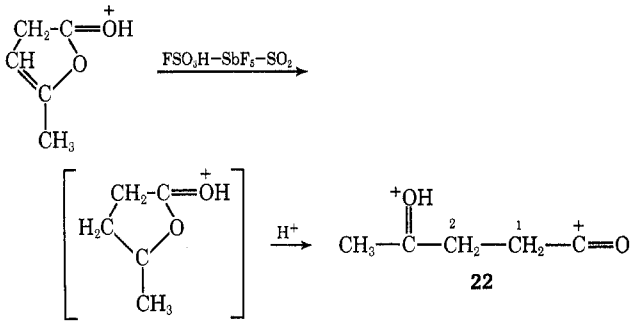

23

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 FSO_3H–SbF_5 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 Complexes[1]

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Protonation of hydroxy ketones was studied in FSO_3H–SbF_5–SO_2 solution. Oxygen diprotonation was observed for all the hydroxy ketones. For comparison, hydroxy ketone–antimony pentafluoride complexes were also studied in sulfuryl chloride fluoride solution.

We have previously reported the observation of protonated ketones,[3] ketocarboxylic acids,[4] hydroxycarboxylic 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 FSO_3H–SbF_5–SO_2 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* FSO_3H–SbF_5 solution diluted with SO_2. In the case of hydroxyacetone the monoprotonated 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 FSO_3H–SbF_5–SO_2 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 monoprotonated 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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(1) Part CVIII: G. A. Olah and A. T. Ku, *J. Org. Chem.*, **35**, 3916 (1970).

(2) National Institutes of Health Predoctoral Research Investigator, 1967–1970.

(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).

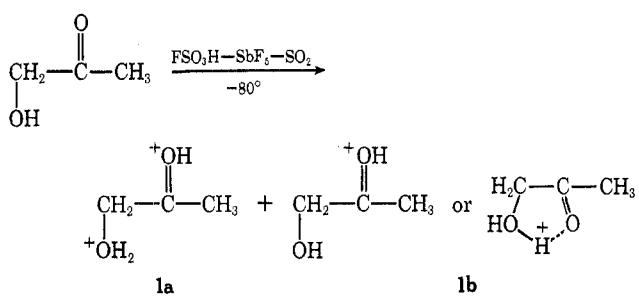
(6) G. A. Olah and E. Namanworth, *J. Amer. Chem. Soc.*, **88**, 5327 (1966).

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

TABLE I
PMR SPECTRAL PARAMETERS[a] OF PARENT AND PROTONATED HYDROXY KETONES

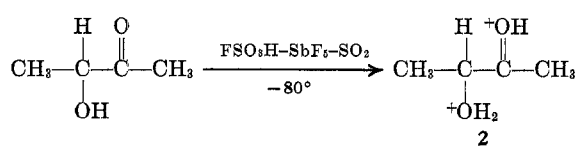
Compd	Registry no.	Solvent	°C	^{+}OH ‖ C	$^{+}OH_2$	OH	H_1	H_2	H_3	H_4
$CH_2(OH)-C(=O)-CH_3$	116-09-6	SO_2	−60			3.58	3.95	1.90		
		$FSO_3H-SbF_5-SO_2$	−80	16.8	12.5		7.16 6.46	3.88 3.63		
$CH_3-CH(OH)-C(=O)-CH_3$	513-86-0	SO_2	−60			4.47	4.11 (q, 7.0)	2.00	1.17 (d, 7.0)	
		FSO_3H-SbF_5	−80	16.87	12.16		6.57	3.50	2.53	
$H_3C-C(CH_3O)(OH)-C(=O)-CH_3$	115-22-0	SO_2	−60			4.00	2.03	1.17		
		$FSO_3-SbF_5-SO_2$	−80	17.03	12.0		3.66	2.20		
$CH_2(OH)-CH(CH_3)-C(=O)-CH_3$	3393-64-4	SO_2	−60			3.50	3.40 (d, 7.0) 3.36 (d, 5.0)	2.58 (m)	1.96	0.83 (d, 7.2)
		$FSO_3H-SbF_5-SO_2$	−50	15.5 (q, 1)	10.6 (t, 3.5)	5.20 (m)	4.26 (m)	3.45 (d, 1)	1.75 (d, 7.2)	

[a] Chemical shifts are in parts per million from external TMS. Coupling constants in hertz are in parenthesis following the multiplicities: d = doublet; t = triplet; q = quartet; m = multiplet.



