

Stable Carbonium Ions. XLII.^{1a}

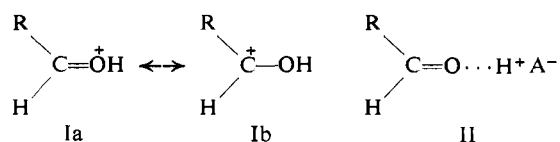
Protonated Aliphatic Aldehydes

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received February 21, 1967

Abstract: A series of protonated aliphatic aldehydes has been studied in $\text{HSO}_3\text{F}-\text{SbF}_5-\text{SO}_2$ solution. O-Protonation was observed at -60° by nmr spectroscopy with negligible exchange rates. Analysis of coupling constants leads to evidence for the structure of protonated aldehydes in solution. Pivaldehyde was found to rearrange to protonated methyl isopropyl ketone in this acid system.

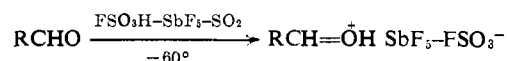
Aliphatic aldehydes are known to form complexes with Lewis and Brønsted acids.² Protonation in acid solutions takes place on the carbonyl oxygen atom (I), or at least a strong donor-acceptor complex II is



formed.³ It has been generally implied that form Ib (e.g., the hydroxycarbonium ion) makes a significant contribution to the protonated species.³ Extensive kinetic and spectral evidence indicates that such species are largely responsible for nucleophilic attack at the carbonyl carbon atom. The structure of protonated aldehydes in solution has not been elucidated. This was the goal of the present investigation.

Results and Discussion

We wish to report the direct observation of protonated aliphatic aldehydes in the extremely strong acid system, $\text{FSO}_3\text{H}-\text{SbF}_5$, using SO_2 as diluent.



Nuclear magnetic resonance observations lead to strong evidence for the structure of the protonated aldehydes in solution.

The protonated aliphatic aldehydes give well-resolved nmr spectra showing very slow exchange rates at -60° . The spectra of protonated aldehydes is characterized by resonances in three distinct regions. The alkyl hydrogens appear at -1 to -3 ppm, the aldehyde hydrogen at about -10 ppm, and the proton on oxygen at -15 to -17 ppm.

In all the samples investigated, the acid was in large excess as indicated by two nmr absorption peaks which can be assigned to the acid system. The more intense of these acid peaks is at -10.9 ppm and, to simplify the spectra, was deleted from Figures 1-6. The other acid peak, of variable intensity, appears at about -10.3

(1) (a) Part XLI: G. A. Olah, J. Sommer, and E. Namanworth, *J. Am. Chem. Soc.*, **89**, 3576 (1967); (b) National Science Foundation Postdoctoral Research Investigator, 1966-1967; (c) National Institutes of Health Postdoctoral Research Investigator, 1966-1967.

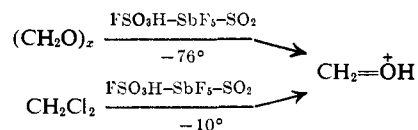
(2) G. A. Olah, Ed., "Friedel-Crafts and Related Reactions," Vol. I, Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1963, p 704.

(3) S. Patai, Ed., "The Chemistry of the Carbonyl Group," Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1966, Chapter 9.

ppm in the region of the aldehyde hydrogen absorption and is shown in Figures 1-6. Assignments of chemical shifts and coupling constants of the investigated protonated aliphatic aldehydes are summarized in Table I.

Proof that the low-field peaks can be assigned to the proton on oxygen and not the aldehyde hydrogen was obtained from experiments using deuterated formaldehyde and acetaldehyde. Protonated formaldehyde- d_2 gives a singlet at -16.75 ppm and no resonance at around -10 ppm. Protonated acetaldehyde- d_4 also gives no resonance around -10 ppm. Protonated ketones also give $=\text{O}^+\text{H}$ resonances from -15 to -16 ppm.⁴ The coupling constants observed are consistent with this assignment. This large deshielding of the proton on oxygen is strong evidence that the positive charge resides primarily on oxygen (Ia) and that contribution from resonance form Ib (hydroxycarbonium ion) is of lesser importance.

