

-20° the upfield peak is completely submerged into one of the acid peaks, while the downfield peak has become resolved into a doublet with a 3-Hz coupling constant. The diprotonated species 10 may be inferred from the data.

Experimental Section

Dialkyl hydrazodiformates were prepared from hydrazine hydrate and the appropriate alkyl chloroformates according to the methods of Diels and Paquin⁷ and Dox.⁸ Di-*t*-butyl hydrazo-

(7) O. Diels and M. Paquin, *Ber. Bunsenges, Phys. Chem.* **46**, 2007 (1913).

(8) A. W. Dox, *J. Amer. Chem. Soc.*, **48**, 1951 (1926).

diformate and azodicarbamate were obtained from Aldrich Chemical Co.

Nmr Spectra.—All spectra were obtained using a Varian Associates Model A-56/60A nmr spectrometer equipped with a variable-temperature probe and using external TMS as reference.

Generation of the Diprotonated Species and Their Cleavage.—Samples of the diprotonated species were prepared by dissolving 1.5 ml of $\text{FSO}_3\text{H}-(\text{HF})-\text{SbF}_5$ (1:1 *M* solution) in an equal volume of sulfur dioxide at -78° . The diester (0.3 g) was dissolved in sulfur dioxide at -78° and this solution was added to the acid solution. Cleavage was attempted by warming the diprotonated species until no further reaction occurred.

Acknowledgment.—Support of the work by a grant from the National Institutes of Health is gratefully acknowledged.

Stable Carbonium Ions. XCIII.¹ Protonated Thion Esters and Dithio Esters and Their Cleavage in Fluorosulfuric Acid-Antimony Pentafluoride Solution

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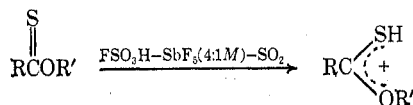
A series of protonated thion esters and dithio esters have been studied in $\text{HSO}_3\text{F}-\text{SbF}_5-\text{SO}_2$ solution. Thio-carbonyl sulfur protonation was observed in both cases at -60° by nmr spectroscopy. Two isomeric species were found for protonated methyl and ethyl thionacetate and protonated methyl dithioacetate at low temperature. Protonated thion esters are quite stable except for isopropyl thionacetate, which cleaved even at -70° . A mechanism for the cleavage reaction is proposed. Protonated *t*-butyl dithio esters underwent alkyl-sulfur cleavage to give protonated dithio acids and *t*-butyl cation.

No investigation of the protonation of thion esters and dithio esters in acid systems was reported so far in the literature. In continuation of previous work relating to the observation of protonated thio carboxylic acids and thio esters,³ we considered it of interest to extend our investigation to the protonation of thion esters and dithio esters in the strong acid system 4:1 *M* $\text{FSO}_3\text{H}-\text{SbF}_5$ solution diluted with SO_2 at low temperature.

Results and Discussion

Protonated Thion Esters.—The following thion esters were protonated in $\text{FSO}_3\text{H}-\text{SbF}_5$ solution diluted with SO_2 at -60° : methyl, ethyl, and isopropyl⁴ thionacetate; methyl and ethyl thionpropionate; and methyl thionbenzoate.

All the thion esters studied were protonated on thiocarbonyl sulfur atom in 4:1 *M* $\text{FSO}_3\text{H}-\text{SbF}_5$ solution diluted with SO_2 and gave well-resolved nmr spectra. As an example, Figure 1 shows the nmr



spectrum of protonated methyl thionacetate. Assignments of the nmr chemical shifts and coupling con-

stants of the thion esters studied are summarized in Table I.

