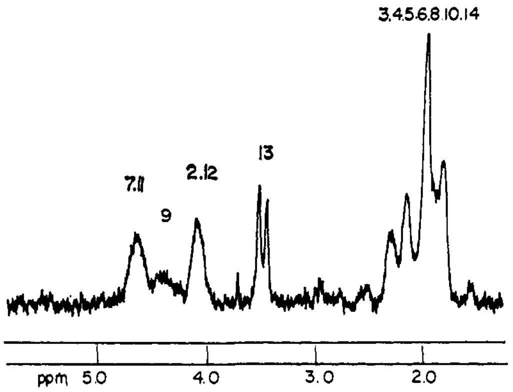


Figure 5. Nmr spectrum of the diamantyl (congressyl) cation (XIII) in neat FSO_3H-SbF_5 solution at −30°.

dard methods. Bicyclo[3.1.0]hexane was prepared according to Simmons and Smith.[17]

Nmr spectra were obtained on a Varian Associates Model A-56-60A nmr spectrometer equipped with a variable-temperature probe. Spin-spin decoupling experiments were done on Varian Associates Model HA-60IL and A-60A spectrometers. Very low temperature work (−120°) was carried out on the HA-60IL instrument using a special low-temperature probe. Table I summarizes the nmr shifts and coupling constants of cycloalkyl cations.

Generation of Cycloalkyl Cations in Neat FSO_3H-SbF_5. In a typical experiment, the cycloalkane and a tenfold (weight) excess of the acid (1:1 mixtures of FSO_3H and SbF_5) were vigorously stirred at room temperature, until they formed a homogeneous colorless mixture. The reaction is carried out under exclusion of moisture and is generally completed in 10 to 30 min.

Generation of Cycloalkyl Cations in $FSO_3H-SbF_5-SOCl_2F$. To a mixture (1:1) of SO_2ClF and FSO_3H-SbF_5 the alkane is added, diluted with SO_2ClF when necessary. On mixing, reaction willoccur at all temperatures above −120°. Un-ionized material will be supervalent. If the acid concentration is decreased, un-ionized alkane will be present in solution together with the carbonium ion.

Quenching of Cycloalkyl Cations. A. With Methanol. The acid solution of the carbonium ion diluted with SO_2ClF or SO_2 is added dropwise to a vigorously stirred slurry of Na_2CO_3 in methanol which is cooled by a Dry Ice-acetone bath. After warming the solution to room temperature, the formed ether is extracted with pentane and isolated after evaporation of the solvent. Methanolysis of all reported ions was carried out and gave generally 70-80% or higher yields of the expected methyl ether.

B. With Water. The solution of the carbonium ion in FSO_3H-SbF_5 or $HF-SbF_5$ is diluted with SO_2ClF or SO_2 and added dropwise to a slurry of ice and sodium carbonate in SO_2 at −78°. After the solution has been warmed up to room temperature the formed alcohol is extracted with ethyl ether and isolated by evaporation of the solvent.

Preparation of Adamantane and Its Derivatives. To 10 g of FSO_3H-SbF_5 (0.032 mol) is added in small amounts 8.6 g (0.064 mol) of tricyclo$[5.2.1.0^{2,6}]$decane over a period of 1 hr. After the addition of 10% of the organic precursor, the adamantyl ion will start to precipitate. Either vigorous stirring or shaking is necessary. After the addition (30 min) has been completed, the slurry is extracted with *n*-pentane. After washing the pentane solution with a solution of sodium carbonate in water, the solvent is evaporated and 4.3 g (0.016 *M*) of adamantane is isolated. Recrystallization is in most cases unnecessary.

1-Adamantanol and methyl 1-adamantyl ether are prepared in the fashion described above for quenching of carbonium ions with methyl alcohol.

Acknowledgment. Support of this work by grants of the National Science Foundation and the National Institute of Health are gratefully acknowledged. Professor P. von R. Schleyer is thanked for a sample of congressane and Professor L. Friedman for a sample of bicyclobutane.

---

[17] H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, 81, 4256 (1959).

