Preparation of 2-Bromo-3-acetoxy-2,3-dimethylbutane. This compound was prepared in the same way as the chloro derivative using N-bromosuccinimide. From 0.05 mole of reagents there was obtained 8.6 g, 77%, of compound, bp 73–77° (9 mm). The analytical sample was a center cut, bp 74°.

Anal. Calcd for $C_8H_{15}BrO$: C, 43.07; H, 6.77; Br, 35.81; O, 14.34. Found: C, 43.31; H, 6.93; Br, 35.36; O, 14.40.

Preparation of 2-Iodo-3-acetoxy-2,3-dimethylbutane. This compound was prepared in the same way as the bromo derivative using N-iodosuccinimide and maintaining the temperature at 0°. From 0.05 mole of reagents there was obtained 7.6 g, 50%, of desired compound. This material was unstable and had to be stored at −78°. It could be stabilized with sodium sulfite. Attempted purification by vacuum distillation resulted in decomposition. This material was used without purification. The absence of appreciable extraneous absorptions in its pmr spectrum indicates better than 90% purity.

Acknowledgment. Support of this work by a grant of the National Science Foundation is gratefully acknowledged. Microanalyses were carried out by Galbraith Laboratories, Knoxville, Tenn. We acknowledge the following undergraduate participants for their participation in this work: Karen Friday, for the preparation of pinacol dichloride; Mark Woolfe, for the preparation of pinacolone dichloride; and Jean Brinnick, for the preparation of 2,3-dimethyl-2-acetoxy-3-iodobutane.

Stable Carbonium Ions. XLIX.[1] Protonated Dicarboxylic Acids and Anhydrides and Their Cleavage to Oxocarbonium Ions

George A. Olah and Anthony M. White[2]

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

Abstract: A series of diprotonated aliphatic dicarboxylic acids (alkylenedicarboxonium ions) have been studied in $HSO_3F-SbF_5-SO_2$ solution. O-diprotonation was observed with negligible exchange rates at low temperature by nmr spectroscopy. Glutaric, adipic, and pimelic acids were found to cleave at higher temperatures, first to the alkylenemonooxocarbonium-monocarboxonium ions, and then to the alkylenedioxocarbonium ions. Only the monooxocarbonium ion was observed in the case of succinic acid. Protonated oxalic and malonic acids did not cleave in the acid system. Protonation of dicarboxylic acid anhydrides in $FSO_3H-SbF_5-SO_2$ solution, even at −90°, leads to a mixture of the corresponding monocarboxonium-monooxocarbonium ion.

The isolation of alkylenedioxocarbonium ion salts from dicarboxylic acid fluorides and antimony pentafluoride has been reported recently.[3] In continuation of our previous work on the observation of the formation of oxocarbonium ions from protonated aliphatic carboxylic acids in FSO_3H-SbF_5,[4] we now report the formation of dioxocarbonium ions from protonated aliphatic dicarboxylic acids.

Results and Discussion

The ionization of saturated dicarboxylic acids in sulfuric acids has been investigated by cryoscopy,[5] and it was concluded that succinic acid and higher members of the series are only partially ionized as diacid bases ($i = 2.6$). Malonic acid was reported to be only monoprotonated ($i = 2.0$) and oxalic acid gave an i factor of 1.3 which increased with time due to decomposition. Pittman[6] has studied the change in nmr band positions of adipic acid in H_2SO_4–oleum and found a downfield shift in the α-proton signal in 17% oleum, but was unable to assign the species under observation on the available evidence.

In the strong acid system, FSO_3H-SbF_5, all the aliphatic dicarboxylic acids studied were completely diprotonated, and we were able to observe, in certain cases, cleavage to the corresponding monocarboxonium–monooxocarbonium ion and dioxocarbonium ions.

$$HO_2C(CH_2)_nCO_2H \xrightarrow[-60^\circ]{FSO_3H-SbF_5-SO_2}$$

$$H_2\overset{+}{O}_2C(CH_2)_n\overset{+}{C}O_2H_2 \xrightarrow[\Delta(-H_2O)]{FSO_3H-SbF_5-SO_2}$$

$$H_2\overset{+}{O}_2C(CH_2)_n\overset{+}{C}O \xrightarrow[\Delta(-H_2O)]{FSO_3H-SbF_5-SO_2} \overset{+}{O}C(CH_2)_n\overset{+}{C}O$$

The following aliphatic dicarboxylic acids were examined in $FSO_3H-SbF_5-SO_2$ solution: oxalic, malonic, glutaric, adipic, and pimelic acids.