Protonated Formaldehyde. Protonated formaldehyde can be generated either by passing formaldehyde from the pyrolysis of paraformaldehyde over a stirred solution of $\text{HSO}_3\text{F}-\text{SbF}_5$ in SO_2 at -76° or by the reaction of methylene chloride with $\text{HSO}_3\text{F}-\text{SbF}_5$ diluted with SO_2 at the boiling point of SO_2 (-10°). The reaction of methylene chloride in the acid system is



not yet well understood. The nmr spectra also show the presence of CH_2F_2 , $\text{CH}_2\text{ClSO}_2\text{F}$, and $\text{CH}_2\text{FSO}_2\text{F}$ formed by halogen exchange and reaction of an intermediate ion (probably the halomethyl cation) with sulfur dioxide. In both cases, an identical nmr spectrum showing an ABX pattern was obtained (Figure 1). It consists of an X portion of four lines centered at -16.73 ppm for the proton on oxygen and an AB portion consisting of a five-line, singlet-quartet pattern centered at -10.10 ppm for the methylene hydrogens III. Solution of this ABX spectrum⁵ using the AB part gives the geminal coupling constant, $J_{2,3} = 22.2$ cps, the *cis* coupling constant, $J_{1,2} = 8.7$ cps, and the *trans* coupling constant, $J_{1,3} = 21.1$ cps. As a check of this calculation, the

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

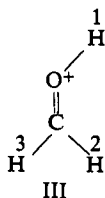
(5) (a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 132; (b) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Resonance Spectroscopy," Vol. I, Pergamon Press Inc., New York, N. Y., 1965, p 357.

Table I. Nmr Chemical Shifts^a (δ , ppm) and Coupling Constants (cps) of Protonated Aldehydes at -60° in $\text{HSO}_3\text{F}-\text{SbF}_5-\text{SO}_2$ Solution

Protonated aldehydes	H ₁ , J _{1,2}	H ₂ , J _{1,3}	H ₃ , J _{2,3}	H ₄		H ₅
				J _{1,4}	J _{2,4}	
	-16.73		-10.18			
	8.7	21.1	22.2			
	-15.11	-10.10			-3.30	
	9.0			<0.3	3.5	
	-15.47	<i>b</i>			-3.33	
	19.5			1.2	...	
	-15.03	-10.15			-3.65	-1.37
	8.8			0.8	<0.3	
	-15.22	-10.25			-3.83	-1.56
	8.8			0.8	<0.3	
	-15.30	-10.17			...	-1.38
	9.0					

^a From external capillary of TMS. ^b Not observed due to solvent acid interference.

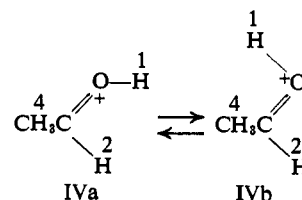
sum of the *cis* and *trans* coupling constants ($J_{1,2} + J_{1,3}$), obtained from the X portion of the spectrum, gave a value of 29.6 cps. The *cis* coupling constant of 8.7 cps and *trans* coupling constant of 21.1 cps are comparable with many analogous olefinic systems.⁶



Protonated Acetaldehyde. The nmr spectrum of protonated acetaldehyde gives a complex pattern (Figure 2). The proton on oxygen gives rise to a doublet centered at -15.11 ppm and a doublet of quartets centered at -15.47 ppm. This clearly indicates the presence of two forms of protonated acetaldehyde, in which the proton is either *cis* (IVa) or *trans* (IVb) to the hydrogen

(6) Reference 5b, Vol. 2, pp 710-749.

on the carbonyl carbon. The isomer ratio is approximately 80% *cis* to 20% *trans* at -60° .