Stable Carbonium Ions. LV.[1] Protonated Alicyclic Ketones

George A. Olah and Mihai Calin[2]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received June 12, 1967*

Abstract: The pmr parameters of O-protonated alicyclic ketones in $SbF_5-FSO_3H-SO_2$ and FSO_3H-SO_2 solutions at −60° have been determined. Analysis of the pmr data leads to the conclusion that the structure of protonated ketones is best represented by the oxonium ion resonance form, with little contribution from the hydroxycarbonium ion form.

Evidence has been presented recently[3] that protonation of aliphatic ketones leads to an equilibrium mixture of stereoisomers observable by pmr spectroscopy. It was considered that the cause of stereoisomerism is the double-bond character of the protonated carbonyl group. There is evidence from the pmr study that the hydroxycarbonium ion as a resonance form contributes only in a minor way to the structure of the protonated species, the main resonance form being the oxonium ion. In other words, the nature of this carbon-oxygen bond is only slightly modified by protonation and the positive charge is located mainly on the oxygen atom. The present pmr study was undertaken to provide additional experimental support for this suggestion. Pmr studies of protonated alicyclic ketones have not been reported in the literature.[4]

---

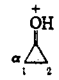
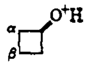
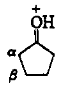
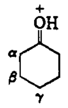
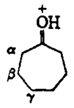
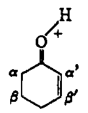
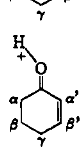
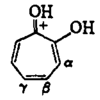
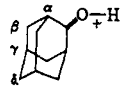
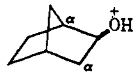
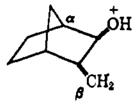
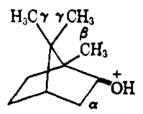
[1] Part LIV: G. A. Olah, J. Lukas, *J. Amer. Chem. Soc.*, 90, 933 (1968).

[2] National Institutes of Health Postdoctoral Research Investigator, 1966-1967.

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

[4] After our work was completed, in a communication M. Brookhart, G. C. Levy, and S. Winstein, *ibid.*, 89, 1735 (1967), reported the observation of the $C{=}OH^+$ absorption in some protonated alicyclic ketones as deshielded singlets.

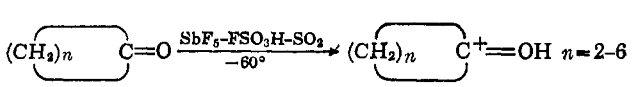
Table I. Pmr Shifts (in ppm) and Coupling Constants (in Hz) of Protonated Alicyclic Ketones[a]

	α-H$_1$	β-H$_2$	γ-H$_3$	δ-H$_4$		OH$^+$
	−2.8 (−1.6)	−2.8 (−1.6)				*b*
	−4.0 (−3.1)	−2.7 (−2.0)				−14.9[c]
	−3.4 (−2.1)	−2.5 (−2.1)				−14.7[d]
	−3.3 (−2.3)	−2.6 (−1.8)	−2.4 (−1.8)			−14.1[e]
	−3.5 (−2.5)	−2.1 (−1.7)	−2.0 (−1.7)			−13.8[e]
	α′ −7.1 (−5.95)	β′ −9.0 (−7.0)	α −3.0 (−2.2)	β −2.3 (−2.2)	γ −3.3 (−2.2)	−12.3 (50%)
	α′ −7.1 (−5.95)	β′ −9.0 (−7.0)	α −3.0 (−2.2)	β −2.3 (−2.2)	γ −3.3 (−2.2)	−12.4 (50%)
	−9.06 (−7.26)	−8.80 (−7.26)	−8.80 (−7.26)			
	−3.5 (−2.56)	−2.73 (−2.06)	−2.40 (−2.06)	−2.30 (−2.06)		−13.85
	−3.9 (−2.6)					−14.1
		−7.1 (−5.5)				−13.5 (72.7%) −14.1 (27.3%)
		−1.3 (−0.98)	−1.2 (−0.92)			−14.1

[a] Chemical shifts of alicyclic ketones in parentheses. [b] Not observable in SO$_2$–FSO$_3$H. [c] Pentuplet, J_{OH-CH_2} = 1.2 Hz. [d] Pentuplet, J_{OH-CH_2} = 1.1 Hz. [e] Unresolved multiplet.

