

toward the  $\pi$ -cloud loop on the ring carbon atoms. In the infrared the differences between the positions of the OH group above the plane of the  $C_2-C_1-C_6$  carbon atoms in **7**, **9**, and **10** are not sufficient to reflect any significant differences in the  $\text{OH}\cdots\pi$  bonds. In the nmr, however, maximum shielding of a hydrogen is experienced when it is held close to the center of the aromatic ring where the induced ring currents cause increased shielding.<sup>6</sup> The degree of shielding of a proton by an isotropic group of electrons is known to depend on both  $r$  and  $\theta$ .<sup>7</sup>

Table II. Shielding Parameters for  $\text{OH}\cdots\pi$  Bonded Alcohols

Norbornanol <sup>a</sup>	— $a$ (ring radii)—			$\theta^b$	$\sigma_{\text{H}}$ , ppm	$\Delta\mu$ , $\text{cm}^{-1}$
	$Z$	$P$	$r$			
<b>10</b>	1.4	0.8	1.6	29	0.64	28
<b>9</b>	1.4	1.1	1.8	38	0.52	30
<b>7</b>	1.6	1.3	2.1	39	0.19	30
<b>8</b>	1.4	1.1	1.8	38	0.18	10

<sup>a</sup> The  $Z$  axis is normal to the plane of the aromatic ring at its center, and the  $P$  axis is in the plane of the ring, both measured in ring radii (1.39 Å) (see C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958)). Then  $r$  measures the distance of  $Z_0, P_0$  to the H atom. <sup>b</sup>  $\theta$  is the angle between the  $Z$  axis at  $P_0$  and the H atom.

Table II shows that **10**, corresponding to the smallest values of  $r$  and  $\theta$ , reflects the greatest shielding, as expected. While  $\theta$  is approximately the same in **7** and **9**, the greater  $r$  value for the former alcohol apparently leads to the lesser degree of shielding.

The values of  $r$  and  $\theta$  have been measured assuming that the preferred benzene ring-hydroxyl hydrogen orientation is that of maximum interaction with the hydrogen perpendicular to the  $P$  axis. On this basis, the experimental data for **8** initially appear to be out of line when compared to its di-*exo*-analog **9**. In **8** the phenyl orientation for maximum  $\text{OH}\cdots\pi$  interaction is one in which an *o*-phenyl hydrogen displays an unfavorable steric interaction with the *endo*-5 hydrogen. To relieve the steric strain the benzene ring can rotate somewhat, thus increasing the value of  $\theta$  and decreasing considerably the extent of the  $\text{OH}\cdots\pi$  interaction evidenced by nmr and infrared.

In conclusion, it has been shown that numerous structural features related to the magnitude of inductive, steric, and conformational effects in bicyclic systems can be probed by an examination of relative values of the slope ( $(d\gamma/dx)_x=0$ ) and the OH signal at infinite dilution ( $\gamma_0$ ). The nmr analysis of  $\pi$ -interaction effects appears to be superior to the infrared method, since the former method better reflects the differences in structure. This analysis should be useful as an analytical tool for structural assignments and as an instrument for detecting the extent of interaction of aromatic rings and other unsaturated systems with functional groups and thereby elucidating physical and chemical behavior.

(6) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, London, 1965, p 140.

(7) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

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### O—H Chemical Shift, Conformation, and Electron Delocalization in Protonated Carbonyl Compounds<sup>1</sup>

Sir:

While studying classical and nonclassical carbonium ions in  $\text{SO}_2\text{-FSO}_3\text{H-SbF}_5$  we have observed the  $\text{C}=\text{O}-\text{H}$  proton signal in the nmr spectra of various protonated aldehydes, ketones, and carboxylic acids. In the usual nmr observations of such species, rapid proton exchange with the medium averages the  $\text{C}=\text{O}-\text{H}$  proton signal with the solvent signal. In very acidic media at sufficiently low temperatures, however, such proton exchange becomes slow enough to permit nmr observation of the  $\text{C}=\text{O}-\text{H}$  proton resonance. The  $\text{C}=\text{O}-\text{H}$  signal for protonated acetone was first observed by MacLean and Mackor<sup>2a</sup> in  $\text{HF-BF}_3$  at  $-75^\circ$ , while very recently Birchall and Gillespie<sup>2b</sup> have reported protonated acetone in  $\text{FSO}_3\text{H-SbF}_5$ , several acetophenones in  $\text{FSO}_3\text{H}$ , and  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{CH}_2\text{COOH}$ , and  $\text{C}_6\text{H}_5\text{COOH}$  in  $\text{FSO}_3\text{H-SbF}_5$ . Still more recently, MacLean and Mackor<sup>2d</sup> have reported protonation of formic acid in  $\text{HF-BF}_3$ .