1a 1b

3-Hydroxy-2-butanone (acetoin) in $FSO_3H-SbF_5-SO_2$ solution is also O-diprotonated **2.** The pmr spectrum of **2** at −80° showed the $^{+}HO{=}C$ proton at δ 16.9 and the $^{+}OH_2$ protons at δ 12.16. At −80°, the resonances are broad. The methyl protons appeared at δ

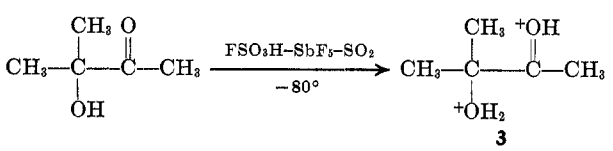


2

2.53, the acetyl methyl protons at δ 3.50, and the methine proton at δ 6.57. As the absorptions of the protons on oxygen are again broad with no resolvable couplings, no structural assignment could be made.

At −40°, protonated acetoin starts to undergo cleavage reactions. The solution gives a complicated nmr spectrum with so far unidentified products.

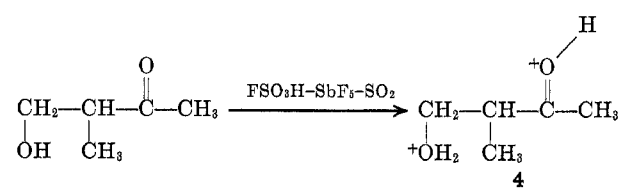
3-Hydroxy-3-methyl-2-butanone in $FSO_3H-SbF_5-SO_2$ is also diprotonated **3.** The proton on the acetyl



3

oxygen appears at δ 17.05. The $-\overset{+}{O}H_2$ protons are not observed in 1:1 *M* $FSO_3H-SbF_5-SO_2$ solution. They are obscured by the acid solvent peak at δ 12.0. However, both the $-C{=}\overset{+}{O}H$ and $\overset{+}{O}H_2$ protons could be observed when the hydroxy ketone is protonated in 4:1 *M* $FSO_3H-SbF_5-SO_2$ solution diluted with SO_2 at −100° and are observed at δ 17.1 and 12.0, respectively. The chemical shifts and coupling constants of the alkyl protons are summarized in Table I. The nmr spectrum of **3** in $FSO_3H-SbF_5-SO_2$ solution showed no significant change from −80 to 0°.

1-Hydroxy-2-methyl-3-butanone is also diprotonated in FSO_3H-SbF_5 solution diluted with SO_2. The nmr

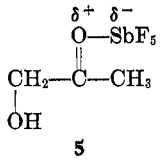


4

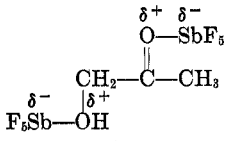
spectrum, recorded at −60°, showed the $\overset{+}{O}H_2$ and $-C{=}\overset{+}{O}H$ proton at δ 10.8 and 15.7, respectively. At higher temperature, such as −50°, the $\overset{+}{O}H_2$ resonance is shown to be a sharp triplet with a coupling constant of 3.5 Hz, and the absorption at δ 15.5 ($^{+}OH{=}C$) is also a well resolved quartet with a coupling constant of about 1 Hz, indicating that this proton is coupled with the acetyl methyl protons. The acetyl methyl absorption at δ 3.46 is accordingly a doublet having a coupling constant of 1 Hz. Comparison of the 1-Hz coupling constant with that of protonated simple ketones[3] indicates that the proton on the keto oxygen and the acetyl methyl group are in a cis relation. Thus protonated 1-hydroxy-2-methyl-3-butanone has the shown structure **4.** Solutions of **4** are stable and the

pmr spectra showed no significant changes up to room temperature.

Hydroxy Ketone–Antimony Pentafluoride Complexes. Nuclear Magnetic Resonance Studies.—The nmr spectrum of **hydroxyacetone** in SbF_5 diluted with SO_2ClF at −60° showed the absorptions for the methyl and methylene protons at δ 3.65 and 6.15, respectively. These absorptions, having a chemical shift close to those of the monoprotonated species **1b**, are assigned to the donor:acceptor complex **5**. The OH proton resonance is not observed and is probably due to the proton exchange. Two very weak absorptions at δ 7.16 and 3.96 with chemical shifts similar to those observed for diprotonated hydroxyacetone **1a** are also observed, and are assigned to the methylene and methyl protons of the dicomplexed species **6**.