Results and Discussion

Protonated alicyclic ketones give well-resolved spectra in SbF$_5$–FSO$_3$H–SO$_2$ solution at −60°. At higher temperature the rate of proton exchange increases and the peak corresponding to the proton on oxygen broadens.



$$(CH_2)_n\ C{=}O \xrightarrow[-60^\circ]{SbF_5\text{-}FSO_3H\text{-}SO_2} (CH_2)_n\ C^+{=}OH \quad n = 2\text{-}6$$

It was recently found by Turro[5] that cyclopropanone could be synthesized in high yield. Some data on the acid stability were obtained by Turro and Hammond[6] who assumed a slow rate in the rearrangement of protonated cyclopropanone to the hydroxyallyl cation. Hydroxyallyl cations of this type have not been reported previously in the literature but they could be formed by opening the cyclopropanone ring in strong acid solution. The opening of the cyclopropanone ring is indeed very rapid in SbF$_5$–FSO$_3$H–SO$_2$ solution even at −100°. The nmr spectrum of protonated cyclopropanone could be observed, however, in FSO$_3$H–SO$_2$ solution at −80° and shows two peaks at −5.7 and −2.8 ppm with no fine structure (Figure 1). We tentatively interpret this spectrum in terms of a mixture of protonated cyclopropanone (I) and hydroxyallyl cation (II) (65% I and 35% II). Our previous observations of protonated carbonyl compounds show that in FSO$_3$H–SO$_2$ solution the rate of proton exchange cannot be lowered sufficiently by

---

(5) N. J. Turro and W. B. Hammond, *J. Amer. Chem. Soc.*, **88**, 3673 (1966).

(6) N. J. Turro and W. B. Hammond, *ibid.*, **89**, 1028 (1967).

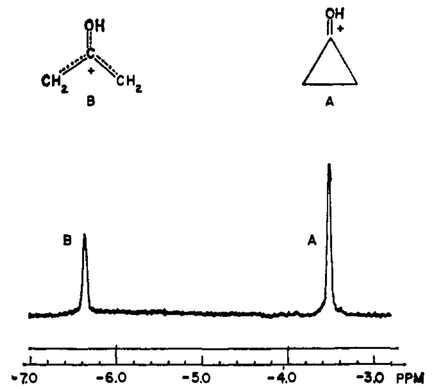


Figure 1.

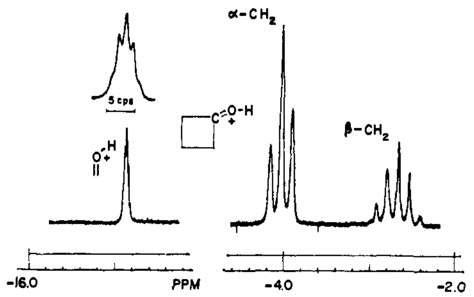
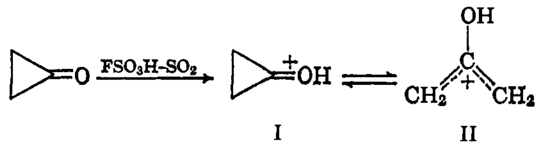
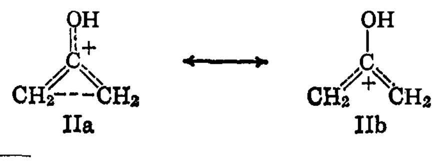


Figure 2.

cooling the sample to −60 to −80° and under these conditions it is not possible to observe the resonance peak of the proton on oxygen. The chemical shifts observed are those expected for the methylene protons of I and II. The ring hydrogens of cyclopropanone (I) are shifted 1.2 ppm downfield. Due to the scarcity of cyclopropanone, our experiments were carried out with extremely small samples which have not allowed the recovery of adequate amounts of the products of the hydrolysis of the protonated ketone for an adequate structural determination. Our results, therefore, for the time being must be considered only tentative and need further confirmation.



