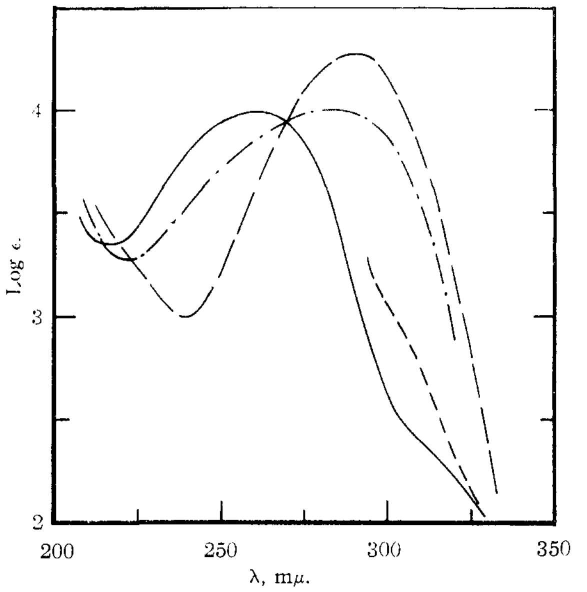


Fig. 2.—Ultraviolet absorption spectra of tetrahydrothiapyran-3,5-dione 1-oxide: in 0.01 *N* ethanolic hydrogen chloride, —; in absolute ethanol ($C = 10^{-3}$ *M*), - - - - -; in absolute ethanol ($C = 10^{-4}$ *M*), —·—; in 0.01 *N* ethanolic sodium ethoxide, — — —.

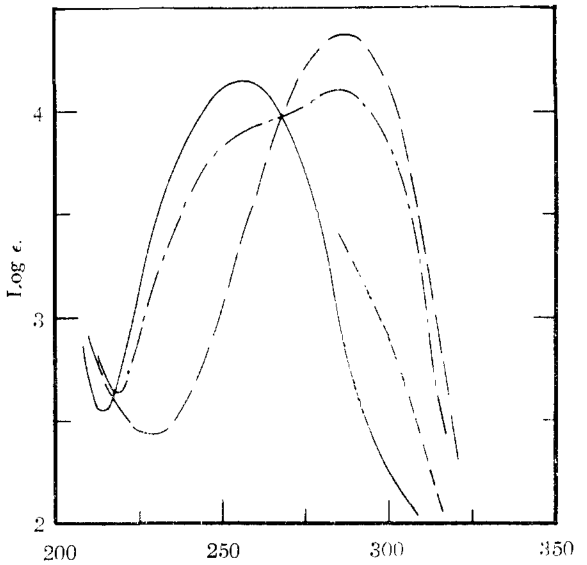
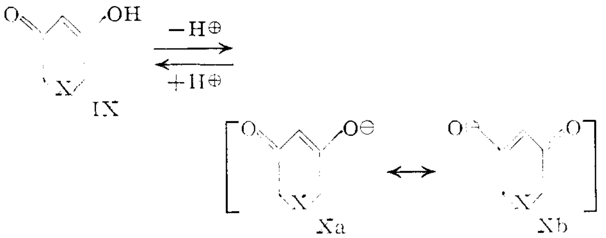


Fig. 3.—Ultraviolet absorption spectra of tetrahydrothiapyran-3,5-dione 1,1-dioxide: in 0.01 *N* ethanolic hydrogen chloride, —; in absolute ethanol ($C = 10^{-3}$ *M*), - - - - -; in absolute ethanol ($C = 10^{-4}$ *M*), —·—; in absolute ethanol ($C = 10^{-5}$ *M*) and in 0.01 *N* ethanolic sodium ethoxide, — — —.

are responsible for the ultraviolet absorption characteristics of I, II and VII.



IX

Xa

Xb

This view is compatible with the observation that both the sulfoxide I and the sulfide VII react readily with diazomethane to give monomethyl derivatives with properties corresponding to those expected for the enol methyl ethers.[14] Thus the non-acidic nature of the products, their failure to give a color with ferric chloride, and the near identity of their spectra with those of the *undissociated* forms of the parent compounds (*i.e.*, I and VII in acidic media, where ionization is suppressed) can be understood only on the basis of their formulation as methyl ethers of the enolic species IX (X = SO or S).

Nothing in the acidimetric or spectroscopic behavior of I, II and VII suggests that enolization proceeds beyond the monoenol stage in any of these compounds. While this result does not necessarily imply that the sulfinyl and sulfonyl groups are intrinsically incapable of participating in prototropic aromatizations of the type postulated, it does support the view that any conjugative ability possessed by these groups must be of a much lower order than that possessed by the carbonyl group. The possibility of producing the desired effect by incorporating the sulfinyl or sulfonyl groups into rings with a potentially greater tendency toward aromatization (as, for example, in the sulfonyl analogs of resorcinol and phenol) remains to be explored, and further work along these lines is now in progress.

SWARTHMORE, PENNA.

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[14] The sulfone II also consumed one equivalent of diazomethane when treated with an excess of this reagent in ether solution, but the only isolable product was a dark-colored resinous solid which resisted all attempts at purification. It is significant to note, however, that this material gave no color with ferric chloride, failed to evolve carbon dioxide from aqueous sodium bicarbonate, and dissolved in aqueous sodium hydroxide with the production of a deep red-violet color.