The  $\text{C}=\text{O}-\text{H}$  proton nmr signal represents a powerful tool in the study of substituent or electron-delocalization effects, and thus it represents a new tool in the study of nonclassical species. Besides casting some light on the electronic distribution in the protonated species, the  $\text{C}=\text{O}-\text{H}$  nmr signal furnishes information regarding conformation and configuration. In the present communication we illustrate some of the kinds of protonated species we have observed and the information derived from the spectra (Table I).

The nmr<sup>3</sup> of acetaldehyde in  $\text{SO}_2\text{-FSO}_3\text{H-SbF}_5$  at  $-52^\circ$  shows two doublets, integrating together for one O—H proton, one at  $\delta$  14.78 ( $J = 8.5$  cps) and the other at  $\delta$  15.14 ( $J = 18.5$  cps), in *ca.* 5:1 ratio, respectively. This is interpreted as an equilibrium mixture of *syn* and *anti* conformational isomers I and II. The assignment of the  $\delta$  14.78 doublet to the *syn* isomer and the  $\delta$  15.14 doublet to the *anti* isomer is based on an assumed steric preference of I over II and an analogy between *syn* and *anti* coupling constants ( $J_{\text{anti}} > J_{\text{syn}}$ ) and *cis* and *trans* olefinic coupling constants ( $J_{\text{trans}} > J_{\text{cis}}$ ). The spectrum of protonated methyl ethyl ketone at  $-60^\circ$  shows two O—H singlets, one at

(1) (a) Research supported in part by the National Science Foundation; (b) research sponsored in part by the U. S. Army Research Office (Durham).

(2) (a) C. MacLean and E. L. Mackor, *J. Chem. Phys.*, **34**, 2207 (1961); (b) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **43**, 1045 (1965); (c) these authors have shown that the  $\text{C}=\text{O}-\text{H}$  chemical shift in substituted acetophenones is quite sensitive to *para* substituents and follows a  $\rho\sigma^+$  relationship; (d) H. Hogeveen, A. F. Bickel, C. W. Hilbers, E. L. Mackor, and C. MacLean, *Chem. Commun.*, 898 (1966); (e) our observations and interpretation of the behavior of protonated  $\text{HCOOH}$  are the same as those of Hogeveen, *et al.*

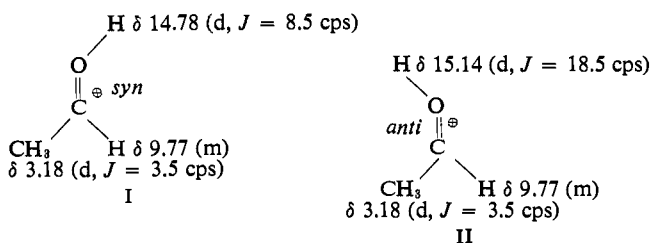
(3) All chemical shifts ( $\delta$ ) are reported in parts per million downfield from TMS using internal  $\text{CH}_2\text{Cl}_2$  ( $\delta$  5.30) as the secondary standard.