The doublet at -15.11 ppm ($J_{1,2} = 9.0$ cps) can be assigned to IVa and the doublet of quartets at -15.47 ppm ($J_{1,2} = 19.5$ cps) to IVb. These assignments are consistent with those for protonated formaldehyde and with the following observations. In the other aldehydes studied, only the upfield doublet appears even down to -70° . As the steric bulk of the alkyl group increases, it can be assumed that IVa, in which the alkyl group is *trans* to the proton on oxygen, will be favored. Apparently the substitution of methyl for hydrogen in going from acetaldehyde to propional-

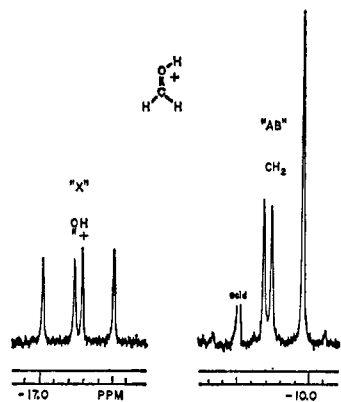


Figure 1.

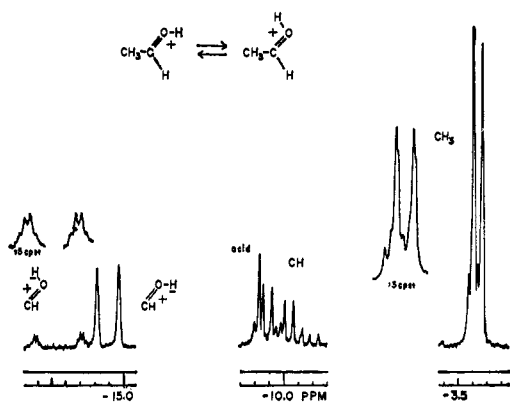


Figure 2.

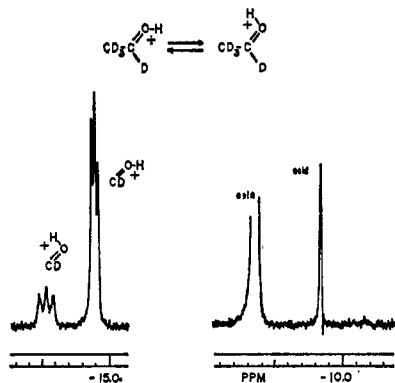


Figure 3.

dehyde is enough to upset this equilibrium in favor of IVa. The downfield position of the proton on oxygen in IVb from IVa (0.36 ppm) may be attributed to deshielding caused by steric repulsion between the methyl hydrogens and the proton on oxygen.

The doublet at -15.47 ppm is clearly further split into a pair of quartets.^{6a} This small but significant

(6a) NOTE ADDED IN PROOF. In a communication just published and unknown to us previously (M. Brookhart, G. C. Levy, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1735 (1967)), the proton on oxygen of the two isomers of protonated acetaldehyde was reported as a pair of doublets, the carbonyl hydrogen as a multiplet, and the methyl groups as a doublet. The proton on oxygen of protonated propionaldehyde was reported as a doublet. We have no explanation for the failure to observe allylic couplings which were observed under similar conditions in our work. We feel that the observation and analysis of the allylic couplings is an essential part of the assignment of isomers unless such assignments are to be based "on an assumed steric preference" only.

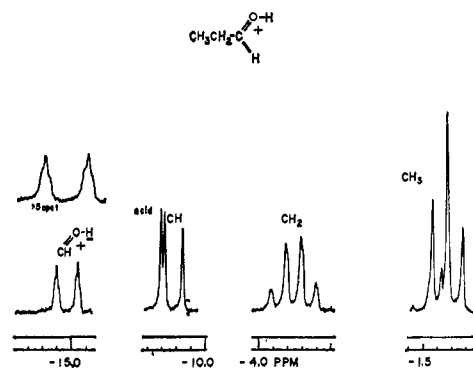


Figure 4.