Diprotonated Dicarboxylic Acids (Alkylenedicarboxonium Ions). Dicarboxylic acids, with the exception of oxalic acid, gave well-resolved nmr spectra in FSO_3H-SbF_5 solution diluted with SO_2. To observe the protons on oxygen, it was necessary to record the spectra, in general, at lower temperatures (−90°) than in the case of the monocarboxylic acids[3] because of the more weakly basic nature of the diacids. At these low temperatures, the C–H protons sometimes show broadening, and the coupling constants between methylene protons were evaluated from spectra recorded at −40°. Table I summarizes the coupling constants and chemical shifts. Representative spectra are given in Figures 1–4. Integration of the peaks indicated four protons

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[1] Part XLVIII: G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, **89**, 4744 (1967).

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

[3] G. A. Olah and M. B. Comisarow, *J. Am. Chem. Soc.*, **88**, 3313 (1966).

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

[5] A. Wiles, *J. Chem. Soc.*, 996 (1953).

[6] C. U. Pittman, Jr., Ph.D. Thesis, The Pennsylvania State University, 1964.

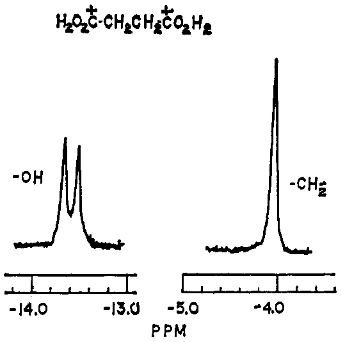


Figure 1.

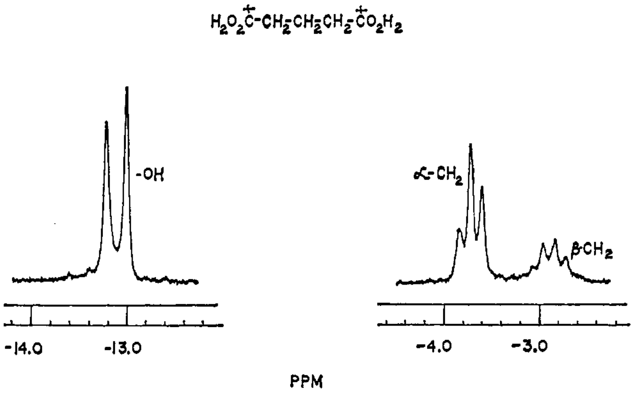


Figure 2.

on oxygen. This shows that all investigated dicarboxylic acids exist in the acid solution as diprotonated species.

$$(CH_2)_n(CO_2H)_2 \xrightarrow{FSO_3H-SbF_5-SO_2} (CH_2)_n(CO_2H_2)^{2+}$$

Table I. Nmr Chemical Shifts (in ppm)[a] and Coupling Constants (in Hz) of Protonated Dicarboxylic Acids (Alkylenedicarboxonium Ions)

Acid	Temp, °C	OH	CH_2
$(COOH)_2$	−90	−15.70	
$(CH_2)(COOH)_2$	−90	−14.60	−5.23
$(CH_2)_2(COOH)_2$	−70	−13.68	−4.08
		−13.52	
$(CH_2)_3(COOH)_2$	−70	−13.25	−3.70[a]
		−13.05	−2.87[b]
$(CH_2)_4(COOH)_2$	−60	−12.98	−3.53[b]
		−12.72	−2.35[c]
$(CH_2)_5(COOH)_2$	−60	−12.77	−3.43[b]
		−12.50	−2.08[d]

[a] Referred to external TMS. [b] Triplet, J = 7 Hz. [c] Pentuplet, J = 7 Hz. [d] Multiplet.

In the case of oxalic acid, the large deshielding observed suggested that this acid, too, was diprotonated. At −90° both the protons on oxygen and the acid solvent had nmr signals which were considerably broadened, indicative of exchange. We attempted to confirm that oxalic acid was indeed diprotonated by integration of the $-OH^+$ protons against an internal standard (tetramethylammonium hexafluoroantimonate) but found that the low solubility of protonated oxalic acid at −90° prevented us from obtaining reproducible results.

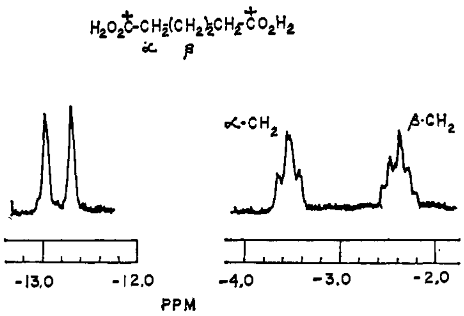


Figure 3.

