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 HSO_3F-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 HSO_3F-SbF_5 (1:1) diluted with SO_2 or by the reaction of methylene chloride (or methylene-d_2 chloride) with HSO_3F-SbF_5 (1:1) diluted with SO_2 and heated for a few minutes to −10°.

Acknowledgment. Generous support of the work by grants of the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

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 $HSO_3F-SbF_5-SO_2$ 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

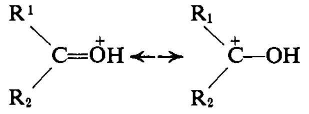
We wish to report the nmr observation of protonated aliphatic ketones in the extremely strong acid system, FSO_3H-SbF_5, using SO_2 as diluent. Analysis of the

$$R_2C{=}O \xrightarrow[-60°]{FSO_3H-SbF_5-SO_2} R_2C{=}OH^+ \; SbF_5FSO_3^-$$

resonance positions and the coupling constants leads to strong evidence for the structure of protonated ketones in acidic solutions.[7a]

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



Ia Ib

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 center[9] (~3.0 ppm) is consistent with this suggestion.

---

(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).

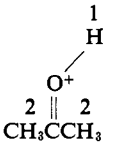
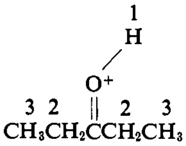
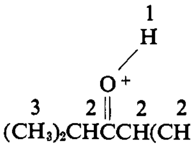
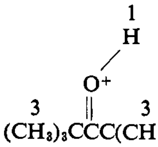
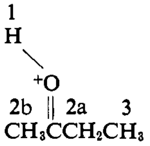
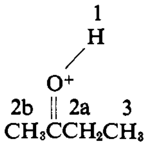
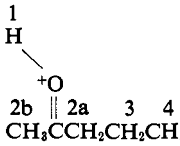
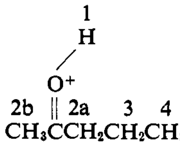
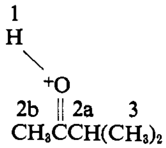
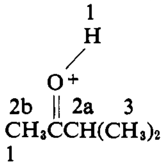
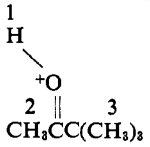
(7) T. J. Sekuur and P. Kranenburg, *Tetrahedron Letters*, 4793 (1966).

(7a) NOTE ADDED IN PROOF. In a communication just published and unknown to us previously (M. Brookhart, G. C. Levy, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1735 (1967), the $C{=}OH^+$ protons in protonated acetone and methyl ethyl ketone were reported as *singlets* in $SO_2-FSO_3H-SbF_5$ 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 $C{=}OH^+$ 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.

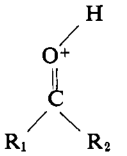
(8) For simplicity, the solvent acid peaks were deleted from Table I and the spectra.

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

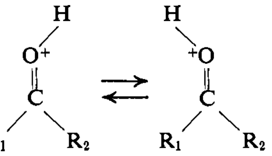
Table I. Nmr Chemical Shifts (δ, ppm) and Coupling Constants (cps) of Protonated Ketones at −60° in FSO_3H–SbF_5–SO_2 Solution

Protonated ketone	H_1, $J_{1,2cis}$	H_2	H_3	H_4
 CH_3CCH_3	−14.93 1.0	−3.45		
 $CH_3CH_2CCH_2CH_3$	−14.06 1.0	−3.70	−1.65	
 $(CH_3)_2CHCCH(CH_3)_2$	−13.86 0.4	−3.90	−1.76	
 $(CH_3)_3CCC(CH_3)_3$	−13.51 ...	...	−1.98	
 $CH_3CCH_2CH_3$	−14.26 1.0	a −3.73 b −3.33	−1.66	
 $CH_3CCH_2CH_3$	−13.91 1.0	a −3.73 b −3.33	−1.66	
 $CH_3CCH_2CH_2CH_3$	−14.30 1.0	a −3.66 b −3.33	−2.13	−1.30
 $CH_3CCH_2CH_2CH_3$	−14.16 1.0	a −3.66 b −3.33	−2.13	−1.30
 $CH_3CCH(CH_3)_2$	−14.41 1.2	a −3.68 b −3.19	−1.65	
 $CH_3CCH(CH_3)_2$	−13.95 1.2	a −3.68 b −3.19	−1.65	
 $CH_3CC(CH_3)_3$	−14.23 1.2	−3.38	−1.98	

