

magnetically nonequivalent. The α -methylene protons appeared as multiplet at δ 5.03, the γ -methylene protons as a triplet at δ 3.48, and the β -methylene protons centered at δ 2.66.

At room temperature, protonated 4-hydroxybutyric acid rearranged slowly to the corresponding protonated γ -butyrolactone **11**. The nmr spectrum of this solution cooled back to -80° showed the $\text{C}=\overset{+}{\text{O}}\text{H}$ proton at δ 12.25 and 12.03 with a relative area ratio of 75:25%, indicating that two isomeric species of protonated lactone **11** are formed. The three methylene groups a, b, and c of the protonated lactone appeared as triplets and quintet at δ 5.45, 3.53, and 2.75, respectively. It is noted that the nmr spectrum showed no $-\overset{+}{\text{O}}\text{H}_2$ absorptions and of course the coupling between $-\overset{+}{\text{O}}\text{H}_2$ and the methylene protons is absent. The nmr spectrum is

identical with that of the protonated authentic γ -butyrolactone.

Experimental Section

Materials.—All hydroxycarboxylic acids used in this study were commercially available materials.

Nmr Spectra.—Varian Associates Model A-56/60A spectrometer with variable temperature probe was used for all spectra.

Preparation of Protonated Hydroxycarboxylic Acids.—The procedure used for the preparation of solutions of protonated hydroxycarboxylic acids was identical with that described previously.¹⁴

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

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

Stable Carbonium Ions. CVIII. Protonated Lactones and Their Cleavage Reactions in Fluorosulfuric Acid–Antimony Pentafluoride Solution¹

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A series of lactones were protonated in fluorosulfuric acid–antimony pentafluoride solution at low temperature. With the exception of protonated δ -valerolactone, α -acetyl- γ -butyrolactone, coumarin, dihydrocoumarin, and 4-hydroxycoumarin, two isomeric species were found for all the protonated lactones studied. Structure assignments for these two isomers are proposed. Protonated lactones in $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$ solution are stable except protonated β -butyrolactone which undergoes alkyl-oxygen cleavage and deprotonation to give protonated crotonic acid at -40° . Protonated α -angelicalactone at -60° undergoes acyl-oxygen cleavage to give the corresponding protonated ketooxocarbonium ion.

In continuation of our preceding study of the protonation of hydroxycarboxylic acids,¹ we felt it of interest to study the protonation and cleavage reactions of lactones in $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$ solution.

Extensive kinetic studies were carried out on the hydrolysis of β -lactones.³ With the exception of Hogeveen's recent report⁴ of the behavior of α, α -dimethyl- β -propiolactone in hydrogen fluoride–boron trifluoride solution, no study of lactones in superacid media has been reported. We wish now to report such a systematic study of the protonation and cleavage reactions of lactones in superacid media.

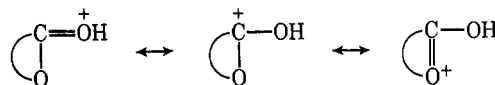
Results and Discussion

In $\text{FSO}_3\text{H}-\text{SbF}_5$ solution diluted with SO_2 generally at -80° , all the lactones studied, *e.g.*, β -propiolactone, β -butyrolactone, γ -butyrolactone, γ -valerolactone, α -bromo- γ -butyrolactone, α -bromo- γ -valerolactone, α -acetyl- γ -butyrolactone, δ -valerolactone, α -angelicalactone, coumarin, dihydrocoumarin, and 4-hydroxy-

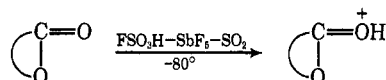
coumarin, were protonated on the carbonyl oxygen atom.

The protonated lactones give well resolved pmr spectra. Assignments of the pmr chemical shifts and coupling constants of the parent and protonated lactones are summarized in Table I.

The proton on oxygen of protonated lactones occurs at lower field than those in protonated alcohols^{5,6} and ethers⁷ but are more shielded than those in protonated aliphatic ketones⁸ and aldehydes,⁹ similar to those in protonated alkylcarboxylic acids¹⁰ and esters.¹¹ This is consistent with the partial double bond character in the protonated lactones.