The hydroxyallyl cation shows the methylene protons at −5.7 ppm, a downfield shift of 4.1 ppm. Direct observation of the allyl cation has been reported.[7] The chemical shift of the methylene protons is −8.97 ppm. It seems that the difference in the methylene chemical shifts of hydroxyallyl and allyl cations are due to the delocalization of the positive charge not only to the two methylene groups but also to the oxygen atom. The structure of the hydroxyallyl cation is better represented by IIa than IIb.



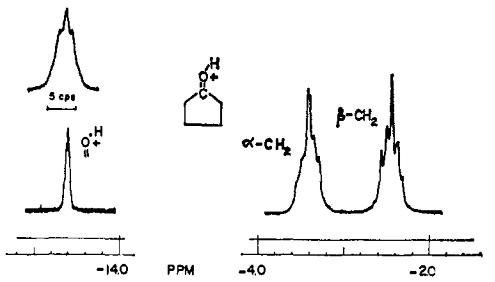
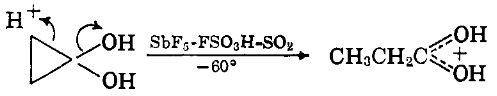


Figure 3.

Protonation of cyclopropanone hydrate in SbF_5–FSO_3H–SO_2 results in a different ring opening from that observed for protonated cyclopropanone. The pmr spectrum of the acidic solution of cyclopropanone hydrate shows two low-field peaks at −12.7 and −12.3 ppm, a quartet at −3.7 ppm, and a triplet at −1.9 ppm. This pattern is that observed for protonated propionic acid under the same conditions.[8]



Under the acidic conditions thus, cyclopropanone hydrate undergoes ring opening with formation of propionic acid.

Protonations of the higher homologs of the alicyclic ketone series give the expected simple nmr spectra (summarized in Table I). The proton on oxygen appears substantially deshielded (−14.9 to −13.8 ppm) with the deshielding increasing as it goes from cycloheptanone to cyclobutanone. The α-hydrogens of the protonated alicyclic ketones are shifted downfield to different degrees. In protonated cyclobutanone (Figure 2) and cyclopentanone (Figure 3) the α-hydrogens are shifted 0.9 and 1.3 ppm, respectively. The shift is 1.0 ppm for protonated cyclohexanone and cycloheptanone. The change in deshielding of the α-hydrogens could be related to charge distribution in the ring conformation, conformer stability, and solvation. It is difficult to determine *a priori* the contribution of each of these terms. Related to the ring conformation and stability of the conformers is also the spin–spin coupling of the proton on oxygen with the α-methylene hydrogens. It has been pointed out that the magnitude of the coupling constant depends on the angle between the carbon–oxygen and the α-carbon–hydrogen bonds.[3,9] The magnitude of the coupling decreases rapidly with increasing ring size. Well-resolved J_{H-OH} coupling is found only for protonated cyclobutanone and cyclopentanone although small coupling is also indicated for protonated cyclohexanone and cycloheptanone by line broadening. The pmr spectra of protonated cyclobutanone and cyclopentanone show the proton on oxygen as a pentuplet (J_{OH-CH} = 1.1 and 1.2 Hz).

Pmr data on the conformation of cyclobutanone have been obtained recently[10a] which confirm the findings based on far-infrared studies[10b] that the carbon skelton of cyclobutanone is planar. It is also generally accepted

---

[7] G. A. Olah and M. Comisarow, *J. Amer. Chem. Soc.*, **86**, 5682 (1964).

[8] G. A. Olah and A. M. White, *ibid.*, **89**, 3591 (1967).

[9] S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

[10] (a) L. L. Combs and L. K. Runnels, *J. Chem. Phys.*, **44**, 2209 (1966); (b) J. R. Durig and R. C. Lord, *ibid.*, **45**, 51 (1966).