Protonated Thionacetates.—The proton on sulfur of protonated thionacetates (Figure 1, Table I) appeared as a singlet at δ 6.86–7.15, which is at a lower field than in protonated aliphatic thiols and sulfides.⁵ In the SH region, another small quartet appeared at δ 7.00 and 6.76 for protonated methyl and ethyl thionacetate, respectively. Double-irradiation experiments indicated that this SH proton is coupled with the thioacetyl protons. The small doublets for the thioacetyl protons of this minor isomer of both protonated methyl and ethyl thionacetate were also observed (Table I). Such a long-range coupling was also observed in protonated thioacetic acid.³ This indicates that two isomeric species (95:5) are present in both protonated methyl and ethyl thionacetate. Protonated isopropyl thionacetate gave only an SH singlet at δ 6.86.

Protonated Thionpropionates.—Protonated methyl and ethyl thionpropionate (Table I) show the proton on sulfur as a singlet at δ 7.00 and 6.86, respectively. No coupling of this proton with the thioacetyl methyl hydrogens or with the α protons of the alkyl groups was observed.

Protonated Methyl Thionbenzoate.—The proton on sulfur in protonated methyl thionbenzoate appears as a singlet at δ 7.13. Chemical shifts are summarized in Table I.

The Structure of Protonated Thion Esters.—Both protonated methyl and ethyl thionacetate show not only a strong, intense singlet for the SH proton but also give a small quartet in the SH region owing to another

(1) Part XCII: G. A. Olah, C. L. Jeuell, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3961 (1969).

(2) National Institutes of Health Predoctoral Research Investigator.

(3) G. A. Olah, A. T. Ku, and A. M. White, *J. Org. Chem.*, **34**, 1827 (1969).

(4) Protonated isopropyl thionacetate could be observed only below -80° .

(5) G. A. Olah, D. H. O'Brien, and C. U. Pittman, Jr., *J. Amer. Chem. Soc.*, **89**, 2996 (1967).

TABLE I

NMR SPECTRAL PARAMETERS FOR PROTONATED THION ESTERS IN 4:1 M FSO₃H-SbF₅ DILUTED WITH SO₂ AT -60°^a

Compd	Registry no.	SH	H ₁	H ₂	H ₃	H ₄
	22479-55-6	7.15	3.33	4.73		
	22479-55-6	7.00 (q, 1)	3.16 (d, 1)	4.73		
	22479-56-7	6.85	3.13	4.95 (q, 7.0)	1.73 (t, 7.0)	
	22479-56-7	6.76 (q, 1)	2.96 (d, 1)	4.95 (q, 7.0)	1.73 (t, 7.0)	
	22479-57-8	6.86 ^b	3.21 ^b	5.63 ^b (m)	1.78 ^b (d, 7.5)	
	22479-58-9	7.00	3.60 (q, 7.0)	4.86	1.40 (t, 7.0)	
	22479-59-0	6.86	3.55 (q, 7.5)	5.05 (q, 7.5)	1.45 (t)	1.83 (t)
	22479-60-3	7.13	7.76-8.43	5.00		

^a Chemical shifts are in parts per million from external TMS. Multiplicity is indicated as follows: d, doublet; t, triplet; q, quartet; m, multiplet. The coupling constants are indicated in hertz next to the multiplicity. ^b At -80°.

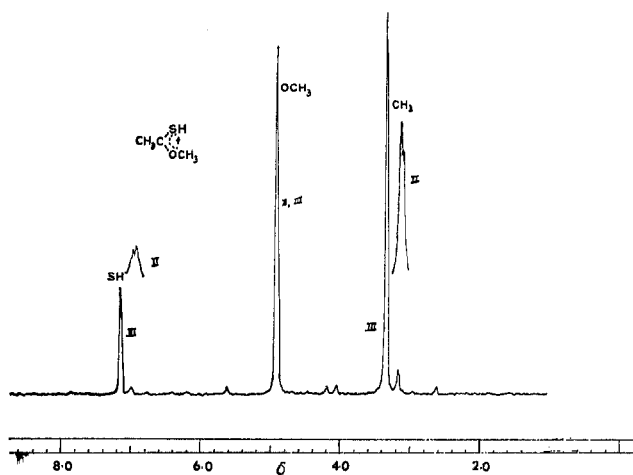
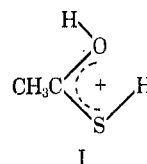
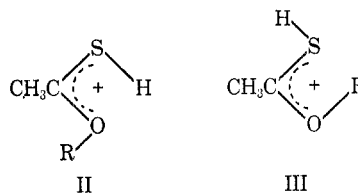