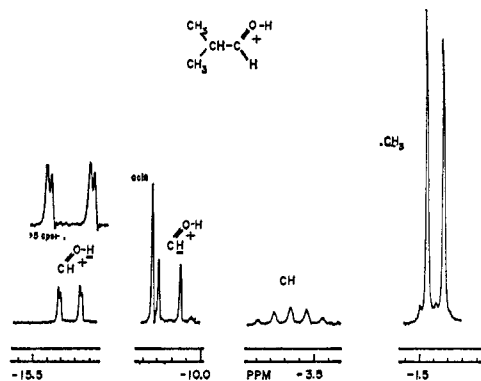


Figure 5.

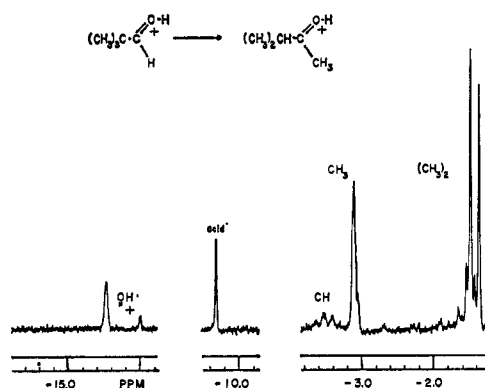


Figure 6.

coupling can be attributed to the *cis* allylic coupling between the proton on oxygen and the methyl hydrogens in IVb ($J_{1,4} = 1.2$ cps). The expected further splitting of the doublet at -15.11 ppm into a pair of quartets by *trans* allylic coupling could not be resolved and is probably about 0.3 cps. The size of *trans* allylic coupling is usually smaller than *cis* allylic coupling in olefinic systems.⁷

The aldehyde proton of protonated acetaldehyde appears as a doublet ($J_{1,2} = 9.0$ cps) of quartets ($J_{2,4} = 3.5$ cps) centered at -10.10 ppm.

An acid peak which can be assigned to the $\text{HSO}_3\text{F}-\text{SbF}_5$ system is found at -10.20 ppm and is indicated in Figure 2.^{7a} The aldehyde proton of IVb was not

(7) S. Sternhall, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(7a) NOTE ADDED IN PROOF. This peak of variable intensity is due to small amounts of water. However, it has not been definitely established

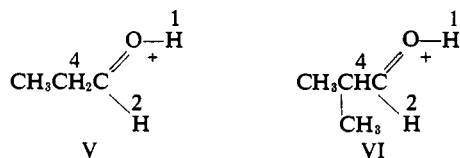
observed, perhaps because of the low concentration of this species and interference of the acid peak.

The methyl hydrogens appear as a pair of doublets at -3.30 ppm. The small doublet, assigned to the methyl group of IVb, is slightly downfield from the large doublet assigned to the methyl group of IVa. The doublet assigned to the methyl group of IVa could be further resolved into a pair of doublets. This gives a value for the *trans* allylic coupling with the proton on oxygen of about 0.3 ppm.

The position of the methyl groups at -3.30 ppm is further evidence for the location of the positive charge in protonated aldehydes. In the methyloxocarbenium ion ($\text{CH}_3\text{C}^+=\text{O}$), in which the positive charge is substantially on the oxocarbon, the methyl hydrogens appear at -4.35 ppm,^{8,9} considerably more deshielded than the hydrogen α to the carbonyl carbon in protonated aldehydes. The spectrum of protonated acetaldehyde- d_4 (Figure 3) proves that the resonances in the -15.0 - to -15.5 -ppm region can be assigned to the proton on oxygen. No resonances appear in the -10.0 -ppm region except those due to the acid. The proton on oxygen appears as a pair of triplets at -15.10 and -15.45 ppm caused by *cis* (IVa, $J_{\text{H-D}} = 1.5$ cps) and *trans* (IVb, $J_{\text{H-D}} = 2.9$ cps) coupling with the carbonyl deuterium.