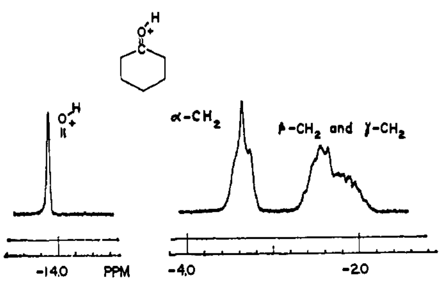


Figure 4.

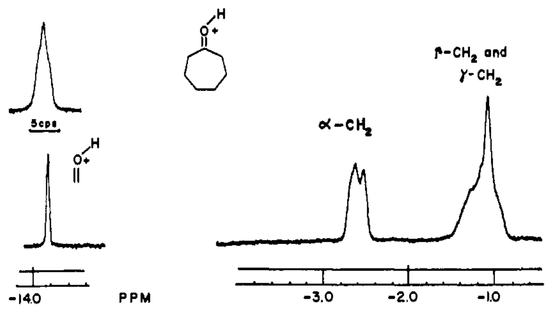


Figure 5.

that cyclopentanone exists in the half-chair conformation[11,12] and cyclohexanone exists in a chair conformation. The latter has the α-equatorial hydrogens approximately eclipsed with the carbon–oxygen bond.[12] It has been assumed[12] that there is a low barrier to the twist conformation of cyclohexanone because the interaction between the neighboring equatorial hydrogens and the carbonyl oxygen is partially eliminated in the twist conformation. From the magnitude of the spin–spin coupling of the proton on oxygen with the α-methylene hydrogens some information concerning the ring conformation of the protonated alicyclic ketones can be deduced. For a carbon skeleton the allylic coupling was found[6] to be a minimum when the dihedral angle mentioned above is 0° and consequently the coupling would be at a maximum when the angle is 90°. It is noteworthy that the proton on oxygen in protonated cyclobutanone and cyclopentanone appears as a pentuplet. The quintuplet structure of the proton on the carbonyl group in protonated cyclobutanone probably results from the methylene groups being coupled to each other and both coupled to the proton on oxygen. The spectrum is deceptively simple, and the observed coupling constant is an average of the *cis-* and *trans-*allylic coupling constants. An analogous *trans*-allylic coupling was encountered in protonated diisopropyl ketone and to a lesser degree in protonated diethyl ketone.[3] The dihedral angle in protonated cyclohexanone (Figure 4) is optimum for an allylic coupling only for the axial hydrogens of the chair conformation and a triplet should be expected for the proton on oxygen. In the twist conformation, the dihedral angle becomes smaller and so does the coupling. The experimental facts can be interpreted in terms of a changing conformation even at low temperature and the small coupling observed is an average of the coupling in different conformers. The unresolved resonance of the proton on oxygen in protonated cycloheptanone (Figure 5) can be explained in the same manner.

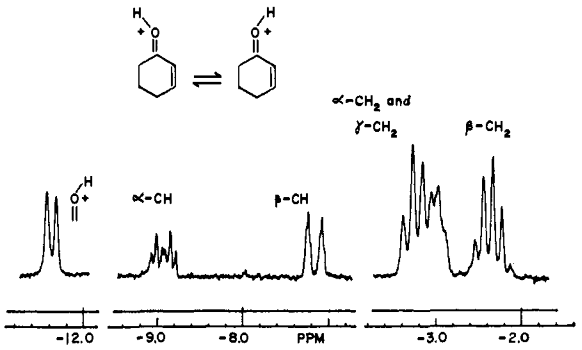


Figure 6.

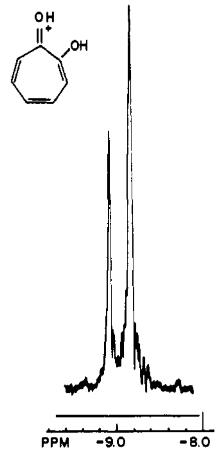
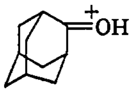


Figure 7.