With the exception of protonated δ -valerolactone, α -acetyl- γ -butyrolactone, coumarin, dihydrocoumarin, and 4-hydroxycoumarin, all the lactones studied gave two low field peaks in the $\text{C}=\overset{+}{\text{O}}\text{H}$ region at low temperature. This indicates the existence of hindered rotation about the C–O bond. In all cases no coupling was



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(1) Part CVII: G. A. Olah and A. T. Ku, *J. Org. Chem.*, **35**, 3913 (1970).

(2) National Institutes of Health Predoctoral Research Investigator, 1970.

(3) For references, see A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1965, Chapter 12.

(4) H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **87**, 1303 (1968).

(5) G. A. Olah and E. Namanworth, *J. Amer. Chem. Soc.*, **88**, 5327 (1966).

(6) G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, **89**, 3576 (1967).

(7) G. A. Olah and D. H. O'Brien, *ibid.*, **89**, 1725 (1967).

(8) G. A. Olah, M. Calin, and D. H. O'Brien, *ibid.*, **89**, 3586 (1967).

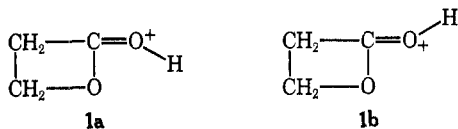
(9) G. A. Olah, D. H. O'Brien, and M. Calin, *ibid.*, **89**, 3582 (1967).

(10) G. A. Olah and A. M. White, *ibid.*, **89**, 3591 (1967).

(11) G. A. Olah, D. H. O'Brien, and A. M. White, *ibid.*, **89**, 5694 (1967).

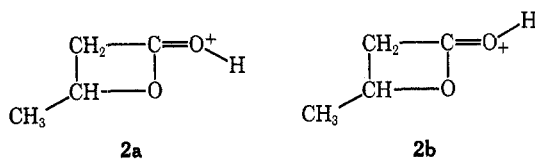
observed between the proton on oxygen and the α -alkyl protons. At higher temperatures, in some of the cases, only the major $\text{C}=\text{O}^+\text{H}$ resonance is observed.

Protonated β -propiolactone in 1:1 $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$ solution at -80° showed two low field absorptions in the $\text{C}=\text{O}^+\text{H}$ region at δ 14.2 and 14.4 with relative area ratio of 60:40, respectively, indicating that two isomeric species (1a and 1b) are present. The two



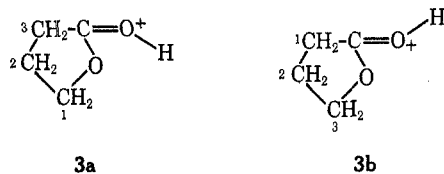
methylene groups appeared as broad peaks at δ 5.50 and 4.13. At higher temperatures, such as -40° , the lower field $\text{C}=\text{O}^+\text{H}$ peak begins to broaden, owing to exchange with the acid solvent system, and finally disappears. At -20° , the methylene protons appear as two well resolved triplets with a coupling constant of 6.0 Hz.

The pmr spectrum of protonated β -butyrolactone in $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$ solution, recorded at -60° , showed the $\text{C}=\text{O}^+\text{H}$ proton as two singlets at δ 12.9 and 13.0 with relative area ratio of 52:48, indicating two forms (2a and 2b) are present. It should be noted that the

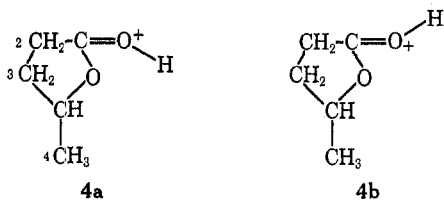


relative area ratio of the higher field $\text{C}=\text{O}^+\text{H}$ resonance with the lower field one is less than that of protonated β -propiolactone. The methylene doublet of protonated β -butyrolactone appears at δ 3.51, methine multiplet at δ 5.66, and the methyl doublet at δ 1.75.

Protonated γ -butyrolactone, 3a and 3b, in the same solvent system at -80° , showed the proton on oxygen as two singlets with relative area ratio of 75:25 at δ 12.30 and 12.51. The resonance at δ 12.51 begins to broaden as temperature increases, and at -60° only the major resonance at δ 12.30 is observed. The α - and γ -methylene triplets appear at δ 3.60 and 5.50, respectively, and the β -methylene protons appear as quintet at δ 2.80.