Protonated Propionaldehyde and Isobutyraldehyde.

The nmr spectra of these protonated aldehydes display the same gross features as that of protonated acetaldehyde (Figures 4 and 5). However, in both cases, no evidence was found for the presence of more than one form. Another significant difference is the absence of further splitting of the carbonyl hydrogen resonances which would be expected to give a doublet of triplets for propionaldehyde and a doublet of doublets for isobutyraldehyde. The olefinic coupling between the proton on oxygen and the aldehyde hydrogen ($J_{1,2}$) is 8.8 cps in both cases, consistent with the *cis* arrangement of these two hydrogens (V and VI). The *trans* allylic



coupling is larger than for acetaldehyde ($J_{1,4} < 0.3$ cps) and shows a pair of triplets for the proton on oxygen of propionaldehyde ($J_{1,4} = 0.8$ cps) and a pair of doublets for isobutyraldehyde ($J_{1,4} = 0.8$ cps).

Although definite conformational assignments cannot be made on the basis of these small couplings, the difference in the *trans* allylic coupling, the coupling between the methyl hydrogens and the aldehyde hydrogen in acetaldehyde, and the lack of any observable coupling between the α -hydrogens and the aldehyde hydrogen in propionaldehyde and isobutyraldehyde are most probably due to different conformations about the α -carbon-carbonyl carbon bond.¹⁰

whether this resonance is due exclusively to H_3O^+ or to an intermediate hydrolysis product of the acid system, $\text{HSO}_3\text{F}-\text{SbF}_5$. The main acid peak at -10.7 ppm was generally deleted from the spectra for simplicity.

(8) G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *J. Am. Chem. Soc.*, **85**, 1328 (1963); G. A. Olah, W. S. Tolgyesi, and E. B. Baker, *ibid.*, **84**, 2733 (1962).

(9) F. P. Boer, *ibid.*, **88**, 1572 (1966).

(10) G. J. Karabatsos and N. Hsi, *ibid.*, **87**, 2864 (1965).

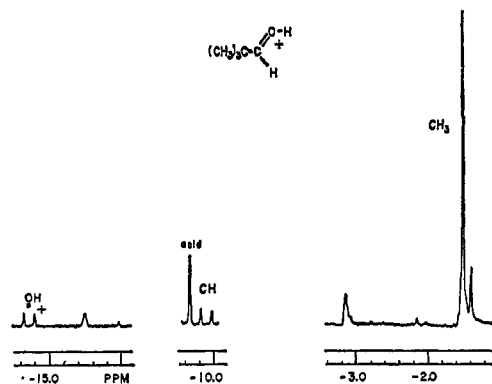
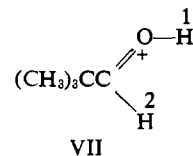
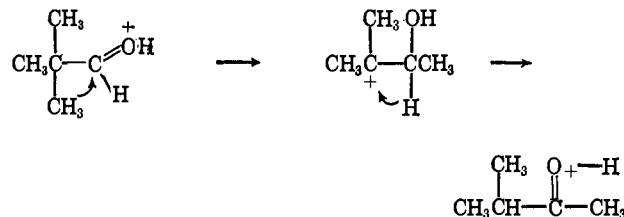


Figure 7.

Pivaldehyde. When the protonation of pivaldehyde was attempted in a solution of $\text{HSO}_3\text{F}-\text{SbF}_5$ (1:1) diluted with SO_2 at -60° , no peaks could be attributed to protonated pivaldehyde (Figure 6). The spectrum is that of protonated methyl isopropyl ketone,⁴ which was obtained in excellent yield on quenching the solution. In order to observe the spectrum of protonated pivaldehyde, it was necessary to prepare the sample in the less acidic medium, $\text{HSO}_3\text{F}-\text{SbF}_5$ (4:1) diluted with SO_2 at -70° (Figure 7). Even under these conditions protonated pivaldehyde slowly rearranged to protonated methyl isopropyl ketone, and minor peaks attributable to this protonated ketone can be seen in Figure 7. The spectrum of protonated pivaldehyde (VII) gave a doublet at -15.30 ppm ($J_{1,2} = 9.0$ cps) for the proton on oxygen, a doublet at -10.17 ppm ($J_{1,2} = 9.0$ cps) for the aldehyde hydrogen, and a singlet at -1.38 ppm for the methyl hydrogens.