In order to confirm the allylic-type coupling in protonated ketones we investigated protonated 2-adamantanone (III), the rigid structure of which seemed suitable for this purpose. The pmr spectrum of protonated 2-adamantanone (Figure 11) shows the O–H resonance as a sharp singlet at −13.85 ppm. This is exactly what is to be expected because the α-hydrogens and the proton on oxygen are eclipsed corresponding to a minimum of an allylic-type spin–spin coupling. The analogy between the allylic coupling in C=C systems with the related coupling in $C{=}^{+}OH$ systems observed in the present work is justified by this observation.



III

Protonated 2-cyclohexen-1-one (Figure 6) gives rise to two stereoisomers, IVa and IVb. The protons on oxygen are less deshielded than in protonated cyclohexanone and appear as singlets at −12.3 and −12.4 ppm. The olefinic β-hydrogens are more deshielded than the α-hydrogens as a consequence of the delocalization of the positive charge through the conjugated double bond. The proton on oxygen could be observed only at −90°. In the pmr spectrum of protonated tropolone (Figure 7), the downfield shift of the ring hydrogens is larger than those observed for protonated alicyclic ketones and the exchanging protons on both oxygens are not visible in the spectrum even at −95°.

---

(11) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 251.

(12) M. Hanack, "Conformation Theory," Academic Press Inc., New York, N. Y., 1965, p 78.

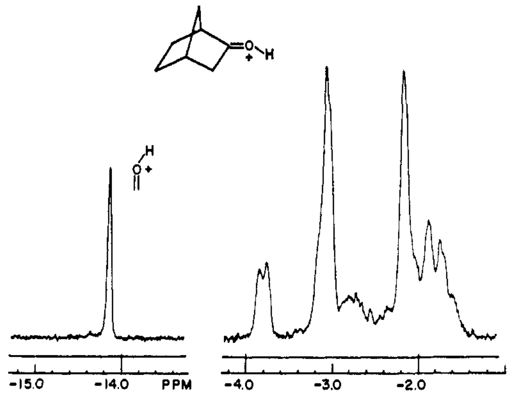


Figure 8.

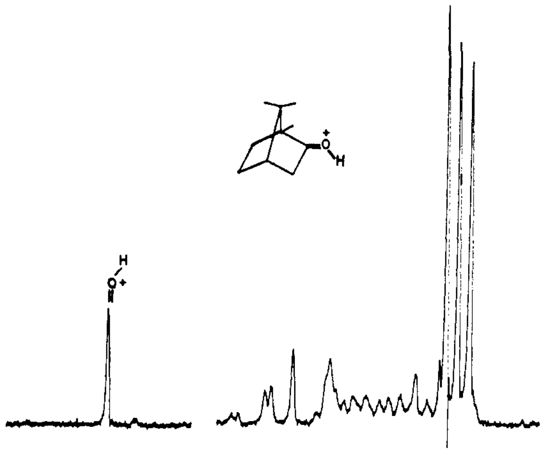
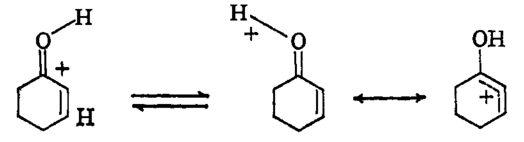
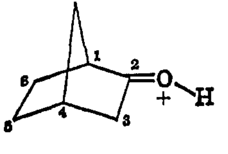


Figure 9.

The spectra of protonated bicyclic ketones such as 2-norbornanone (Figure 8) and *dl*-camphor (Figure 9) show the protonated carbonyl resonance as singlets at −14.1 ppm. One would expect the existence of *syn* and *anti* isomers for the proton on oxygen. It seems in these cases that one of the isomers is preferred. Knowing that the stability of stereoisomers is sterically controlled, that the *cis*-allylic coupling is generally larger than the *trans*-allylic, and also that the allylic coupling is at a minimum when the hydrogen on the α-carbon is eclipsed with the plane of the carbonyl group, we can make a reasonable assumption about the stereochemistry of the observed isomer. Thus the hydrogen on oxygen is *cis* to the hydrogens in the 3 position of the norbornanone ring. The same conclusion is true for protonated camphor.



