cis-**2-Hydroxycyclopentylacetic Acid Lactone (IV).**—Rearrangement of 5 g (0.040 mol) of norcamphor oxime yielded (after the usual work-up) 1.40 g (28%) of low boiling [85–87° (2 mm)] material. Judging from the infrared spectrum, this material is nearly pure IV (n^{23}_{D} 1.4747). Further purification by preparative glpc gave a clear colorless liquid, n^{23}_{D} 1.4742 [lit. bp 120–121° (12 mm),[8] n^{25}_{D} 1.4727[14]]. Comparison of the infrared spectrum of the above material with that of an authentic sample[8] showed the materials to be identical.

Registry No.—I, 4576-48-1; III, 16994-00-6; V HCl, 16994-01-7; VI, 279-82-3.

Acknowledgment.—The authors wish to thank the Research Council and the Department of Chemistry of the University of Dayton for partial support of this investigation. The authors are also indebted to Professor P. G. Gassman of The Ohio State University, under whose direction the early part of this study was carried out.

(14) W. E. Noland, J. H. Cooley, and P. A. McVeigh, *J. Amer. Chem. Soc.*, **79**, 2976 (1957).

The Behavior of Thioxanthenol Sulfoxides in Trifluoroacetic Acid and Its Anhydride

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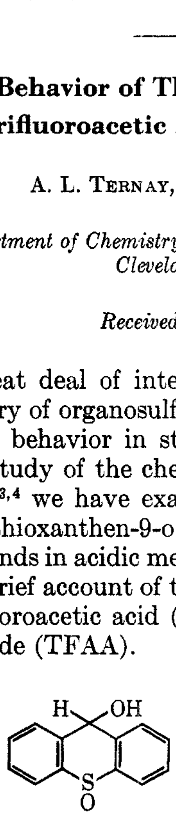
A great deal of interest has been generated in the chemistry of organosulfur compounds and, particularly, in their behavior in strongly acidic media.[2] As part of our study of the chemistry of the thioxanthene ring system,[3,4] we have examined the reactions of the isomeric thioxanthen-9-ol 10-oxides (1)[3,4] and related compounds in acidic media. We would now like to present a brief account of the reactions of these compounds in trifluoroacetic acid (TFA) and in the corresponding anhydride (TFAA).



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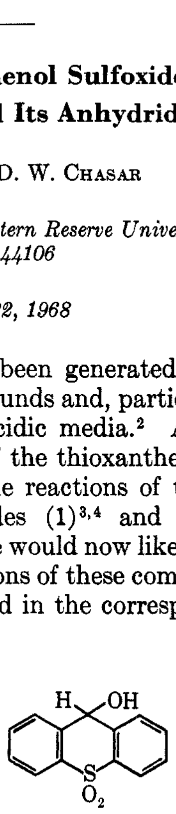

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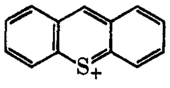
cis and *trans* 1 produce identical nmr spectra in TFA. These spectra consist of singlets at 404 and 396 Hz (relative intensities *ca.* 4:1) and a complex aromatic region. Comparison of these spectra with those of the isomeric acetates of 1[4] ($CDCl_3$ solvent) indicates that these signals represent the *trans* and *cis* trifluoroacetates of 1, the *trans* isomer being present to a larger extent. (The *cis* and *trans* acetates of 1 exhibit methine resonances ($CDCl_3$) at 396 and 412 Hz, respectively.[5]) Thus far we have not been able to isolate and directly characterize any of the trifluoroacetates that will be discussed, apparently because of their rapid hydrolysis. The nmr spectrum of thioxanthen-9-ol 10,10-dioxide (2) in TFA, in addition to a complex aryl multiplet, contains a group of resonances which constitute an "AB quartet" centered at 232 Hz. In deuteriochloroform 5 exhibits an "AB quartet" centered at 238 Hz.

The nmr spectrum of the thioxanthylium ion (3) (perchlorate counterion) in TFA is similar to that of 3 in 96% sulfuric acid.[6] The nmr spectrum of a dilute solution of thioxanthenol (4) in TFA is virtually identical with that of 3. However, more concentrated (*i.e.* near saturation) solutions of 4 in TFA result in a spectrum exhibiting two distinct singlets. One of these (572 Hz) represents the C-9 proton of the thioxanthylium ion while the other signal (395 Hz) is ascribed to the trifluoroacetate of 4.