Figure 1.—The nmr spectrum of protonated methyl thionacetate.

isomeric species amounting to about 5%. In this minor isomer the SH proton is coupled with the thioacetyl protons, which appear as doublets at δ 3.16 and 2.96 for protonated methyl and ethyl thionacetate, respectively. Such long-range coupling was also observed in one of the isomers of protonated thioacetic acid in which the SH proton was *trans* to the thio-



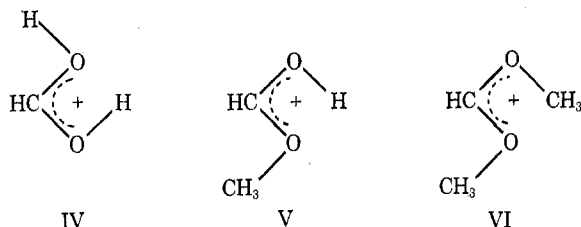
acetyl protons (I). The reason for this assignment was given in our previous paper on protonated thio acids.³ In accordance with the assignment of the structure of protonated thioacetic acid, the SH proton in the minor isomer of both protonated methyl and ethyl thionacetate should have a *trans* relationship with the thioacetyl protons (II, R = CH₃, C₂H₅).



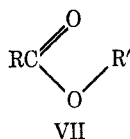
The SH proton of the major isomer of protonated thionacetates consequently should be *cis* to the thioacetyl protons and have structure III.

The orientation of the R group cannot be decided on the basis of the available data. However, it has been

shown⁶ that protonated methyl formates of simple carboxylic acid have two isomeric forms (IV and V), in which the OH proton, the methine proton, and the methyl group are in a *cis,trans* relationship. In addition, the isomer observed for dimethoxy carbonium ion also has the *cis,trans* structure VI.⁷ On the basis



of these observations, the orientation of the group R in protonated thionacetates is suggested to be as shown in II and III. This structural assignment is consistent with the fact that the preferred conformation of esters⁸ is the one in which the alkyl group is coplanar and "cis" to the carbonyl oxygen (VII), thus minimizing the interaction between the lone pairs on oxygen.⁹



Cleavage of Thion Esters.—We have reported previously³ the cleavage action of protonated thionacetates in strong acid media in which acyl-sulfur cleavage was observed for primary and secondary thiol acetates and alkyl-sulfur cleavage was observed for *t*-butyl thiolacetates. Protonated thion esters are, however, quite stable. With the exception of protonated isopropyl thionacetate, all the protonated thion esters studied gave no significant change¹⁰ in $\text{FSO}_3\text{H-SbF}_5$ solution between -60 and 15° . Protonated isopropyl thionacetate, on the other hand, could be observed only below -80° and cleavage occurred even at -75° . At -70° the nmr spectrum (Figure 2) showed the resonances of protonated isopropyl thiolacetate, protonated isopropanethiol, and methyloxocarbenium ion (acetyl cation, $\text{CH}_3\text{C}^+=\text{O}$). We have reported previously³ that protonated isopropyl thiolacetate is stable in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$ solution at -70° . Thus the methyloxocarbenium ion and protonated isopropanethiol formed from protonated isopropyl thionacetate at -70° cannot be due to the cleavage of intermediately formed protonated isopropyl thiolacetate.