The acidic rearrangement of α -hydroxy- and α -phenylaldehydes is well known.¹¹ The rearrangement of pivaldehyde to methyl isopropyl ketone has been effected with aluminum chloride¹² and concentrated sulfuric acid.¹³ Danilov obtained methyl isopropyl ketone by the reaction of pivaldehyde in 70% sulfuric acid in a sealed tube at 130° . The rearrangement at -70° in $\text{HSO}_3\text{F}-\text{SbF}_5$ is in sharp contrast to these conditions and reflects the great acid strength of the system.¹⁴ The driving force in this reaction is most probably the rearrangement of the protonated aldehyde to the more stable tertiary carbonium ion followed by a



(11) Reference 4, p 771, and references therein cited.

(12) H. Hopff, C. D. Nenitzescu, D. A. Isacescu, and I. P. Cantuniari, *Ber.*, **69**, 2244 (1936).

(13) S. Danilov and E. Vanus-Danilov, *ibid.*, **59**, 377 (1926).

(14) N. C. Deno and P. S. Scholl (unpublished results) report rearrangement in 1 min at 25° in 95% H_2SO_4 .

hydride shift to give protonated methyl isopropyl ketone. No evidence was found under these conditions for the rearrangement of isobutyraldehyde to methyl ethyl ketone, which would require the intermediacy of a secondary carbonium ion.

Experimental Section

Materials. All aldehydes were commercially available materials and were distilled just prior to use. Methylene- d_2 chloride and acetaldehyde- d_4 were obtained from Merck Sharp and Dohme, Ltd. and were 99% isotopically pure.

Nmr Spectra. Varian Associates Model A56-60A and HA-60-IL nmr spectrometers with variable-temperature probes were used for all spectra. Coupling constants (Table I) are believed accurate to ± 0.1 cps.

Preparation of Protonated Aldehydes. Samples of protonated aldehydes were prepared by dissolving approximately 1.5 ml of

$\text{HSO}_3\text{F-SbF}_5$ (1:1 molar solution) in an equal volume of sulfur dioxide and cooling to -76° . The aldehyde (approximately 0.2 ml) was dissolved in 1 ml of sulfur dioxide, cooled to -76° , and with vigorous agitation slowly added to the acid solution. Samples prepared in this manner gave nmr spectra which showed no appreciable chemical shift difference with temperature or small concentration variations. The acid was always in excess of the aldehyde as indicated by the large acid peak at about -10.9 ppm.

Protonated formaldehyde and protonated formaldehyde- d_2 were prepared by passing formaldehyde from the pyrolysis of paraformaldehyde over the surface of a cooled, stirred solution of $\text{HSO}_3\text{F-SbF}_5$ (1:1) diluted with SO_2 or by the reaction of methylene chloride (or methylene- d_2 chloride) with $\text{HSO}_3\text{F-SbF}_5$ (1:1) diluted with SO_2 and heated for a few minutes to -10° .

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Stable Carbonium Ions. XLIII.^{1a} Protonated Aliphatic Ketones

George A. Olah, Mihai Calin,^{1b} and Daniel H. O'Brien^{1c}

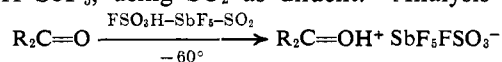
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received February 21, 1967

Abstract: The protonation of a series of aliphatic ketones was studied in $\text{HSO}_3\text{F-SbF}_5\text{-SO}_2$ solution by nmr spectroscopy at -60° . Exchange rates were negligible under the used conditions. Analysis of the spectra allowed the elucidation of the structure of protonated ketones in the strong acid solution.