In protonated symmetrically substituted aliphatic ketones II (1–4), only one resonance is found for the proton on oxygen. For protonated asymmetrically substituted aliphatic ketones III (1–4), two resonances are found for the proton on oxygen, except for protonated methyl *t*-butyl ketone III (4).



II (1), $R_1 = R_2 = CH_3$
(2), $R_1 = R_2 = CH_3CH_2$
(3), $R_1 = R_2 = (CH_3)_2CH$
(4), $R_1 = R_2 = (CH_3)_3C$

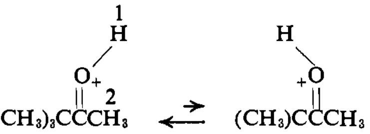


IIIa IIIb

(1), $R_1 = CH_3$; $R_2 = CH_3CH_2$
(2), $R_1 = CH_3$; $R_2 = CH_3CH_2CH_2$
(3), $R_1 = CH_3$; $R_2 = (CH_3)_2CH$
(4), $R_1 = CH_3$; $R_2 = (CH_3)_3C$

This observation is explained by the existence of two isomers of protonated asymmetrically substituted ketones in which the proton on oxygen is in two magnetically nonequivalent environments depending on its relationship to alkyl groups R_1 and R_2.

Assignment of the observed $=OH^+$ resonances to isomer IIIa or IIIb is based on the allylic coupling constants between the proton on oxygen and the α hydrogens (proved by spin–spin decoupling experiments). In analogous olefinic systems, *cis* allylic coupling is usually larger than *trans* allylic coupling.[10] In the protonated ketones studied, the *cis* allylic coupling was consistently large enough to be observed (0.8–1.2 cps) while further splitting caused by *trans* allylic coupling was not observed. The observed *cis* allylic coupling is best described by using protonated methyl *t*-butyl ketone as an example (Figure 8). The large difference in steric requirements of the *t*-butyl group compared to the methyl group allows only the observation of the isomer in which the proton on oxygen is *trans* to the *t*-butyl group (IVa). The proton on oxygen appears as a quartet at −14.23 caused by *cis* allylic coupling to the α-methyl hydrogens ($J_{1,2}$ = 1.2 cps). The α-methyl hydrogens appear as a doublet at −3.38 ppm ($J_{2,1}$ = 1.2 cps). Irradiation at the $=OH^+$ resonance caused the methyl doublet to collapse to a singlet and irradiation at the methyl resonance caused the $=OH^+$ quartet to collapse to a singlet.



IVa, ~100% IVb

Protonated Acetone. Protonated acetone gives rise to a quartet ($J_{1,2}$ = 1.0 cps) at −14.93 ppm for the proton on oxygen caused by *cis* allylic coupling to one of the methyl groups (Figure 1). The methyl group of protonated acetone appears as a complex multiplet centered at −3.45 ppm. Apparently the chemical shift difference between the magnetically nonequivalent methyl groups is too small to allow the observation of two methyl groups. This lack of shift difference is further complicated by long-range coupling between the methyl groups comparable to that observed in ace-

---

(10) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

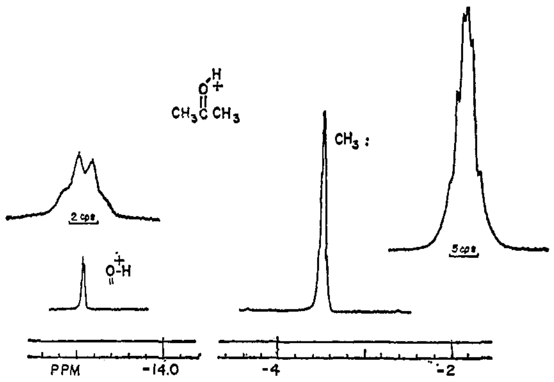


Figure 1.