A possible mechanism which accounts for the formation of the products in the cleavage reaction involves a

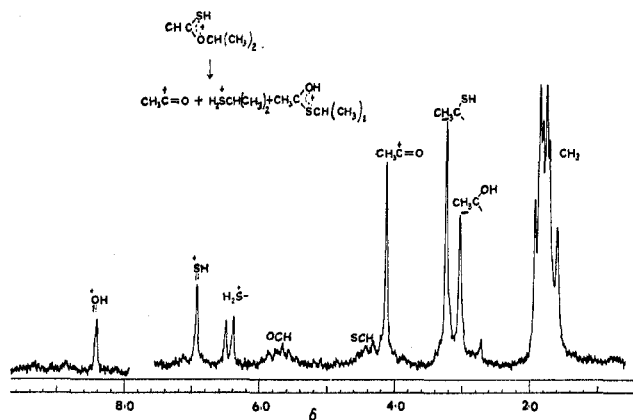
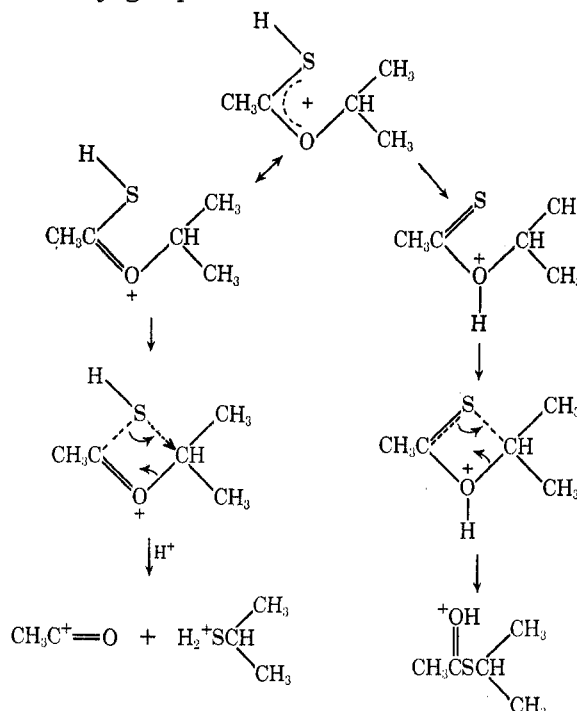
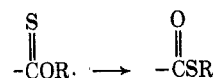


Figure 2.—The nmr spectrum of the cleavage reaction of protonated isopropyl thionacetate.

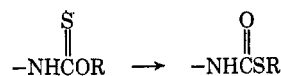
four-membered cyclic transition state formed by nucleophilic attack of the sulfur atom on the α carbon of the alkyl group.



A number of examples of rearrangement reactions of this type are known, which are formally similar to the Schönberg rearrangement¹¹ involving the migration of a group from oxygen to sulfur in the system



These are best known in the thionocarbamate system, the so called Newman-Kwart rearrangement,¹² and involve a change of the type



(6) G. A. Olah, D. H. O'Brien, and A. M. White, *J. Amer. Chem. Soc.*, **89**, 5694 (1967).

(7) A. M. White and G. A. Olah, *ibid.*, **91**, 2943 (1969); R. F. Borsch, *ibid.*, **90**, 5303 (1968).

(8) G. J. Karabatsos, N. Hsi, and C. E. Orzech, Jr., *Tetrahedron Lett.*, **38**, 4639 (1966), and references cited therein.

(9) N. L. Owen and N. Sheppard, *Proc. Chem. Soc. (London)*, 264 (1963).

(10) This reflects the stability of $\text{RC}^+=\text{O}$ relative to $\text{RC}^+=\text{S}$, the latter being the expected result of thioacyl-oxygen cleavage if this were to occur. We have had no evidence for the formation of this ion so far.

(11) H. R. Al-Kazimi, D. S. Tarbell, and D. H. Plant, *J. Amer. Chem. Soc.*, **77**, 2479 (1955); D. H. Powers and D. S. Tarbell, *ibid.*, **78**, 5363 (1956).

(12) M. S. Newman and H. A. Karnes, *J. Org. Chem.*, **31**, 3980 (1966); H. Kwart and E. R. Evans, *ibid.*, **31**, 410 (1966); H. M. Rells and G. Pezzolato, *ibid.*, **33**, 2249 (1968); K. Miyazaki, *Tetrahedron Lett.*, 2793 (1968).