Our recent investigation of protonated alcohols,² ethers,³ sulfides,⁴ and aldehydes^{1a} lead us now to the investigation of protonated ketones. Protonation of ketones in acidic solutions has been indicated by ultraviolet and infrared measurements.⁵ Birchall and Gillespie studied the nmr spectra of protonated acetone and aromatic ketones.⁶ Substituted benzophenones were also investigated.⁷ No systematic nuclear magnetic resonance study of the structure of protonated aliphatic ketones has been made.

Results and Discussion

We wish to report the nmr observation of protonated aliphatic ketones in the extremely strong acid system, $\text{FSO}_3\text{H-SbF}_5$, using SO_2 as diluent. Analysis of the resonance positions and the coupling constants leads to strong evidence for the structure of protonated ketones in acidic solutions.^{7a}



(1) (a) Part XLII: G. A. Olah, D. H. O'Brien, and M. Calin, *J. Am. Chem. Soc.*, **89**, 3582 (1967); (b) National Institutes of Health Postdoctoral Research Investigator, 1966-1967; (c) National Science Foundation Postdoctoral Research Investigator, 1966-1967.

(2) G. A. Olah, J. Sommer, and E. Namanworth, *J. Am. Chem. Soc.*, **89**, 3576 (1967); G. A. Olah and E. Namanworth, *ibid.*, **88**, 5327 (1966).

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

(4) G. A. Olah, D. H. O'Brien, and C. U. Pittman, Jr., *ibid.*, **89**, 2996 (1967).

(5) S. Patai, Ed., "The Chemistry of the Carbonyl Group," John Wiley and Sons, Inc., New York, N. Y., 1966, Chapter 9.

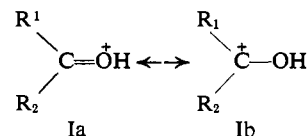
(6) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **43**, 1045 (1965).

(7) T. J. Sekuur and P. Kranenburg, *Tetrahedron Letters*, 4793 (1966).

(7a) NOTE ADDED IN PROOF. In a communication just published and unknown to us previously (M. Brookhart, G. C. Levy, and S. Weinstein, *J. Am. Chem. Soc.*, **89**, 1735 (1967), the $\text{C}=\text{OH}^+$ protons

Protonated ketones give well-resolved nmr spectra below -20° showing very slow exchange rates. Chemical shift values and coupling constants for the protonated aliphatic ketones studied are summarized in Table I.⁸

The Proton on Oxygen. The proton on oxygen in protonated ketones was found substantially deshielded and is generally between -13.5 and -15.0 ppm. This large deshielding of the proton on oxygen indicates



that the positive charge resides mainly on oxygen (Ia) and that resonance form Ib (e.g., the dialkylhydroxycarbonium ion) is of lesser significance. The relatively small deshielding of the hydrogens on the α -carbon atom (~ 1.2 ppm) when compared to the deshielding of hydrogens α to a carbonium ion center⁹ (~ 3.0 ppm) is consistent with this suggestion.

in protonated acetone and methyl ethyl ketone were reported as singlets in $\text{SO}_2\text{-FSO}_3\text{H-SbF}_5$ solution at -60° . We have no explanation for the lack of observation of coupling and fine structure under conditions similar to those reported in our present paper. Assignment of the conformation of isomers is based in our work primarily on the analysis of coupling constants which we consider an essential part of our work. Similarly we must call attention to the fact that in protonated cyclic ketones the $\text{C}=\text{OH}^+$ proton generally gives rise to well observable coupling and fine structure, not, as reported by Brookhart, *et al.*, to singlets. Our work in this regard is being published in detail.

(8) For simplicity, the solvent acid peaks were deleted from Table I and the spectra.

(9) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgsey, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).