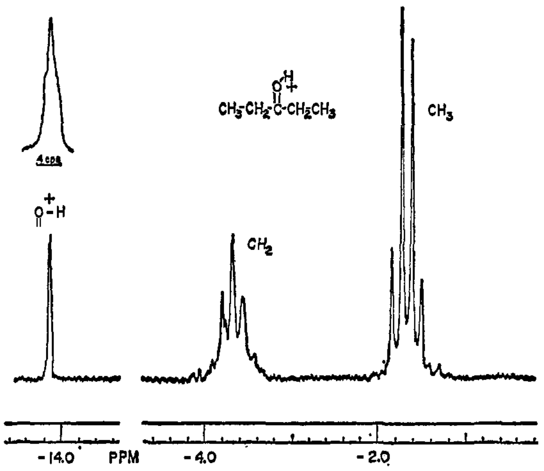


Figure 2.

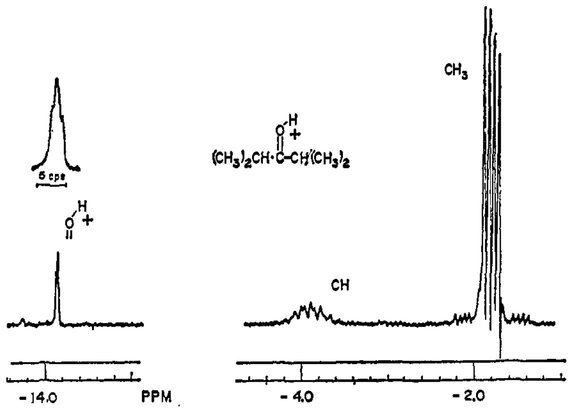


Figure 3.

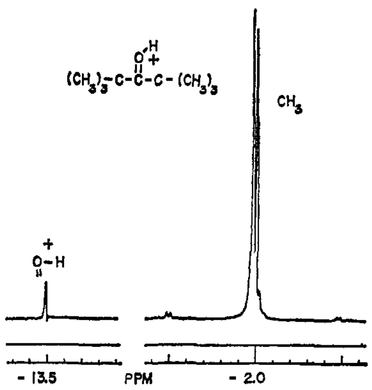


Figure 4.

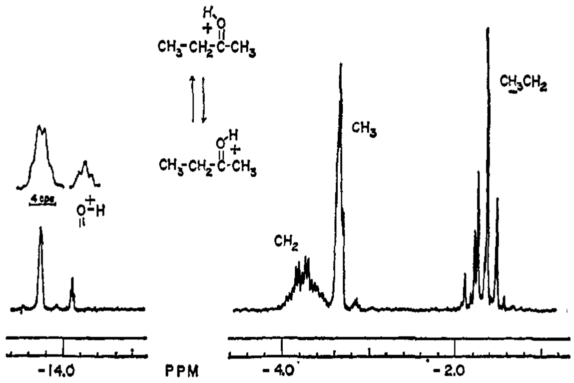


Figure 5.

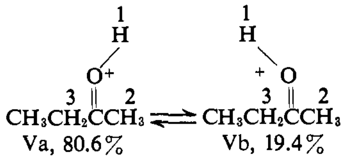
tone itself.[11] Irradiation of the proton on oxygen in protonated acetone does not cause the methyl resonances to collapse into two singlets, indicating that such long-range coupling is present.

Protonated Diethyl Ketone. Protonated diethyl ketone gives rise to a triplet ($J_{1,2}$ = 1.0 cps) at −14.06 ppm for the proton on oxygen caused by *cis* allylic coupling with one of the methylene groups (Figure 2). The methylene hydrogens appear as a complex multiplet at −3.70 ppm. The methyl hydrogens appear as a pair of overlapping triplets centered at −1.65 ppm. These triplets are separated by 7.0 cps. This separation is a measure of the magnetic nonequivalence of the methyl groups *cis* and *trans* to the proton on oxygen.

