Preparation of Strong Acid Solutions.—Solutions were made up with at least 3 mol of 1:1 FSO₃H-SbF₅ for each site available for protonation in the solute, and the solutions were further diluted with ca. 3 mol of sulfur dioxide for each mol of 1:1 FSO₃H-SbF₅. The aromatic amino acids were diluted in a solution of 9:1 FSO₃H-SbF₅.

Few of the starting compounds investigated dissolved in sulfur dioxide, and the solutions were made up slowly, at low temperature, by vigorous agitation of the suspensions with the acid solusolutions, resulting in homogeneous solutions of the protonated substrates.

The presence of a large excess of acid was ensured by observing the characteristic acid peak at ca. δ 11.

Registry No.—Protonated histidylhistidine, 22493-22-7; protonated triglycine, 22493-23-8.

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Stable Carbonium Ions. LXXXIV.1 Diprotonation of Dialkyl Hydrazodiformates and Their Cleavage to Diprotonated Hydrazodiformic Acid and Alkylcarbonium Ions

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A series of dialkyl hydrazodiformates $[(RO_2CNH)_2]$ has been investigated in $FSO_3H-SbF_5-SO_2$ and $from FF-SbF_5-SO_2$ and $from FF-SbF_5-SO$ SO₂ solution. Carbonyl oxygen protonation was observed in all cases, regardless of substituents, by means of low-temperature pmr spectroscopy. With certain of the diprotonated dialkyl hydrazodiformates, cleavage occurred in the extremely strong acid systems at higher temperatures to give stable alkylcarbonium ions and diprotonated hydrazodiformic acid [(NHCO₂H₂+)₂]. Diprotonation of the related azodicarbonamide in strong acid media was also observed by low-temperature pmr spectroscopy.

In an earlier study we reported the observation of protonated alkyl carbamates.3

$$\begin{array}{c} \begin{array}{c} R \\ R' \end{array} > N - C \stackrel{O}{\longleftarrow} O R \xrightarrow{FSO_{5}H - SbF_{5} - SO_{2}} \\ & \stackrel{R}{\longrightarrow} N - C \stackrel{+}{\longleftarrow} OH \xrightarrow{OH} OH \xrightarrow{A} R > N - C \stackrel{+}{\longleftarrow} OH OH OH \end{array} + R''^{+}$$

R, R' = alkyl or hydrogen; R'' = alkyl

For example, in the pmr spectrum of protonated ethyl N-methyl carbamate, the proton on oxygen appears at δ 9.71 as an overlapping doublet on top of a singlet. The OH proton is expected to show two absorptions owing to cis and trans isomers (1 and 2) if on

the pmr time scale rotation about the C-N bond is slow. That one of the OH resonances is a doublet (J = 2.8)Hz) is presumably due to long-range coupling in 1 with the NH proton.

Olah and Calin³ observed that at temperatures as low as -60° protonated alkyl carbamates undergo alkyloxygen cleavage to give carbonium ions and protonated carbamic acids and that the rate of cleavage is tertiary alkyl carbamates > secondary > primary > methyl.

Dialkyl hydrazodiformates are bisalkyl carbamates. In an extension of our studies of protonation of weak organic bases, we investigated the chemistry of these compounds in superacid media. Protonation of the following dialkyl hydrazodiformates was examined in FSO₃H(HF)-SbF₅-SO₂ solution: dimethyl, diethyl, di-n-propyl, di-n-butyl, and di-isobutyl hydrazodiformate.

As in the case with alkyl carbamates, imides, amides,5 and simple dipeptides,6 protonation in the extremely strong acid media is observed exclusively at the carbonyl oxygen atoms for all dialkyl hydrazodiformates studied. The protonated species give well-resolved low-temperature pmr spectra in the superacid media. The spectral parameters for the diprotonated dialkyl hydrazodiformates are summarized in Table I.

As a representative case, the pmr spectrum of diprotonated diethyl hydrazodiformate (Figure 1) can be compared with that of protonated ethyl carbamate.3 The OH proton of protonated ethyl carbamate (3)

$$\begin{array}{c} H \\ H \\ \hline \\ N \end{array} \begin{array}{c} -C \\ OCH_2CH_3 \end{array}$$

shows a doublet (J = 2 Hz) at δ 9.86 caused by coupling to the protons on nitrogen, which show two broad singlets at δ 7.40 and 7.33. The methyl protons show a triplet at δ 1.60 and the methylene protons show a quartet at & 4.86. In the case of diprotonated diethyl hydrazodiformate (4), the chemical shifts of both the

$$\begin{array}{c|c}
 & \uparrow & \text{OH} \\
 & \downarrow & \text{OCH}_2\text{CH}_3 \\
 & \downarrow & \text{OCH}_2\text{CH}_3
\end{array}$$

NH and OH protons are deshielded by about 1 ppm from those in the carbamate, as would be expected for a doubly charged species such as 4. On closer inspection the spectrum very clearly shows the presence of two virtually identical (\$\Delta\$ ca. 2 Hz) ethyl groups. Second-order splitting is ruled out, as Δ is the same for

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Table I.