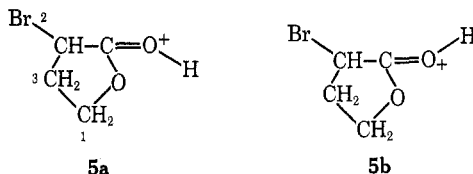


The nmr spectrum of protonated γ -valerolactone, 4a and 4b, at -80° showed the two $\text{C}=\text{O}^+\text{H}$ resonances

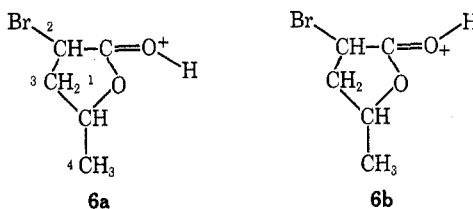


at δ 11.8 and 12.1 with relative area ratio of 75:25. At -70° only the singlet at δ 11.8 is observed. The chemical shifts and coupling constants of the alkyl protons are summarized in Table I.

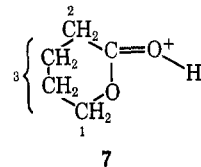
Protonated α -bromo- γ -butyrolactone (5a and 5b) at -60° showed the $\text{C}=\text{O}^+\text{H}$ proton at δ 12.93 and 13.2 with a relative area ratio of 85:15 which is larger than that of protonated γ -butyrolactone. The two $\text{C}=\text{O}^+\text{H}$ singlets are temperature independent and could be seen even at a temperature as high as -40° , indicating that proton exchange remained slow.



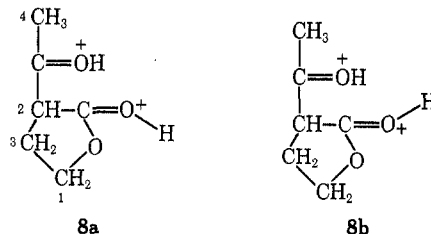
Again two forms (6a and 6b) are observed for protonated α -bromo- γ -valerolactone with relative ratio of 65:35 at δ 12.5 and 12.65, respectively. The isomer ratio is lower than that of protonated α -bromo- γ -butyrolactone, and the $\text{C}=\text{O}^+\text{H}$ resonances are also sharp singlets even at a temperature as high as -40° .



The nmr spectrum of protonated δ -valerolactone (7) at -70° gave only one singlet for the $\text{C}=\text{O}^+\text{H}$ proton at 11.3. No other $\text{C}=\text{O}^+\text{H}$ resonance could be observed even when the temperature of the solution was lowered to -100° . This indicates that only one protonated form was observed.

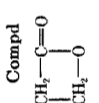
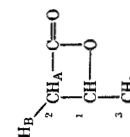
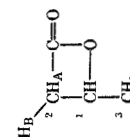
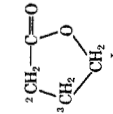
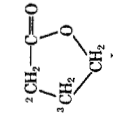
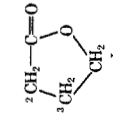
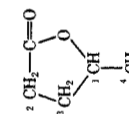
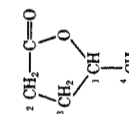
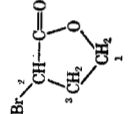
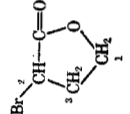
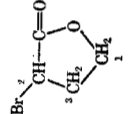
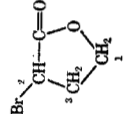


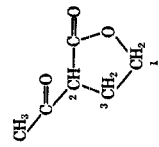
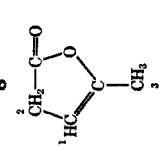
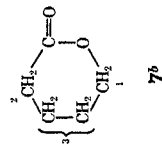
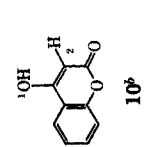
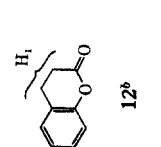
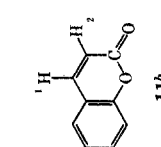
α -Acetyl- γ -butyrolactone in $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$ solution is diprotonated (8a). The pmr spectrum recorded



at -90° showed two sharp singlets at δ 16.6 and 14.03 which are assigned to the protons on the acetyl oxygen and the lactone carbonyl oxygen, respectively. No coupling was observed between the proton on oxygen and the α protons.