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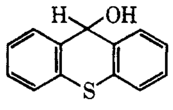

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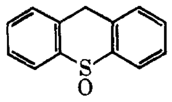

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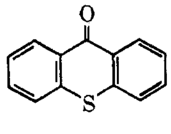

6

Unlike its behavior in 96% sulfuric acid,[7] thioxanthene sulfoxide (5) does not form the thioxanthylium cation (3) in TFA. In this medium the spectrum of 5 contains a group of resonances which constitute an "AB quartet" centered at 238 Hz. In deuteriochloroform 5 exhibits an "AB quartet" centered at 238 Hz.

The behavior of 2 in TFAA is similar to its behavior in TFA. Thus, the spectrum consists of a single resonance at 403 Hz in addition to the signals resulting from the aryl protons. Unlike their behavior in TFA, the stereoisomers of 1 were "dehydrated" to thioxanthone (6) in TFAA. (The base-induced dehydration of 1 to 6 has already been reported.[3b]) This reaction is preceded, however, by the formation of a signal (singlet, 393 Hz) ascribed to the methine proton of one of the corresponding trifluoroacetates (integrated intensity ratio of C-9 H/aryl H 1:8). Both isomers of 1 afforded the same spectrum. Thioxanthene sulfoxide (5) reacts immediately with TFAA to form a red oil which possessed an nmr spectrum (acetonitrile solvent) virtually identical with that of 3. This reaction is similar to that of 5 in 96% sulfuric acid[7] and is presumed to proceed by way of 7.

The nmr spectrum of thioxanthenol (4) in TFAA consists of a singlet (563 Hz) and two regions of complex multiplet absorption (*ca.* 440–490 Hz and *ca.* 400–430

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(1) To whom inquiries should be directed. Support of this research by Public Health Service Grant No. CA-10139 from the National Cancer Institute is gratefully acknowledged.

(2) For a recent review, see H. J. Shine in "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience Publishers, New York, N. Y., 1967, Chapter 6.

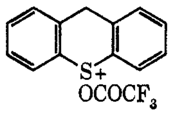
(3) (a) A. L. Ternay, Jr., D. W. Chasar, and M. Sax, *J. Org. Chem.*, **32**, 2465 (1967); (b) A. L. Ternay, Jr., and D. W. Chasar, *ibid.*, **32**, 3814 (1967).

(4) A. L. Ternay, Jr., and D. W. Chasar, *ibid.*, **33**, 2237 (1968).

(5) A referee has suggested that the species observed in solutions of 1 in TFA may actually be the trifluoroacetylsulfoxonium salts of the trifluoroacetates of 1. However, the similarity in the chemical shifts of the methine protons of the isomeric acetates of 1 and the observed resonances in TFA make this unlikely.

(6) H. J. Shine and L. Hughes, *J. Org. Chem.*, **31**, 3142 (1966).

(7) Thioxanthene sulfoxide is converted into the thioxanthylium ion in 96% sulfuric acid.[6]



7

Hz) with integrated intensities of 12:112:50, respectively. The low-field multiplet and the single line are clearly the spectrum of **3** although two "extraneous" singlets occur within the multiplet. The upfield multiplet is assigned to six of the hydrogens of thioxanthone (**6**), the "extraneous" peaks within the multiplet of **3** account for the remaining two protons. Thus 17 (one-third of 50) of the 112 are assignable to **6**. The resulting ratio of integrated intensities (12:95 and 17:50) is consistent with the assigned structures and indicates the ratio of **3** to **6** to be 1.4:1.

The origin of **6** may rest in the disproportionation of **4** to **6** and to thioxanthene (**8**).[8] This is supported by the nmr spectrum of the (red) solution which results when **8** is dissolved in TFAA; the spectrum is that of **3**. No resonance which could be readily assigned to the methine proton of the trifluoroacetate of **4** was observed in solutions of **4** in TFAA.

Shine[6] has suggested that both **4** and **5** would behave in the same manner in 80% sulfuric acid; however, this was not observed in either TFA or TFAA.

Experimental Section

Nmr Spectra.—All of the nmr spectra that have been cited were obtained on a Varian Model A-60 except for those of **4**, **6**, and **8** in TFAA which, for solubility reasons, were obtained on a Varian Model HA-100. Chemical shifts are reported in hertz at 60 MHz downfield from external TMS. Integrated intensities are consistent with the assigned structures. The nmr spectra (deuteriochloroform) of **1**, **2**, and the corresponding acetates have already been discussed.[4]

Compounds.—The preparation and characterization of all of the compounds employed in this study are extant in the literature.[3,4,6]