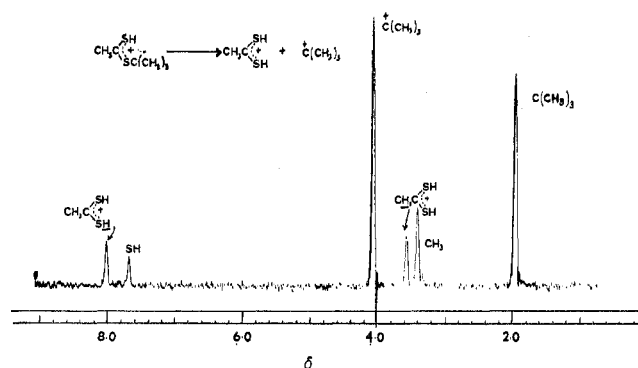
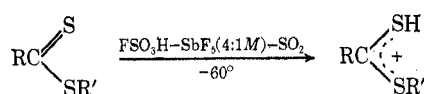
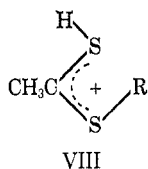


Figure 3.—The nmr spectrum of the cleavage reaction of protonated *t*-butyl dithioacetate.

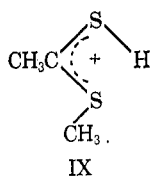
Protonated Dithio Esters.—The following dithio esters were protonated in 4:1 *M* $\text{FSO}_3\text{H-SbF}_5$ solution diluted with SO_2 at -60° : methyl, ethyl, *n*-propyl, isobutyl, and *t*-butyl dithioacetate; *t*-butyl dithio-propionate; and methyl and isopropyl dithiobenzoate. All the dithio esters studied were protonated on the thiocarbonyl sulfur atom and gave well-resolved nmr spectra. The chemical shifts and coupling constants are summarized in Table II.



Protonated dithioacetates (Table II) show the proton on sulfur as a singlet at δ 7.38–7.65. No coupling of this proton with the thioacetyl protons or with the α protons of the alkyl groups was observed. As in the case of protonated thion esters, this SH proton is assigned *cis* to the thioacetyl group. Thus the structure of protonated dithio acetates is VIII.



The reasons for the proposed orientation of the alkyl group are the same as those already discussed in the case of protonated thion esters. At lower temperature, -90° , protonated methyl dithioacetate shows another small quartet due to the SH proton at δ 6.80 with a coupling constant of *ca.* 1 Hz. This indicates the existence of another isomeric species of protonated methyl dithioacetate, in which the SH proton and the thioacetyl group are *trans* to one another. The structure of this second isomer, present in *ca.* 5% amount, probably is as shown in IX.

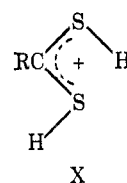


Protonated methyl and isopropyl dithiobenzoate show the proton on sulfur as a singlet (Table II) at δ 7.36 and 7.60, slightly shielded when compared with the proton on sulfur in the corresponding protonated dithioacetates.

Cleavage of Protonated Dithio Esters.—Protonated primary and secondary dithio acetates are very stable. No indication of cleavage was observed even when the solutions were heated up to 100° . Protonated *t*-butyl dithioacetate and dithiopropionate, however, undergo alkyl-sulfur cleavage at -30 to -20° in 4:1 *M* $\text{FSO}_3\text{H-SbF}_5$ solution diluted with SO_2 to give *t*-butyl cation and the corresponding protonated dithio carboxylic acids. As an example, the nmr spectrum of the cleavage reaction of protonated *t*-butyl dithioacetate is shown in Figure 3.

Protonated methyl and isopropyl dithiobenzoate underwent cleavage reaction slowly at room temperature and -20° , respectively, to give as yet unidentified products.