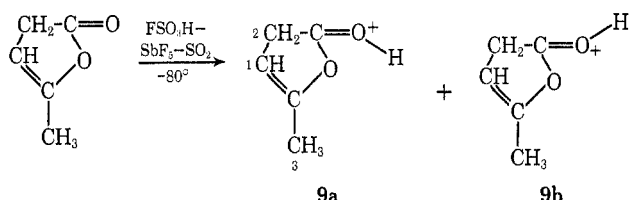
TABLE I
 PMR SPECTRAL PARAMETERS^a OF PARENT AND PROTONATED LACTONES

Compd	Registry no.	Solvent	°C	C=OH ⁺	H ₁	H ₂	H ₃	H ₄	Aromatic H
	57-57-8	SO ₂	-60		4.20 (t, 5.7)	3.40 (t, 5.7)			
	25966-30-7	FSO ₃ H-SbF ₅ , SO ₂	-80	14.4 14.2	5.50 (t, 6.0)	4.13 (t, 6.0)			
	3068-88-0	SO ₂	-60		4.61 (m)	HA 3.40 (q) HB 2.86 (q) J _{AB} = 17.0 J _{AC} = 6.0 J _{BC} = 4.8 3.51	1.31 (d, 6.1)		
	25966-32-9	FSO ₃ H-SbF ₅ , SO ₂	-60	13.0 12.9	5.66 (m)		1.75 (d, 6.2)		
	96-48-0	SO ₂	-60		4.20 (t, 7.0)	2.25 (m)	2.13 (t, 7.0)		
	25966-34-1	FSO ₃ H-SbF ₅ , SO ₂	-80	12.51 12.30	5.50 (t, 8.0)	3.60 (t, 8.0)	2.80 (qt, 8.0)		
	108-29-2	SO ₂	-70		4.60 (m)	2.31 (m)	1.93 (m)	1.21 (d, 6.2)	
	25966-36-3	FSO ₃ H-SbF ₅ , SO ₂	-80	12.1 11.8	5.95 (m)	3.58 (m)	2.66 (m)	1.65 (d, 6.2)	
	5061-21-2	SO ₂	-60		4.30 (m)	4.26 (m)	2.45 (m)		
	25966-38-5	FSO ₃ H-SbF ₅	-60	12.9 13.2	5.88 (m)	5.63 (m)	3.50 (m)		
	25966-39-6	SO ₂	-60		4.81 (m)	4.50 (m)	2.50 (m)	1.40 (d, 6.0)	
	25966-40-9	FSO ₃ H-SbF ₅ , SO ₂	-70	12.65 12.5	6.06 (m)	5.43 (m)	3.03 (m)	1.86 (d, 6.2)	

	517-23-7	SO ₂	-60	16.3 14.3	4.13 (t, 7.2)	3.60 (q, J _{AC} = 9.5) J _{BC} = 8.0)	2.23 (m)	2.10 (s)
8^a	26039-35-0	FSO ₃ H-SbF ₅ , SO ₂	-70	16.3 14.3	5.65 (m)	5.65 (m)	3.60 (m)	3.65 (s)
	591-12-8	SO ₂	-50		5.05 (m)	2.86 (m)	1.78 (m)	
9^b	25966-43-2	FSO ₃ H-SbF ₅ , SO ₂	-80	12.9 12.6	6.01 (m)	4.23 (m)	2.28 (m)	
	542-28-9	SO ₂	-60		4.15 (m)	2.31 (m)	1.66 (m)	
7^b	25966-45-4	FSO ₃ H-SbF ₅ , SO ₂	-70	11.3	5.20 (t, 5.0)	3.19 (t, 5.0)	2.15 (m)	
	91-64-5	SO ₂	-40		7.65 (d, 9.5)	6.15 (d, 9.5)		7.0-7.5
10^b	25966-47-6	FSO ₃ H-SbF ₅ , SO ₂	-70		9.36 (d, 9.2)	7.61 (d, 9.2)		Centered at 8.33
	119-84-6	SO ₂	-60		2.63 (m)			Centered at 7.13
12^b	25966-49-8	FSO ₃ H-SbF ₅ , SO ₂	-80	12.8 (18%) 12.5 (82%)	3.55 (m)			7.47 (s)
	1076-38-6	DMSO-d ₆ CDCl ₃	-40		12.5 (s)	5.70 (s)		7.16-7.96
11^b	25966-51-2	FSO ₃ H-SbF ₅ , SO ₂	-80			6.66 (s)		7.66-8.46