**Table I.** Nmr Chemical Shifts of Protonated Aldehydes, Ketones, and Carboxylic Acids in  $\text{SO}_2\text{-FSO}_3\text{H-SbF}_5$ <sup>a</sup>

Conjugate base	Temp, °C	C=OH <sup>+</sup> , $\delta$
Acetaldehyde	-52	14.78 (d, $J = 8.5$ cps), ~82% 15.14 (d, $J = 18.5$ cps), ~18%
Propionaldehyde	-65	15.12 (d, $J = 9$ cps)
Acetone	-59	14.24 (s)
Methyl ethyl ketone	-60	14.03 (s), ~80% 13.65 (s), ~20%
	+40	13.98 <sup>c</sup> (s)
Cyclobutanone	-62	14.73 (s)
Cyclopentanone	-54	14.17 (s)
Cyclohexanone	-56	14.03 (s)
Cycloheptanone	-55	13.93 (s)
Norcamphor	-60	13.75 (s)
Acetic acid	-57	12.70 (s), ~48% 12.05 (s), ~48% 12.53 (s), ~3%
	-30	12.38 (s)
Formic acid	-75	13.15 (d, $J = 3$ cps), ~38% 12.95 (d, $J = 3$ cps), ~24% 12.73 (d, $J = 14$ cps), ~38%
Propionic acid	-53	12.25 (s), 1.0 proton 12.00 (s), 1.0 proton
Benzoic acid	-53	11.87 (s)
Benzaldehyde	-52	13.29 (d, $J = 8$ cps)
Acetophenone	-52	13.03 (s)
Benzophenone	-58	12.23 (s)
Anthraquinone <sup>b</sup>	-50	13.8 (s), 2.0 protons
Naphthaquinone <sup>b</sup>	-50	14.58 (s), 2.0 protons
1,4-Diacetylbenzene <sup>b</sup>	-50	14.57 (s), 2.0 protons
1,3,5-Tribenzoylbenzene	-30	13.67 (s), 3.0 protons
Cyclopropanecarboxaldehyde	-50	12.62 (d, $J = 8$ cps), ~75% 13.33 (d, $J = 18$ cps), ~25%
Cyclopropyl methyl ketone	-55	12.52 (s), 80% 13.18 (s), 20%
Dicyclopropyl ketone	-52	12.08 (s)
Cyclopropyl phenyl ketone	-50	11.78 (s)
7-Norbornanone	-58	14.30 (s)
7-Norbornenone	-58	12.75 (s)

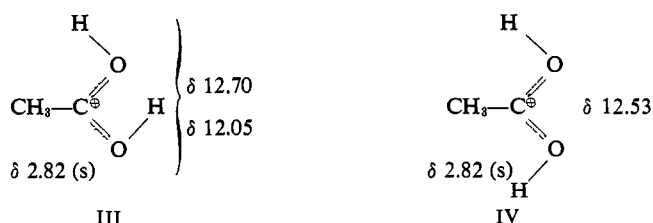
<sup>a</sup> In a 9:7:2 molar  $\text{SO}_2\text{-FSO}_3\text{H-SbF}_5$  mixture. Chemical shifts reproducible to  $\pm 0.05$  ppm. The temperature coefficient of the OH chemical shift is small,  $< -0.005$  ppm/deg. Cf. ref 3. <sup>b</sup> No  $\text{SO}_2$ ; 7:1 molar ratio  $\text{FSO}_3\text{H-SbF}_5$ . <sup>c</sup> 7:2 molar ratio  $\text{FSO}_3\text{H-SbF}_5$ .

$\delta$  14.03 and one at  $\delta$  13.65 (total integration of one proton), in *ca.* 4:1 ratio, respectively. This is also interpreted as a mixture of conformational isomers where the major isomer is probably the one with the O-H proton *syn* to the methyl group. Upon warming to 40° the two singlets collapse to one peak at  $\delta$  13.98, indicating averaging of the two O-H signals by fast conformational equilibration before exchange with solvent becomes rapid.<sup>4</sup> In the case of protonated cyclic ketones (Table I), the O-H resonances of the five-, six-, and seven-membered ketones all occur at  $\delta$  13.9–14.2, while the corresponding protonated cyclobutanone at  $\delta$  14.73 shows the effect of increased angle strain on the C=O—H resonance.



(4) T. J. Sekuur and P. Kranenburg, *Tetrahedron Letters*, 4793 (1966), report two C=O—H resonances for unsymmetrically substituted benzophenones in  $\text{FSO}_3\text{H-SbF}_5$  at  $-40^\circ$  which merge to a singlet at higher temperatures. They attribute this to two conformations in which "the carbonyl group is alternately coplanar with two different aryl systems." We believe this is probably "syn" and "anti" isomerism as observed in the present systems.