Protonated Dithio Carboxylic Acids.—The nmr chemical shifts of protonated dithioacetic and dithiopropionic acid generated by the cleavage of protonated *t*-butyl dithioacetate and dithiopropionate in 4:1 *M* $\text{FSO}_3\text{H-SbF}_5$ solution diluted with SO_2 are given in Table III. The nmr spectrum of protonated dithioacetic acid (Figure 3) showed only one singlet at δ 8.03 for the SH protons even when the temperature was lowered as low as -100° . Integration of the peaks indicated two protons on sulfur. Protonated dithiopropionate, however, as in the case of the protonated simple carboxylic acids,¹³ showed two singlets at the SH region at δ 7.90 and 7.94. This indicates, as in the case of protonated aliphatic carboxylic acids, that the two protons have nonequivalent environments and is interpreted as a consequence of structure X



being the predominant species. In the case of protonated dithioacetic acid, the two SH protons are probably incidently having the same chemical shift, only one singlet was observed for the SH protons.

Experimental Section

Materials.—The thion esters were prepared by the method described by Renson and Bidaine.¹⁴ The imido ester hydrochlorides were first prepared by the reaction of the appropriate nitriles and alcohols with anhydrous hydrogen chloride in dry hexane as solvent at ice-bath temperature. The imido ester hydrochloride was then treated with hydrogen sulfide in quinoline at 0° to give the corresponding thion ester.

Dithio esters were prepared by the reaction of hydrogen sulfide with thio imido ester hydrochlorides in pyridine. The thio

(13) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **89**, 3591 (1967).

(14) M. Renson and J. Bidaine, *Bull. Soc. Chim. Belges.*, **70**, 519 (1961).

TABLE II

NMR SPECTRAL PARAMETERS FOR PROTONATED DITHIO ESTERS IN 4:1 M FSO₃H-SbF₅ SOLUTION DILUTED WITH SO₂ AT -60°^a

Compd	Registry no.	SH	H ₁	H ₂	H ₃	H ₄
	22479-61-4	7.38	3.10	3.30		
	22479-62-5	7.40	3.35	3.66 (q, 7.5)	1.73 (t, 7.5)	
	22479-63-6	7.65	3.50	3.75 (t, 7.5)	2.21 (m)	1.33 (t, 7.5)
	22528-33-2	7.58	3.43	3.58 (d, 7.0)	2.71 (m)	1.31 (d, 7.0)
	22479-64-7	7.70	3.40	1.96		
	22479-65-8	7.62	3.65 (q, 7.5)	1.63 (t)	1.93	
	22479-66-9	7.36	7.76-8.10	3.33		
	22479-67-0	7.60	8.00-8.33	4.55 (m, 7.0)	1.93 (d, 7.0)	

^a See footnote a, Table I.

TABLE III

NMR SPECTRAL PARAMETERS FOR PROTONATED DITHIO CARBOXYLIC ACIDS IN 4:1 M FSO₃H-SbF₅ SOLUTION DILUTED WITH SO₂ AT -60°^a

Compd	Registry no.	SH	H ₁	H ₂
	22479-68-1	8.03	3.57	
	22479-69-2	7.90 7.94	3.83 (q, 7.5)	1.78 (tq, 7.5)

^a See footnote a, Table I.

imido ester hydrochlorides were prepared by the reaction of the appropriate nitrile and mercaptan and anhydrous hydrogen chloride in petroleum ether.¹⁵

Nmr Spectra.—Varian Associates Model A-56/60A and HA 100 spectrometers with variable-temperature probes were used

for all spectra. Chemical shifts are reported in δ (parts per million) from external (capillary) tetramethylsilane.

Preparation of Solutions.—The procedure used for the preparation of solutions of the protonated thion esters and dithio esters was identical with that described previously.⁶

Acknowledgment.—Support of this work by a grant from the National Institutes of Health is gratefully acknowledged.

(15) (a) C. S. Marvel, P. DeRadzifsky, and J. J. Brader, *J. Amer. Chem. Soc.*, **77**, 5997 (1955). (b) In the preparation of methyl and isopropyl dithiobenzoate, anhydrous ether was used as solvent.