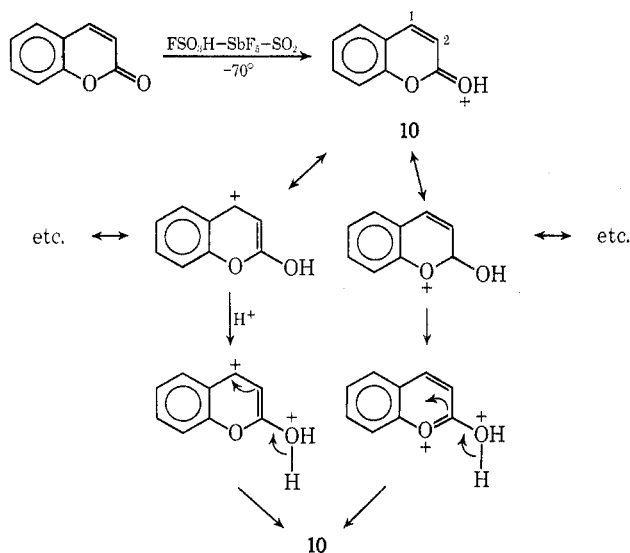
^a Chemical shifts are in parts per million from external TMS. Coupling constants in hertz are given in parenthesis following the multiplicities: d = doublet; t = triplet; q = quartet; m = multiplet; qi = quintet. ^b See text for structure.

Protonated α -angelicalactone (9a and 9b) in $\text{FSO}_3\text{H}-\text{SbF}_5$ solution diluted with SO_2 at -80° gave an nmr spectrum similar to that of the parent compound in SO_2 except it showed additional $\text{C}=\text{OH}^+$ resonances at δ 12.6 and 12.9 (60:40) and the deshielding of the alkyl protons (see Table I). The nmr spectrum also showed additional small resonances at δ 3.53 and 4.80 which can be attributed to the methyl and methylene protons of the cleavage product (see later discussion) and are due to local heating during sample preparation. The in-

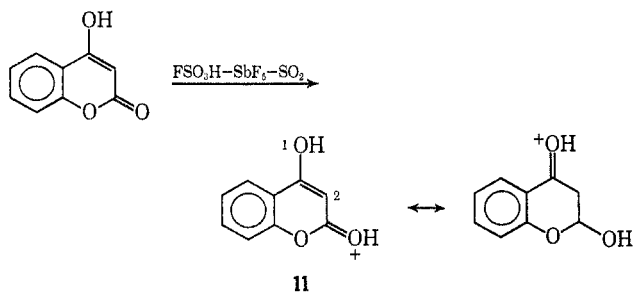


tensities of the resonances of the cleavage product did not increase with time at -80° .

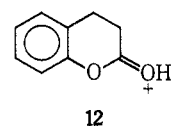
The pmr spectrum of protonated coumarin (10) in $\text{FSO}_3\text{H}-\text{SbF}_5$ solution diluted with SO_2 at -70° showed the two $-\text{CH}=\text{CH}-$ doublets at δ 9.36 ($J = 9.2$ Hz) and 7.63, and the aromatic resonance centered at δ 8.33. The spectrum showed no $\text{C}=\text{OH}^+$ resonance. This is due to the fact that in protonated coumarin the $-\text{OH}$ proton is probably in a keto-enol equilibrating form, and proton exchange occurred.



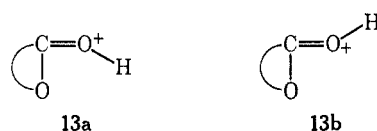
The same reason is suggested for not being able to observe the $\text{C}=\text{OH}^+$ resonance for protonated 4-hydroxy coumarin, 11. Comparison of the chemical shifts of $=\text{CH}$ and the aromatic protons with those of protonated coumarin 10 indicated that 11 probably was only monoprotonated.



Dihydrocoumarin was protonated (12) on the carbonyl oxygen and showed only one $\text{C}=\text{OH}^+$ resonance at δ 12.6 at -60° which is consistent with the observation of protonated δ -valerolactone.