Protonated Diisopropyl Ketone. Protonated diisopropyl ketone gives rise to a resonance at −13.86 ppm for the proton on oxygen (Figure 3). This peak is a triplet ($J_{1,2}$ = 0.4 cps) rather than the doublet which would be expected to result from *cis* allylic coupling with one of the methine hydrogens. This increased complexity may be due to variation of the *cis* and *trans* allylic coupling reflecting differences in conformation about the α-carbon–carbonyl carbon single bond. The methine hydrogens appear as a complex multiplet at −3.90 ppm. The methyl hydrogens appear as a pair of overlapping doublets at −1.76 ppm. The separation of this pair of doublets is 3.6 cps.

Protonated Di-*t*-butyl Ketone. The proton on oxygen appears as a singlet at −13.51 ppm. The methyl hydrogens appear as two slightly separated singlets at −1.98 ppm. The separation of these singlets is 1.6 cps (Figure 4).

Protonated Methyl Ethyl Ketone. Protonated methyl ethyl ketone shows two resonances for the proton on oxygen (Figure 5). One appears at −14.26 ppm and the other at −13.91 ppm. This indicates the presence of two isomers in which the proton on oxygen is either



$$\mathrm{CH_3CH_2\overset{3}{C}\overset{\overset{\overset{1}{H}\diagup}{O^{+}}}{\overset{\|}{C}}\overset{2}{C}H_3} \rightleftharpoons \mathrm{CH_3CH_2\overset{3}{C}\overset{\overset{\overset{1}{H}\diagdown}{{}^{+}O}}{\overset{\|}{C}}\overset{2}{C}H_3}$$

Va, 80.6%   Vb, 19.4%

---

(11) N. van Meurs, *Spectrochim. Acta*, **19**, 1695 (1963).

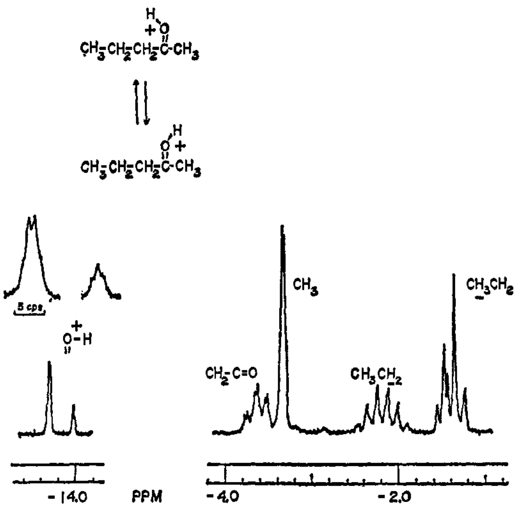


Figure 6.

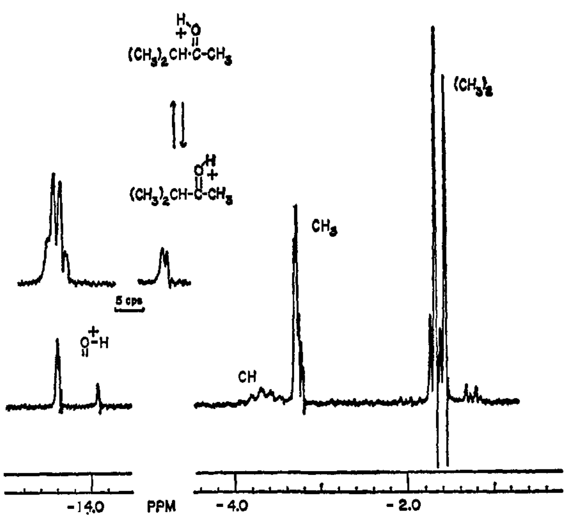


Figure 7.