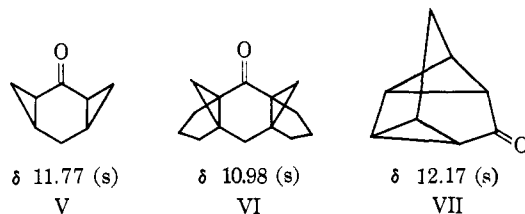
We have also examined several protonated carboxylic acids<sup>2e</sup> (Table I). Birchall and Gillespie<sup>2b</sup> report for protonated acetic acid two one-proton O-H singlets at  $\delta$  12.28 and 12.89 in  $\text{FSO}_3\text{H-SbF}_5$  at  $-75^\circ$ . Besides these two singlets, which occur at  $\delta$  12.05 and 12.70 in  $\text{SO}_2\text{-FSO}_3\text{H-SbF}_5$  at  $-60^\circ$  and which we attribute to isomer III, we observe an additional singlet at  $\delta$  12.53 (3% of the total O-H integration) which we attribute to the presence of isomer IV. We also<sup>2b</sup> observe the O-H resonances collapse to a singlet at  $\delta$  12.38 as the solution is warmed<sup>5</sup> to  $-30^\circ$ .



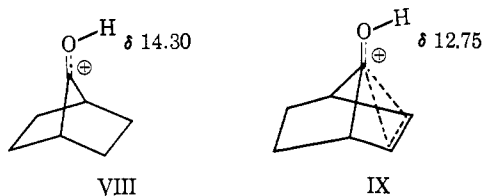
The chemical shift of the C=O—H proton reflects the ability of the carbonyl substituents to donate electron density to the positive center. The O-H resonances of protonated acetaldehyde occur at  $\delta$  15.14 and 14.78 while acetone falls at higher field,  $\delta$  14.24. Protonated benzophenone occurs at  $\delta$  12.23, 2 ppm

(5) The protonated acetic acid slowly forms  $\text{CH}_3\text{-C}\equiv\text{O}^+$  and  $\text{H}_3\text{O}^+$  as evidenced by a second methyl singlet at  $\delta$  3.92 and an  $\text{H}_3\text{O}^+$  singlet at  $\delta$  9.93 which slowly appear at  $-40^\circ$ .

upfield from acetone and *ca.* 2.7 ppm upfield from acet-aldehyde, while protonated acetophenone<sup>2c</sup> falls between acetone and benzophenone at  $\delta$  13.03. The OH chemical shift as a probe of electronic distribution also reflects nonclassical delocalization of positive charge. It is instructive to compare the O-H chemical shifts of protonated cyclopropyl ketones<sup>6</sup> with phenyl- and alkyl-substituted ketones (Table I). In each case the OH chemical shifts of the analogous protonated cyclopropyl and phenyl ketones are nearly equivalent,<sup>7</sup> both occurring at much higher field than the alkyl derivatives. Pronounced electron supply by cyclopropyl groups is further illustrated by the conjugate acids of other interesting dicyclopropyl ketones, *e.g.*, V, VI,<sup>8a</sup> and VII.<sup>8b</sup>



The present technique can be used effectively to illustrate electron delocalization in other nonclassical ions. Thus, it is instructive to compare the O-H resonance of protonated 7-norbornanone (VIII) at  $\delta$  14.30 with the OH resonance of protonated 7-norbornenone (IX) at  $\delta$  12.75.<sup>9</sup> The dramatic upfield shift of 1.55 ppm reflects significant delocalization of the  $\pi$ -olefinic electrons in IX. Another interesting bridged ion is X.<sup>8c</sup> In this species the OH chemical shift at  $\delta$  10.78, at 0.72-ppm higher field than in the case of the classical ion XI,<sup>8d</sup> reflects the extensive involvement of the cyclopropane ring in electron delocalization.<sup>8c</sup>



While our emphasis is on charge and electron-delocalization effects, we must note that the magnetic anisotropy of the protonated carbonyl group helps determine the actual values of the O-H chemical shifts. Deshielding effects due to magnetic anisotropy of the carbonyl group are decreased by protonation, and this explains why the chemical shift of the aldehydic proton

