

TABLE I
NMR PARAMETERS OF DIPROTONATED DIALKYL HYDRAZODIFORMATES

R	Registry no.	Temp, °C	CH ₂	α CH ₂	β CH ₂	γ CH ₂	CH	NH	OH	
Methyl	22479-47-6	-20	4.05 (s) ^b					8.25 (br, 3 NH)	10.80	
			4.02 (s)						8.48 (br, 1 NH)	11.20
Ethyl	22479-48-7	-30	1.42 (t, J = 7 Hz)	4.90 (q, J = 7 Hz)				8.62 (br, 3 NH)	10.90 (s, 3 OH)	
			1.45 (t, J = 7 Hz)	4.93 (q, J = 7 Hz)					8.87 (br, 1 NH)	11.02 (d, J = 2 Hz 1 OH)
n-Propyl	22479-49-8	-20	0.72 (t, J = 7 Hz)	4.67 (m)	1.70 (m)			8.48 (br)	11.01	
Isopropyl	22479-50-1	-60	1.12 (d, J = 7 Hz)				5.30 (m)	8.32 (br, 3 NH)	11.08 (s)	
									8.55 (br, 1 NH)	11.37 (s)
n-Butyl	22479-51-2	-50	0.67 (t, J = 6 Hz)	4.67 (m)	1.57	1.17 (m)		8.60 (br)	11.00 (s)	
Isobutyl	22479-52-3	-60					1.97 (m)		11.13 (s)	
			0.73 (d, J = 6 Hz)	4.47 (m)					8.85 (br)	11.25 (s)
										11.40 (s)
t-Butyl ^c	22479-53-4	-60	3.68 [s, (Me ₃ C) ⁺]					8.72 (br)	11.09 (s)	
Azodicarbonamide	22479-54-5	-80							11.33 (s)	
			-20						8.93 (br)	11.43 (s)
									11.58 (s)	
								8.90 (br)	11.47 (d, J = 3 Hz)	
								10.62 (br)	11.75 (br)	
									11.63 (d, J = 3 Hz)	

^a From external capillary of tetramethylsilane. ^b Letters in parenthesis represent multiplicity of peaks: s, singlet; d, doublet; t, triplet; q, quartet; br, broad. ^c Even at the lowest temperature studied, only the cleavage products were observed.

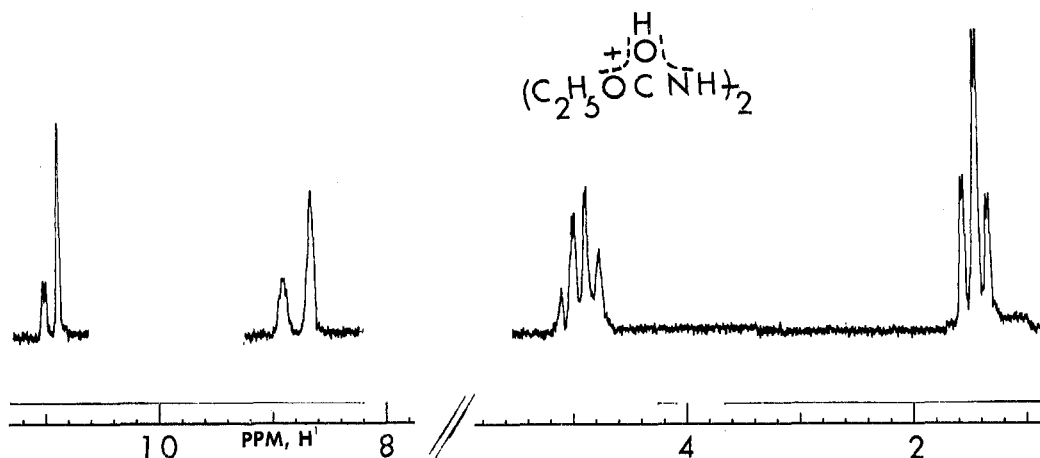
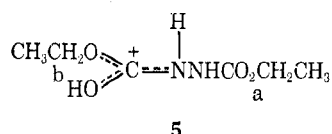
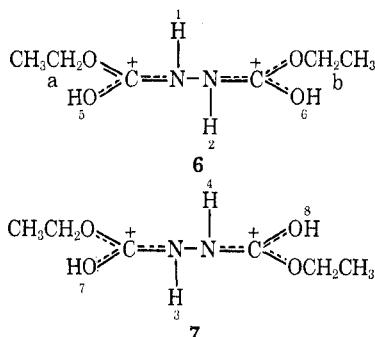


Figure 1.—Pmr spectrum of diprotonated diethyl hydrazodiformate.