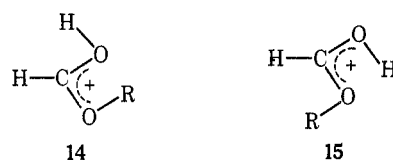


Structure of Protonated Lactones.—Protonated lactones with the exceptions of protonated δ -valerolactone, coumarin, 4-hydroxycoumarin, α -acetyl- γ -butyrolactone, and dihydrocoumarin, all showed two $\text{C}=\text{OH}^+$ resonances. The partial double bond character of the carbon-oxygen bonds and the observation of two OH resonances for the proton on oxygen imply the presence of two isomers (13a and 13b) in protonated lactones.

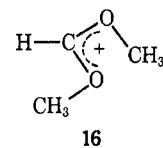


Similar isomers have been observed in the case of other protonated carbonyl compounds.⁸⁻¹¹ No coupling of the proton on oxygen with the α -alkyl protons was observed for protonated lactones. Therefore, no structural assignments could be made on this basis.

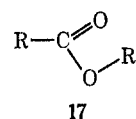
It has been shown, however, that protonated alkyl formates have two isomeric forms (14 and 15)¹¹⁻¹³ in



which the OH proton, the methine proton, and the alkyl group were in a cis-trans relationship. It was also reported¹⁴ that the isomer observed for dimethoxy carbonium ion had the cis-trans structure 16. In addition,



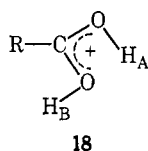
it has been shown that the preferred conformation of esters¹⁵ is the one in which the alkyl group is coplanar and cis to the carbonyl oxygen (17) thus minimizing the interaction between the lone pairs on oxygen.¹⁶



- (12) A. M. White and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2943 (1969).
 (13) H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **86**, 816 (1967).
 (14) R. F. Borsch, *J. Amer. Chem. Soc.*, **90**, 5303 (1968).
 (15) G. J. Karabatsos, N. Asi, and C. E. Orzech, Jr., *Tetrahedron Lett.*, 4639 (1966), and references cited therein.
 (16) N. L. Owen and N. Sheppard, *Proc. Chem. Soc. (London)*, 264 (1963).

In protonated lactones the orientation of the *O*-alkyl group is fixed trans to the OH proton. Thus in order to minimize the lone pair interactions of the two oxygens, the orientation of the C=OH⁺ proton has to be cis to the ether oxygen. Thus we suggest that the predominant species in protonated lactones is that of structure **13a**, in which the C=OH⁺ proton is cis to the ether oxygen. The minor species would then be structure **13b**.

A number of additional facts are consistent with this assignment. The C=OH⁺ absorption of the major isomer of protonated lactones is assumed to be more shielded than that of the minor isomers. This is in agreement with the C¹³ nmr study of protonated carboxylic acids which indicated¹⁷ that proton H_A of **18** has a



more shielded chemical shift than that of H_B. In addition, the inner methyl protons of dimethoxy carbonium ion^{12,14} **16**, and the inner OH proton of protonated alkyl formates **15**, also have more shielded chemical shifts than those of the corresponding outer ones.

Some hydrogen bonding interaction between the OH proton and the neighboring oxygen in spite of the resultant unfavorable four-membered ring is possible and could add to the preponderance of isomer **13a** over **13b**. In addition, if this is the case, the hydrogen bonded proton should be in the shielding zone of the carbonyl.

Hence the C=OH⁺ proton of **13a** should be more shielded than that of **13b**, in agreement with our structural assignment.

It should be noted that the relative isomer ratio of **13a**:**13b** of protonated lactones is found to be increased as the ring size is increased. This is due to the fact that the lone pair interaction of six-membered ring lactones is much larger than that of the four-membered ring lactones. This may be the reason why only one isomer, presumably the major isomer **13a**, is observed for protonated δ -valerolactone and protonated dihydrocoumarin.

Steric effects should also play a role in the isomer distributions of protonated lactones. Substituents at the position α to the carbonyl should tend to increase the amount of the major isomer, while the substituents α to the ether oxygen should decrease the amount of the major isomer. This indeed is in accordance with our observations (see Table II). In the case of protonated α -acetyl- γ -butyrolactone, only one C=OH⁺ resonance for the proton on the lactone carbonyl oxygen was observed, and was assigned to **8a**. It is believed that sterically and electronically isomer **8a** should be favored than **8b**. Thus, the observed data are indeed in accordance with our structural assignment.