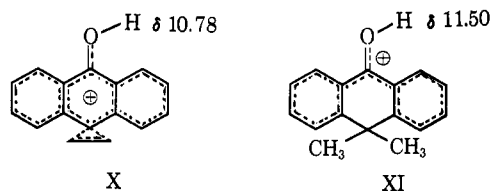
(6) (a) T. J. Sekuur and P. Kranenburg, *Tetrahedron Letters*, 4769 (1966), report a series of protonated substituted phenyl cyclopropyl ketones but do not discuss the significance of the O-H chemical shift; (b) other authors have protonated cyclopropyl ketones in acidic media, but have reported only the C-H proton signals.

(7) From detailed consideration of conformations it is evident that the large upfield shifts of the O-H proton in protonated cyclopropyl carboxaldehyde and cyclopropyl ketones relative to alkyl analogs are not largely due to cyclopropyl ring-current effects.

(8) (a) L. Birladeanu, H. Hanafusa, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 2315 (1966); (b) N. A. LeBel and R. N. Liesemer, *ibid.*, **87**, 4301 (1965); (c) L. Ebersson and S. Winstein, *ibid.*, **87**, 3506 (1965); (d) ions X and XI examined in 5.5:1  $\text{FSO}_3\text{H}-\text{SbF}_5$ .

(9) H. G. Richey and R. K. Lustgarten, *J. Am. Chem. Soc.*, **88**, 3136 (1966), report the C-H proton resonances for protonated 7-norbornenone in  $\text{FSO}_3\text{H}$ .

in the protonated aldehydes is nearly the same as in the free aldehyde. The magnetic anisotropy effects are still large enough in the protonated aldehydes and ketones to contribute appreciable deshielding of the O-H proton. The magnetic anisotropic effect is decreased by charge delocalization, and thus electron delocalization and magnetic anisotropic effects are intertwined. In the case of protonated 7-norbornenone



(IX), one should consider the magnetic anisotropic effect of the "olefinic group" on the O-H proton. Models suggest that this effect is quite small. Also, it is most likely deshielding and thus in the opposite direction from the observed substantial shielding of the O-H proton compared to protonated norbornanone (VIII).

(10) National Institutes of Health Predoctoral Fellow, 1965-1967.

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### Effect of Base Strength upon Orientation in Base-Promoted Elimination Reactions

Sir:

The evidence for the proposal<sup>1</sup> that the size of alkoxide bases significantly affects orientation in base-promoted eliminations is a series of experiments<sup>1b</sup> in which not one but three experimental conditions were changed between each comparative experiment within the series. In addition to a change in base size, the solvent and the strength of the base were changed. The authors recognized this ambiguity in their experiments but presented arguments, which have generally been accepted,<sup>2</sup> to discount these latter two changes as being contributory factors to the results obtained.

(1) (a) H. C. Brown and I. Moritani, *J. Am. Chem. Soc.*, **78**, 2203 (1956); (b) H. C. Brown, I. Moritani, and Y. Okamoto, *ibid.*, **78**, 2193 (1956); (c) H. C. Brown and I. Moritani, *ibid.*, **75**, 4112 (1953); (c) H. C. Brown and R. L. Klimisch, *ibid.*, **88**, 1425 (1966).

(2) (a) The following authors accept the steric proposal: J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p 311; A. H. Corwin and M. M. Bursey, "Elements of Organic Chemistry," Addison-Wesley, Reading, Mass., 1966, p 518; E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt, New York, N. Y., 1959, p 483. (b) The following author assigns an important role to the steric requirement of the base but points out that base strength may in part be responsible for the experimental trends: J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, Book Co., Inc., New York, N. Y., 1962, p 197. (c) The following author assigns an important role to the steric requirement of the base but also reports a system in which the strength of the base and the nature of the solvent are believed to affect relative rates: D. J. Cram in "Steric Effect in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 338-346. (d) The following authors' reports suggest an unwillingness to accept the steric requirement as a major factor: D. V. Banthorpe, "Reaction Mechanisms in Organic Chemistry," Vol. 2, E. D. Hughes, Ed., Elsevier Publishing Co., New York, N. Y., 1963, p 70; W. H. Saunders in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 195.