both the methyl and methylene groups. Another possibility would be the presence of both di- (4) and monoprotonated (5) species in the solution. We



feel that this alternative can be disregarded, one would expect $\delta(\text{CH}_{2a}) - \delta(\text{CH}_{2b})$ to be much greater than the 2-Hz difference observed. The explanation favored is that partial multiple bond formation between carbon and nitrogen in the diprotonated species 4 leads to rotation about the C-N σ bond sufficiently hindered on the nmr time scale at low temperature to permit the observation of *cis* and *trans* isomers, 6 and 7. From the structural formulas, it can be seen that, if the rotational conformers 6 and 7 can be frozen out at low temperature, then in the *ci* sconformer (6) CH_{2a} is magnetically non-equivalent with CH_{2b} . The methylene group labeled CH_{2b} is *cis* to the NH proton, H_1 , whereas CH_{2b} is *trans* to H_2 .

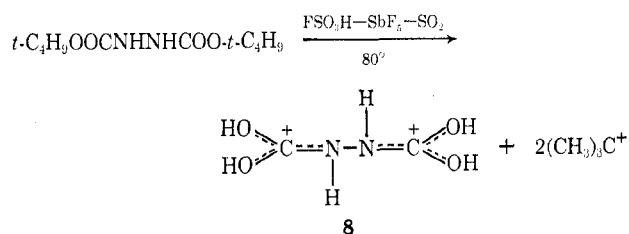


If the diprotonated species exists equally as conformers 6 and 7, then three separate NH resonances should be expected, since $\text{H}_1 \neq \text{H}_2 \neq \text{H}_3 = \text{H}_4$. In fact only NH absorptions are found at δ 8.62 and 8.87 in the area ratio 3:1. This is a reasonable result, since the difference between H_2 and H_3 and/or H_4 is only in the relationship with the oxygen substituents on the carbon at the other end of the molecule. The peak at δ 8.87 (H_1) is somewhat broadened.

As is the case with the NH resonances, there should be three OH resonances ($\text{H}_5 \neq \text{H}_6 \neq \text{H}_7 = \text{H}_8$), but the

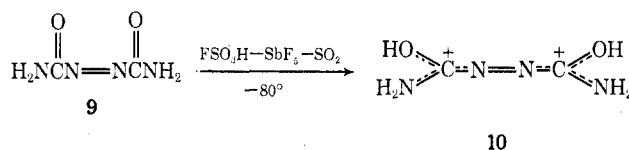
magnetic environment of H_8 is very little different from those of H_7 and H_8 . Indeed a sharp singlet at δ 10.90 (H_6 , H_7 , and H_8) and a doublet ($J = 2$ Hz) at δ 11.02 (H_5) are observed. The doublet presumably arises from coupling of H_5 with H_1 (i.e., $\text{HN}=\text{COH}$ long-range coupling). Table I summarizes the pmr parameters of the diprotonated dialkyl hydrazodiformates investigated.

Di-*t*-butyl hydrazodiformate, when treated in "magic acid" solution, cleaves even at the lowest temperatures attainable to give the *t*-butyl cation and diprotonated hydrazodiformic acid [(+ $\text{H}_2\text{O}_2\text{CNH}$)₂, 8]. The observed enhanced deshielding of the NH and OH protons in 8 compared with those in protonated carbamic acid⁸ ($\text{H}_2\text{N}-\text{CO}_2\text{H}^+$) reflects the dipositive ion nature of 8.



When the di-*n*-butyl- and *sec*-butyl hydrazodiformates were treated with $\text{FSO}_3\text{H-SbF}_5$ solution and then warmed to 20° , they cleaved to give the *t*-butyl cation and diprotonated hydrazodiformic acid. The di-*n*-propyl and diisopropyl derivatives cleave very slowly at 20° , while the diprotonated dimethyl and diethyl hydrazodiformates were stable at 20° . These cleavage results are in good general agreement with the result cited above for the cleavage of protonated alkyl carbamates.

When azodicarbamate 9 was treated in $\text{FSO}_3\text{H-(HF)-SbF}_5\text{-SO}_2$ solution at -78° a clear, brilliant



orange solution was obtained. At -80° , in addition to absorptions attributable to the solvent, only two peaks are seen in the pmr spectrum, a singlet at δ 11.75 (OH) and a broad singlet at δ 10.62 (NH_2). At

-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

GEORGE A. OLAH AND ALICE T. KU²

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received May 5, 1969

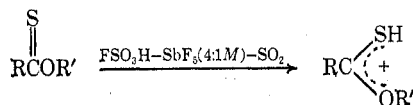
A series of protonated thion esters and dithio esters have been studied in $\text{HSO}_3\text{F}-\text{SbF}_5-\text{SO}_2$ solution. Thio-carbonyl sulfur protonation was observed in both cases at -60° by nmr spectroscopy. Two isomeric species were found for protonated methyl and ethyl thionacetate and 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).