NMR PARAMETERS OF DIPROTONATED DIALKYL HYDRAZODIFORMATES

æ	Registry no.	Temp, °C	CH	a CH ₂	в СН2	δ, ppm ^a	СН	HN	НО
Methyl	22479-47-6	-20	$4.05 (s)^b$ 4.02 (s)					8.25 (br, 3 NH) 8.48 (br, 1 NH)	10.80 11.20
Ethyl	22479-48-7	-30	1.42 ($t_p J = 7 Hz$) 1.45 ($t_p J = 7 Hz$)	4.90 (q, $J = 7 \text{ Hz}$) 4.93 (q, $J = 7 \text{ Hz}$)				8.62 (br, 3 NH) 8.87 (br, 1 NH)	10.90 (s, 3 OH) 11.02 (d, J = 2 Hz 1 OH)
$n ext{-Propyl}$	22479-49-8	-20	0.72 (t, J = 7 Hz)	4.67 (m)	1.70 (m)			8.48 (br) 8.73 (br)	11.01
Isopropyl	22479-50-1	09-	1.12 (d, J = 7 Hz)				5.30 (m)	8.32 (br, 3 NH) 8.55 (br, 1 NH)	11.08 (s) 11.37 (s)
n-Butyl	22479-51-2	-50	0.67 (t, J = 6 Hz)	4.67 (m)	1.57	1.17 (m)		8.85 (br)	11.00 (s) 11.13 (s) 11.25 (s) 11.40 (s)
Isobutyl	22479-52-3	09-	$0.73 (\mathrm{d}, J = 6 \mathrm{Hz})$	4.47 (m)			1.97 (m)	8.72 (br) 8.93 (br)	11.09 (s) 11.33 (s) 11.43 (s) 11.58 (s)
t-Butyl ^e Azodicarbonamide	22479-53-4 22479-54-5	- 60 - 80 - 20	3.68 [s, (Me ₃ C) ⁺]					8.90 (br) 10.62 (br)	11.47 (d, $J = 3 \text{ Hz}$) 11.75 (br) 11.63 (d, $J = 3 \text{ Hz}$)

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

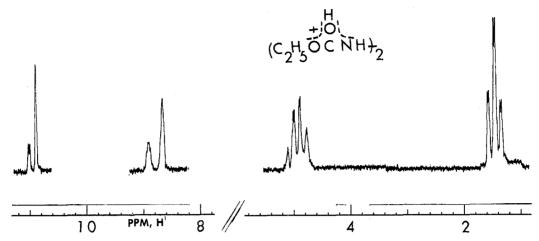


Figure 1.—Pmr spectrum of diprotonated diethyl hydrazodiformate.

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 δ (CH_{2b}) - δ (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 nonequivalent with CH_{2b}. The methylene group labeled CH_{2b} is cis to the NH proton, H₁, whereas CH_{2b} is trans to H₂.

If the diprotonated species exists equally as conformers 6 and 7, then three separate NH resonances should be expected, since $H_1 \neq H_2 \neq H_3 = H_4$. 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 ($H_5 \neq H_6 \neq H_7 = H_8$), but the

magnetic environment of H_6 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.*, HN= $\dot{C}OH$ longrange 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 [(+H₂O₂CNH)₂, 8]. The observed enhanced deshielding of the NH and OH protons in 8 compared with those in protonated carbamic acid³ (H₂N—CO₂H₂+) reflects the dipositive ion nature of 8.

$$t \cdot C_4 H_9 OOCNHNHCOO \cdot t \cdot C_4 H_9 \xrightarrow{FSO_3 H - SbF_5 - SO_2} \\ HO \xrightarrow{\dagger} \begin{array}{c} HO \\ HO \end{array} \xrightarrow{\bullet} \begin{array}{c} HO \\ HO \end{array} \xrightarrow{\bullet} \begin{array}{c} HO \\ H$$

When the di-n-butyl- and sec-butyl hydrazodiformates were treated with FSO₃H–SbF₅ 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 $FSO_3H-(HF)-SbF_5-SO_2$ solution at -78° a clear, brilliant

$$\begin{array}{c|c}
O & O \\
\parallel & \parallel \\
H_2NCN \longrightarrow NCNH_2 & FSO_3H - SbF_5 - SO_2 \\
\hline
9 & HO & C=N \longrightarrow N-C & NH_2
\end{array}$$

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 (NH₂). 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 Paquin and Dox. Di-t-butyl hydrazodiformate 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-temperture 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 $FSO_3H-(HF)-SbF_5$ (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.

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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 HSO₃F-SbF₅-SO₂ solution. Thiocarbonyl 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 $4:1\ M$ FSO₃H-SbF₅ solution diluted with SO₂ at low temperature.

Results and Discussion

Protonated Thion Esters.—The following thion esters were protonated in FSO₃H-SbF₅ 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 FSO₃H-SbF₅ solution diluted with SO₂ 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 constants 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

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⁽⁴⁾ Protonated isopropyl thionacetate could be observed only below