Reaction of Thioxanthenol Sulfoxide (1) with TFAA.—A mixture (*ca.* 1:1) of *cis* and *trans* **1** (0.116 g) was dissolved in 0.3 ml of TFAA. The resulting solution soon developed a red-brown color and later deposited a white, crystalline solid.[9] After *ca.* 2 hr, signals characteristic of **6** appeared in the nmr spectrum of the solution.[10] After 4 hr the reaction mixture was diluted with water (35 ml). The resulting solid was removed by filtration and dried (*in vacuo*, sodium hydroxide) to afford 0.085 g of a light yellow solid, mp 188–196° (lit.[11] mp 209°). The ir spectrum (Nujol mull) of this material was almost identical with that of authentic **6**. A tlc[12] of this material indicated that it was essentially pure **6** contaminated with a trace of the corresponding sulfoxide. The thioxanthone sulfoxide may arise from oxidation by oxygen.

Registry No.—**1**, 7605-20-1; **2**, 10445-85-9; **3**, 261-32-5; **4**, 6783-74-0; **5**, 10133-81-0; **6**, 492-22-8; **7**, 17203-18-8; trifluoroacetic acid, 76-05-1; trifluoroacetic anhydride, 407-25-0.

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[8] The disproportionation of **4** to **6** and **8** has been suggested.[6] We have observed that vpc of chloroform solutions of **4** may result in the formation of **6** and **8** (unpublished results).

[9] Thioxanthone (**6**) is relatively isoluble in TFAA.

[10] R. H. Martin, N. Defay, F. Geerts-Evrard, P. H. Given, J. R. Jones, and R. W. Wedel, *Tetrahedron*, **21**, 1833 (1965).

[11] E. G. Davis and S. Smiles, *Trans. Chem. Soc.*, **97**, 1290 (1910).

[12] The thin layer chromatography was performed employing a glass plate coated with silica containing a fluorescent indicator. Development was achieved with chloroform while ultraviolet light was used for visualization.

A Route to Tetraacyl-1,3-dithiacyclobutanes from Carbon Suboxide and Sulfur Dichloride

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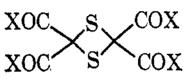
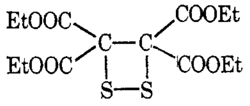
The reaction of carbon suboxide with sulfur dichloride has been found to be a one-step route to the previously unknown 2,2,4,4-tetraacyl-1,3-dithiacyclobutane system. The product, formed from two molecules each of carbon suboxide (C_3O_2) and sulfur dichloride (SCl_2), is the tetraacyl chloride **1**. The direction of addition of the sulfur dichloride, wherein the chlorine adds to the carbonyl carbons, shows that carbon suboxide behaves like ketene in this respect. Ketene has been reported[1] to form thiodiglycolyl chlorides with sulfur dichloride.

Addition of sulfur dichloride to carbon suboxide in a solution of cold ether usually results in the tetraacyl chloride **1** slowly precipitating as orange prisms. Mass spectral analysis shows that the parent ion of **1** has a molecular weight of 340 (theory, 340) and contains four chlorine atoms.[2] The elemental analysis shows the material to be a 2:2 adduct and also shows that no ether was incorporated into the product.

Reaction of the above prisms with ethanol gives a chlorine-free product. The molecular weight and elemental analysis show that this product is also derived from a 2:2 adduct of carbon suboxide and sulfur dichloride and also that it contains four ethyl groups and two sulfur atoms per molecule. The infrared spectrum and nmr spectrum indicate this material to be an ethyl ester and the nmr spectrum shows the four ethyl groups to be in the same environment. These considerations leave only two possible structures, the 1,2- or 1,3-dithiacyclobutane (**4** and **2**, respectively), for these products. Isolation of diethyl malonate upon desulfuration of the ethanol reaction product proves that it is an ester and shows that it possesses the 1,3-dithiacyclobutane structure **2**. Since carbon–carbon cleavage is unlikely under ester formation or the mild conditions of desulfuration, the exclusive formation of diethyl malonate upon desulfuration strongly suggests that the tetraacyl chloride **1** is also a 1,3-dithiacyclobutane. The orange color of the acid chloride, which persists and even intensifies through sublimation and then disappears upon conversion into the ester or amide, is probably due to an intensely colored impurity. Thio ketones, for example, are often highly colored.[3]



1, X = Cl
2, X = OEt
3, X = NEt_2



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[1] D. Harman and C. W. Smith, U. S. Patent 2,514,640 (1950).

[2] J. H. Beynon, "Mass Spectroscopy and its Applications to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960, pp 298–299.

[3] R. Mayer, J. Morgenstern, and J. Fabian, *Angew. Chem. Intern. Ed. Engl.*, **3**, 277 (1964).