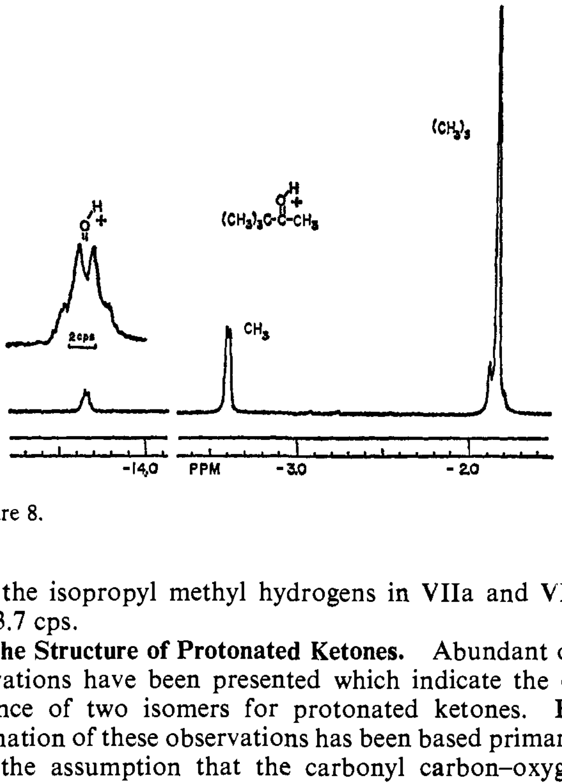


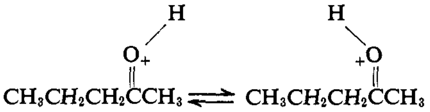
Figure 8.

cis (Va) or *trans* (Vb) to the α-methyl group. The resonance at -14.26 ppm can be resolved into a quartet ($J_{1,2} = 1.0$ cps) caused by *cis* allylic coupling to the α-methyl hydrogens of isomer Va. The resonance at -13.91 ppm can be resolved into a triplet ($J_{1,3} = 1.0$ cps) caused by *cis* allylic coupling to the methylene hydrogens in isomer Vb.

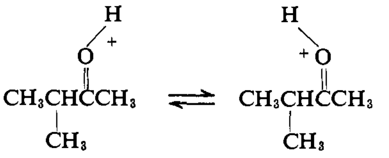
The methylene hydrogens appear as a complex multiplet at -3.73 ppm and the α-methyl hydrogens as a complex multiplet at -3.33 ppm. The α-methyl group could not be resolved into two distinct methyl groups which would be expected because of the presence of isomers Va and Vb and is perhaps further complicated by long-range coupling to the methylene hydrogens.

The methyl hydrogens of the ethyl group appear as a pair of overlapping triplets of unequal intensity centered at -1.66 ppm. The centers of these two triplets are separated by 4.5 cps, reflecting the nonequivalence of these methyl groups in isomers Va and Vb.

Protonated Methyl Propyl and Methyl Isopropyl Ketone. These protonated ketones display the same characteristic $=\mathrm{OH}^+$ resonances as protonated methyl ethyl ketone (Figures 6 and 7). *cis* Allylic coupling gives rise to quartets for VIa and VIIa and a triplet and doublet for VIb and VIIb, respectively. Irradiation of the α-methyl hydrogens of protonated methyl isopropyl ketone at -3.19 ppm caused the $=\mathrm{OH}^+$ quartet at -14.41 ppm (VIIa) to collapse to a singlet while the $=\mathrm{OH}^+$ doublet at -13.95 ppm (VIIb) remained unchanged. The overlapping triplets for the methyl hydrogens of the propyl group in VIa and VIb were separated by 4.5 cps and the overlapping doublets for the isopropyl methyl hydrogens in VIIa and VIIb by 3.7 cps.