IVa IVb IVc



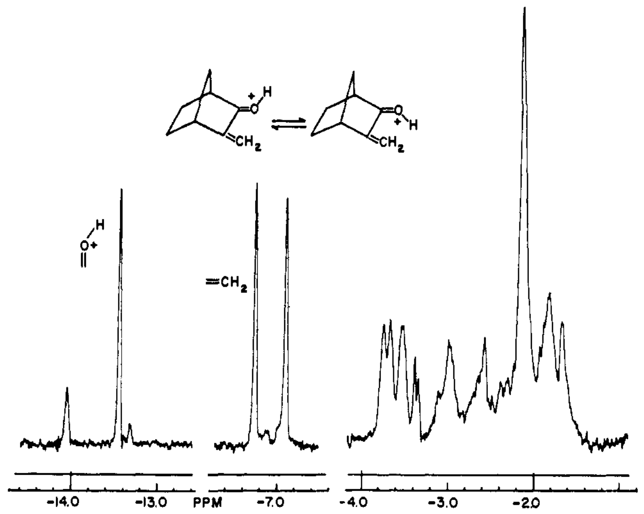


Figure 10.

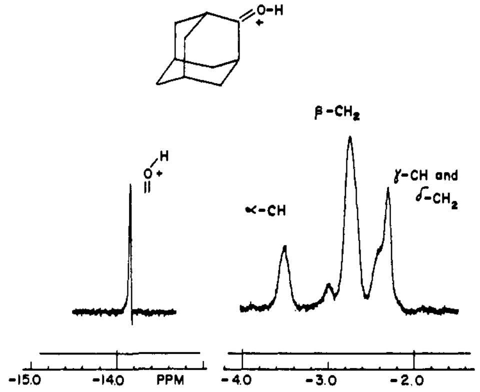
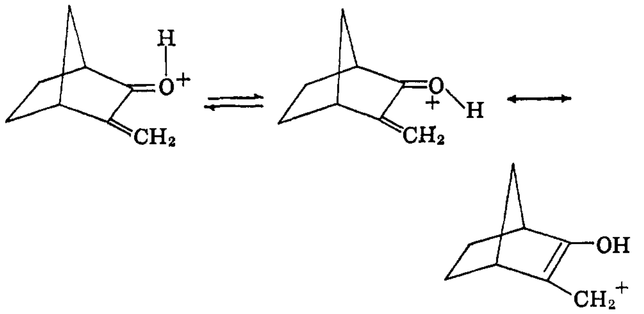


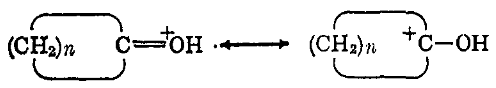
Figure 11.

It should be noted that the *cis*-allylic coupling with the C-3 hydrogens is not measurable although the absorption peak is broad even at −85°.

In protonated 3-methylene-2-norbornanone (Figure 10) the hydrogen on oxygen appears at −14.1 and −13.5 ppm corresponding to two isomers and is close to the chemical shifts observed for the protonated carbonyl in saturated alicyclic ketones. Significant contribution to the structure of the hydroxycarbonium ion resonance from V seems very limited.



From the pmr data of protonated saturated alicyclic ketones it can be concluded that VI represents the major resonance and the hydroxycarbonium ion from VII is of lesser importance.



VI VII

Experimental Section

Materials. Samples of cyclopropanone and cyclopropanone hydrate were kindly given by Professor N. J. Turro whom we thank for his help. All the other alicyclic ketones were reagent grade commercial chemicals and used without further purification.

Nmr Spectra. A Varian Associates Model A-56-60A nmr spectrometer with variable-temperature probe was used for all spectra. External TMS was used as reference (sealed capillary tube). The coupling constants are accurate to within 0.1 Hz.

Preparation of Protonated Alicyclic Ketones. Samples of protonated ketones were prepared by dissolving 1.5 ml of SbF_5–FSO_3H (1:1 *M* solution) in an equal volume of sulfur dioxide and cooling to −78°. The ketone (0.2–0.3 ml) was dissolved in 1 ml of sulfur dioxide, cooled to −78°, and with vigorous agitation dropwise added to the acid solution. The cyclopropanone was used as 0.5 *M* solution in methylene chloride. The excess of acid was always indicated in the spectra by the intense peak at −10.9 ppm. This peak and that of H_3O^+ at about −10.5 ppm were deleted from the spectra (Figures 1–11) for simplicity.