5

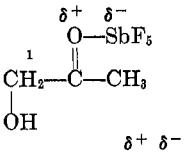
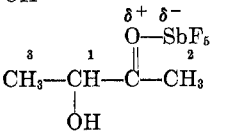
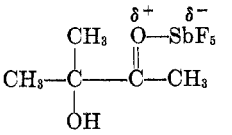
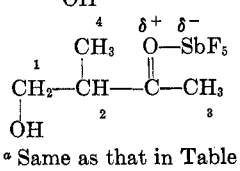


6

Donor:acceptor complexes with antimony pentafluoride are also observed for **3-hydroxy-2-butanone** (acetoin), **3-hydroxy-3-methyl-2-butanone,** and **4-hydroxy-3-methyl-2-butanone** in SO_2ClF solution. The chemical shifts and coupling constants of these hydroxyketone–antimony pentafluoride complexes are summarized in Table II. The pmr spectra showed only the absorptions due to the monodonor:acceptor complexes, with complexing on the carbonyl oxygen atoms.

TABLE II

PMR CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS OF HYDROXY KETONE–ANTIMONY PENTAFLUORIDE COMPLEXES IN SO_2ClF SOLUTION AT −60°

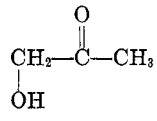
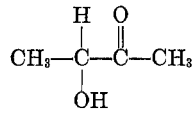
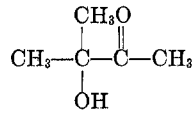
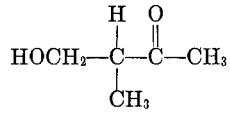
Compd	H_1	H_2	H_3	H_4
	6.15 (s)	3.65 (s)		
	6.16 (m)	3.40 (s)	2.26 (d, 6.0)	
	3.46 (s)	2.40 (s)		
	4.81 (m)	3.93 (m)	3.11 (s)	1.60 (d, 7.0)

[a] Same as that in Table I.

Infrared Spectroscopic Studies.—Solutions of the hydroxy ketone complexes in antimony pentafluoride (with small amount of SO_2ClF) were pressed between Irtran plates, all operations being carried out in a drybox, as the compounds are sensitive to moisture. Infrared spectra were obtained on a Beckman IR-10 infrared spectrophotometer. The main characteristic data obtained are summarized in Table III.

TABLE III

INFRARED C=O STRETCHING FREQUENCIES (CM^{-1}) OF HYDROXY KETONE–ANTIMONY PENTAFLUORIDE COMPLEXES

Compd	$\nu_{C=O}$, hydroxy ketone	$\nu_{C=O}$, hydroxy ketone–SbF_5 complex	$\Delta\nu_{CO}$
	1715	1615	100
	1721	1605	116
	1716	1601	115
	1709	1630	79

All the investigated hydroxy ketone–antimony pentafluoride complexes show significantly shifted carbonyl stretching frequencies at 1601 to 1630 cm^{-1} indicative of donor:acceptor complex nature. Thus the hydroxy ketone–antimony pentafluoride complexes are clearly formed by carbonyl oxygen coordination.

Experimental Section

Materials.—All of the hydroxy ketones used were commercially available.

Nmr Spectra.—A Varian Associates Model A-56/60A spectrometer with variable temperature probe was used for all spectra. Chemical shifts are reported in ppm (δ) from external (capillary) tetramethylsilane.

Preparation of Superacid Solutions.—The procedure used for the preparation of FSO_3H–SbF_5–$SO_2(SO_2ClF)$ solutions of the protonated hydroxy ketones was identical with that described previously.[8]

Solutions of the hydroxy ketone–antimony pentafluoride complexes were obtained by preparing saturated solution of antimony-pentafluoride in sulfuryl chloride fluoride at −20°. Portions (2 ml) of this solution were cooled to −78°, causing some antimony-pentafluoride to crystallize from solution. To this suspension was added dropwise with efficient stirring, approximately 0.3 g of the appropriate hydroxy ketone in ~0.5 ml of sulfuryl chloride fluoride.

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

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