Cleavage of Protonated Lactones.—In general, protonated lactones in FSO₃H-SbF₅SO₂ solution are stable. No cleavage was observed for protonated five- and six-membered ring lactones (except protonated

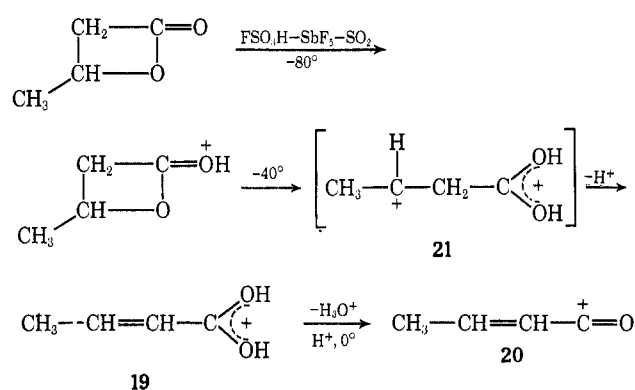
TABLE II
PER CENT ISOMER DISTRIBUTIONS OF PROTONATED LACTONES IN
FSO₃H-SbF₅-SO₂ SOLUTION AT -80°

Compd	% isomer	
	13a	13b
1	60	40
2	52	48
3	75	25
4	75	25
5	85	15
6	65	35
9	60	40
8	100	
7	100	

α -angelicalactone) even when solutions were heated up to +65°.

Protonated β -propiolactone (**1a** and **1b**) in FSO₃H-SbF₅-SO₂ solution, in contrast to Hogeveen's study on α,α -dimethyl- β -propiolactone⁴ and kinetic studies in weaker acidic systems, is stable and the nmr spectrum showed no significant change from -80° to room temperature.

Protonated β -butyrolactone (**2a** and **2b**) is stable up to -50°. At higher temperature cleavage occurred. At 0°, the nmr spectrum showed the absorptions for protonated crotonic acid (**19**) which has been studied previously,¹⁸ and the absorptions for the propenyloxocarbenium ion (**20**). This indicates that alkyl-oxygen cleavage occurred to form the secondary carbonium ion (**21**) which is not stable and is deprotonated to give the protonated crotonic acid (**19**) which in turn undergoes further dehydration to give the corresponding oxocarbenium ion **20**. The nmr spectrum, recorded at 0°,



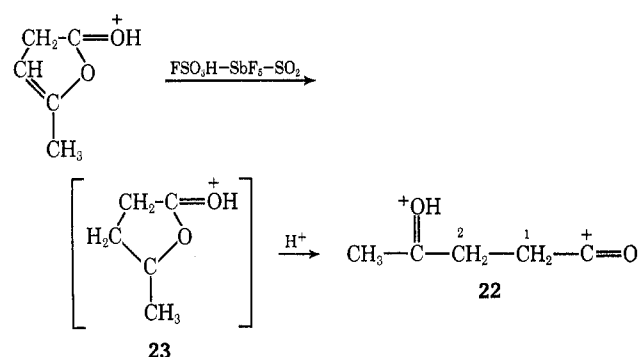
also shows a singlet at δ 9.53 and some multiplets at δ 4.3-5.1 which are not understood at the present time.

Protonated α -angelicalactone in excess FSO₃H-SbF₅ solution at -60° underwent acyl-oxygen cleavage to give the corresponding protonated ketooxocarbenium ion **22**. The nmr spectrum recorded at -60° showed methylene protons at δ 4.80 (broad), the methyl singlet at δ 3.53, and the proton on oxygen at δ 16.2 which is more deshielded than that of protonated simple ketones⁸ and is similar to that of protonated ketooxocarbenium ion studied previously.¹⁹ The two resonances of the two methylene groups (1 and 2) of ion **22** are well separated on a HA 100 nmr spectrum and having chemical shifts of δ 4.96 and 4.71, respectively.

(18) G. A. Olah and M. Calin, *ibid.*, **90**, 405 (1968).

(19) G. A. Olah, A. T. Ku, and J. Sommer, *J. Org. Chem.*, **35**, 2159 (1970).