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

Stable Carbonium Ions. LVI.[1a] Diphenylpyridinyl- and Phenylmethylpyridinylcarbonium Ions

George A. Olah and Mihai Calin[1b]

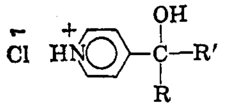
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received June 12, 1967*

Abstract: As model compounds for the study of dication systems, the isomeric diphenyl-2-, -3-, and -4-pyridinyl- and phenylmethylpyridinylcarbonium ions were investigated by nmr spectroscopy in SbF_5–FSO_3H–SO_2 solution at −30°. The *p*-tolylmethyl-4-pyridinylcarbonium ion was also investigated in the same acid system.

The stability of dicarbonium ions is known to be related to the distance and the type of separation of the positive charges. We have recently observed simple alkyldicarbonium ions[2] and alkylenedioxodicarbonium ions.[3] Looking for model compounds in the investigation of dication systems we felt it of interest to extend our studies to the isomeric diphenylpyridinyl- and phenylmethylpyridinylcarbonium ions. In the isomeric diphenyl- and phenylmethyl-2-, -3-, and -4-pyridinylcarbonium ions the proximity effects of the two positive charges can be compared. The behavior of diphenyl-2-pyridylmethanol and diphenyl-4-pyridylmethanol in 100% sulfuric acid has been studied by their vibrational spectra and by cryoscopy of the systems.[4] We wish to report now a systematic nmr investigation of isomeric diphenyl-2-, -3-, and -4-pyridyl- as well as phenylmethylpyridylmethanols in the extremely strong acid system fluorosulfonic acid–antimony pentafluoride (1:1 *M*).

Results and Discussion

In order to gain a better understanding of the pyridinylcarbonium ions to be investigated, first we studied the corresponding monocations (pyridinylmethanols). The isomeric diphenyl- and phenylmethyl-2-, -3-, and -4-pyridinylmethanols were investigated as the hydrochloride salts in sulfur dioxide solution at −60°.



R = phenyl or methyl

It was found that they give well-resolved nmr spectra with the rate of exchange of the proton on nitrogen slow enough to observe this resonance peak as a broad singlet. Comparison of the chemical shifts of the free bases with those of the conjugated acids (pyridinium hydrochlorides) helps to understand the charge distribution in the pyridinium ring systems. For any given pyridine isomer, the deshielding effect of N-protonation is generally independent of substituents on the pyridine ring (data summarized in Table I and II).

The nmr spectra of the N-protonated phenylmethylpyridylmethanols show a significant deshielding of the pyridinium ring hydrogens. The effect on the pyridine ring hydrogens is smaller for the C-2 and C-6 hydrogens than for the C-3, C-4, and C-5 hydrogens. The same observation can be made from the nmr study of diphenylpyridinylmethanol. The methyl and phenyl hydrogens are not deshielded (compared with the starting phenylmethyl- and diphenylpyridylmethanols), and their resonance position changes only within the limits of the solvent effect.

The NH^+ proton is observable in the nmr spectra only at low temperature and is at a rather low field. The significance of the deshielding effect was discussed for the pyridinium ion itself,[5] as were deshielding effects on

---

[1] (a) Part LV: G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, **90**, 938 (1968); (b) National Institutes of Health Postdoctoral Research Investigator, 1966–1967.

[2] J. M. Bollinger, C. A. Cupas, K. J. Friday, M. L. Woolfe, and G. A. Olah, *J. Amer. Chem. Soc.*, **89**, 156 (1967).

[3] G. A. Olah and M. B. Comisarow, *ibid.*, **88**, 3313 (1966).

[4] H. A. Smith and L. W. Holley, *ibid.*, **80**, 3714 (1958).

[5] W. M. S. Gil and J. N. Murell, *Trans. Faraday Soc.*, **60**, 248 (1964).