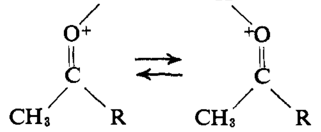
VIa, 80%   VIb, 20%



VIIa, 84.6%   VIIb, 15.4%

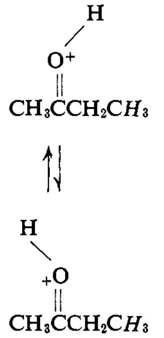
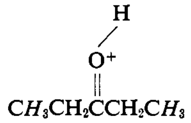
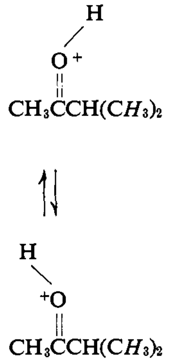
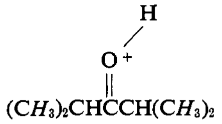
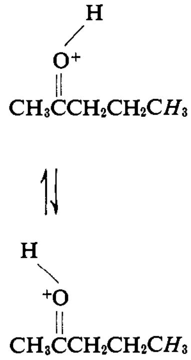
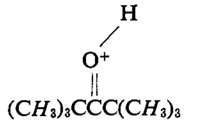
The Structure of Protonated Ketones. Abundant observations have been presented which indicate the existence of two isomers for protonated ketones. Explanation of these observations has been based primarily on the assumption that the carbonyl carbon–oxygen bond maintains its double-bond character in protonated ketones. Two further observations which are present in the nmr spectra of protonated ketones warrant discussion.

Where chemical shift differences could be measured, the β- or α-alkyl group *cis* to the proton on oxygen in the asymmetrically substituted methyl ketones VIIIa was slightly more deshielded than the β- or α-alkyl group *trans* to the proton on oxygen (VIIIb) (Figures 5–8). In the symmetrically substituted ketones (Figures 2–4) where only one isomer is present, the β-alkyl



VIIIa   VIIIb

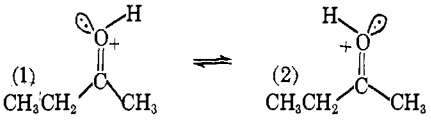
Table II. β-Alkyl Chemical Shift Differences[a]

Protonated ketone	ΔHz	Protonated ketone	ΔHz
	8.0		7.0
	3.7		3.6
	4.5		1.6

[a] Chemical shift difference between center of multiplets of alkyl group given in italics.

groups were of equal intensity and could not be definitely assigned but the small chemical shift differences were comparable in size to the chemical shift differences for the corresponding asymmetrically substituted ketones. These shift differences are summarized in Table II. It can be seen that this difference decreases as the number of β-alkyl groups increases. In the asymmetric protonated methyl ketones, the $=OH^+$ resonance of the *trans* isomer VIIIb was at lower field (15.0–22.0 cps) than the *cis* isomer VIIIa.

It has been proposed in theoretical treatments of the unprotonated carbonyl bond that the two lone pairs of electrons on oxygen maintain s and p character.[12] Protonation of oxygen's p lone pair of this model leads to no convenient explanation of these alkyl chemical shift differences or of the relative position of the $=OH^+$ resonances. A more convenient model for protonated ketones is obtained through the sp^2 hybridization of oxygen. This would lead to nonbonded interaction between the sp^2 lone pair on oxygen and the alkyl group *trans* to the proton on oxygen and to localization of the positive charge in the area of the oxygen–proton bond. Using this model for protonated methyl ethyl ketone, we would expect that the methyl group 1 of IXa would be slightly shielded compared to methyl group 2 of IXb, as is observed. Nonbonded interaction of the sp^2 lone pair in IXa with the β-methyl group would also lead to deshielding of the proton on oxygen in IXa compared to IXb, as is observed. It must be pointed out, however, that hybridization and charge distribution arguments may not be the only factors affecting the nmr shifts. Anisotropy and other factors may also have substantial effects.



IXa IXb

Experimental Section

Materials. All ketones were commercially available materials and were distilled just prior to use.

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

Preparation of Protonated Ketones. Samples of protonated ketones were prepared by dissolving approximately 1.5 ml of HSO_3F-SbF_5 (1:1 molar solution) in an equal volume of sulfur dioxide and cooling to −76°. The ketone (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 differences 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.

Acknowledgment. Support of this research by grants of the National Institute of Health and the National Science Foundation is gratefully acknowledged.

---

[12] Reference 6, Chapter 1, and references cited therein.