(17) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **89**, 7072 (1967).



It should be mentioned that ion 22 was not formed by dehydration of protonated acetylpropionic acid which was studied previously.¹⁹ Obviously, the double bond in α -angelicalactone does assist the formation of ion 22. It is possible that the diprotonated species

(23) could be the intermediate for the formation of ion 22. In excess FSO₃H-SbF₅ solution, ion 23 is not observed.

Experimental Section

Materials.—All lactones were commercially available materials. Liquid lactones were redistilled before use.

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

Preparation of Protonated Lactones.—The procedure used for the preparation of solutions of protonated lactones was identical with that described previously.¹¹

Registry No.—Fluorosulfuric acid, 7789-21-1; antimony pentafluoride, 7783-70-2.

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

Stable Carbonium Ions. CIX. Protonation of Hydroxy Ketones in Fluorosulfuric Acid-Antimony Pentafluoride-Sulfur Dioxide Solution and the Study of Hydroxy Ketone-Antimony Pentafluoride Complexes¹

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Protonation of hydroxy ketones was studied in FSO₃H-SbF₅-SO₂ solution. Oxygen diprotonation was observed for all the hydroxy ketones. For comparison, hydroxy ketone-antimony pentafluoride complexes were also studied in sulfuric acid solution.

We have previously reported the observation of protonated ketones,³ ketocarboxylic acids,⁴ hydroxy-carboxylic acids,⁵ and lactones.¹ No investigation relating to protonation of hydroxy ketones has been reported so far in the literature. In continuation of our work of protonation of heteroorganic compounds, we considered it of interest to extend our investigation to the protonation of hydroxy ketones in the fluorosulfuric acid-antimony pentafluoride superacid system.

Results and Discussion

Protonated Hydroxy Ketones.—The pmr parameters of protonated hydroxyketones have been measured in FSO₃H-SbF₅-SO₂ solution at -80°. It was found that 1-hydroxy-2-propanone (acetol, hydroxyacetone), 3-hydroxy-2-butanone (acetoin), 3-hydroxy-3-methyl-2-butanone, and 4-hydroxy-3-methyl-2-butanone are diprotonated in excess 1:1 M FSO₃H-SbF₅ solution diluted with SO₂. In the case of hydroxyacetone the monoprotinated form was also observed. In all cases there is no indication of resolvable fine structure in the OH resonance. The peaks are broad indicating

exchange of the proton on oxygen with the solvent acid system. The pmr parameters of both the parent and the protonated hydroxy ketones are summarized in Table I.

The pmr spectrum of diprotonated hydroxyacetone (acetol, 1) in excess 1:1 FSO₃H-SbF₅-SO₂ solution at -80° showed two low field absorption peaks at δ 12.5 and 16.8 with a relative area ratio of 2:1. These two absorptions are assigned to the proton on the alcohol and ketone oxygen atom, respectively. The protons on oxygen of protonated hydroxyacetone are much more deshielded than those of protonated methanol^{6,7} and acetone.³ The effect of the double positive charge is considered to be responsible for this strong deshielding. The nmr spectrum shows two singlets for the methyl protons at δ 3.88 and 3.63, and two sets of methylene resonance at δ 7.16 and 6.46. The higher field methyl and methylene protons tend to increase with decreasing acid concentration. We consequently assign the lower field methylene (δ 7.16) and methyl (δ 3.88) absorptions to the diprotonated species (1a) and the higher field resonances to the monoprotinated species (1b). The protons on oxygen for 1b are not observed probably owing to proton exchange. The proton on oxygen for 1a could only be observed at temperatures below -80°. At these low temperatures the absorptions are broad and show no resolvable coupling with the α protons. Hence no structural assignment could be made.

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(3) G. A. Olah, M. Calin, and D. H. O'Brien, *J. Amer. Chem. Soc.*, **89**, 3586 (1967).

(4) G. A. Olah, A. T. Ku, and J. Sommer, *J. Org. Chem.*, **35**, 2159 (1970).

(5) G. A. Olah and A. T. Ku, *ibid.*, **35**, 3913 (1970).

(6) G. A. Olah and E. Namanworth, *J. Amer. Chem. Soc.*, **88**, 5327 (1966).

(7) G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, **89**, 3576 (1967).