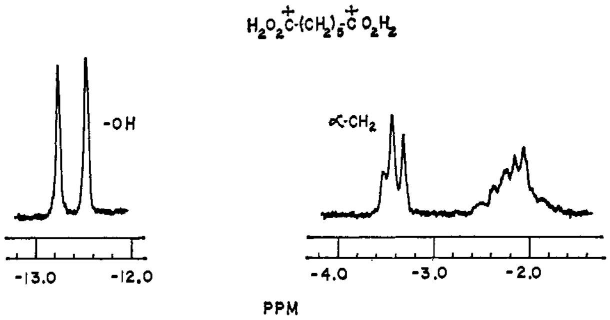
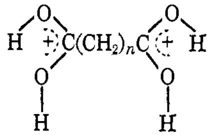


Figure 4.

Succinic, glutaric, adipic, and pimelic acids all have two peaks of equal area in the hydroxyl region at low temperature indicating, as in the case of aliphatic monocarboxylic acids, that protonation is occurring on the carbonyl oxygen and that the two protons have nonequivalent environments. This is interpreted, as in the case of protonated monocarboxylic acids,[4] as a consequence of structure I being the predominant species.



I

The temperature at which collapse to a single absorption occurs decreased with decreasing separation of the acid functions, and in the case of malonic and oxalic acids, only a single absorption peak was observed at the lowest temperature studied (−90°).

The chemical shift of the OH peaks appears to be very dependent on chain length, and the results suggest a correlation between the basicity of the carbonyl oxygens and the chemical shift of the hydroxyl protons. A similar correlation has been noted in the case of protonated cyclic ketones for which basicity data are available.[7]

Diprotonated "Squaric Acid." 1,2-Dihydroxycyclobutenedione ("squaric acid") is to be considered as a dicarboxylic acid. In many of its reactions[8,9] squaric acid behaves as a strong organic acid because of the resonance stabilization of its dianion. The dication, if squaric acid were diprotonated and the hydroxycarbonium ion was a contributor to the structure,

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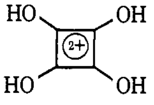
(7) G. A. Olah and M. Calin, *J. Am. Chem. Soc.*, **89**, 4736 (1967).

(8) G. Maaks and P. Hegenberg, *Angew. Chem. Intern. Ed. Engl.*, **5**, 888 (1966).

(9) D. T. Ireland and H. F. Walton, *J. Phys. Chem.*, **71**, 751 (1967).

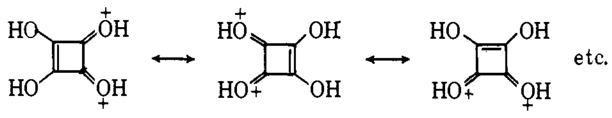
would formally be a Hückel aromatic system. The cyclobutenium dication form (II) would be expected to exert a strong stabilizing influence with significant delocalization of the positive charge from the oxygen atoms into the ring.



II

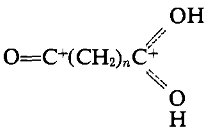
We have found that in all other oxygen-protonated species examined, the chemical shift of the proton on oxygen is a good measure of the distribution of charge in the molecule. Observation of the hydroxyl protons in diprotonated squaric acid should thus provide a measure of the contribution from the dicyclobutenium dication form of the molecule. The only previous report of protonated species from squaric acid is the suggestion that the changes in the ultraviolet absorption spectrum of squaric acid found in acidic media (1 *M* sulfuric acid) was a result of protonation.[9]

We found that squaric acid in $FSO_3H-SbF_5-SO_2$ solution at −90° gives a single peak in the nmr spectrum at −14.50 ppm. This large deshielding is comparable with that found in diprotonated malonic acid, and we feel that this result implies that there is no significant contribution of the cyclobutenium dication to the stability of this molecule. We suggest that the predominant resonance forms of diprotonated squaric acid are of the type indicated below.



On raising the temperature, exchange with the solvent is observed, as in other protonated dicarboxylic acids. At −70°, we observed the appearance of a new peak at −13.67 ppm. This was about 10% of the area of the low-field OH^+ peak and disappeared on lowering the temperature again to −90°. As yet the identity of this new species has not been established.

Cleavage of Alkylenedicarboxonium Ions to Alkylenemonooxocarbonium–Monocarboxonium Ions. The ease with which alkylenedicarboxonium ions (diprotonated dicarboxylic acids) can be dehydrated diminishes with decreasing separation between the acid functions. Pimelic, adipic, and glutaric acids cleave under conditions similar to the protonated monocarboxylic acids previously studied[4] ($t_{1/2}$ about 1 hr at −20°), the changes in the nmr spectra being consistent with the formation of a monooxocarbonium–monocarboxonium ion having the structure III.


$$O{=}C^+(CH_2)_nC\overset{\displaystyle OH}{\underset{\displaystyle \overset{|}{O}H}{\overset{+}{}}}$$

III

The downfield shifts of the methylene protons on cleavage of the diprotonated dicarboxylic acid to the monooxocarbonium ion are very similar to the shifts found in the dehydration of protonated alkylcarboxylic acids and are about 1.0, 0.5, and 0.2 ppm for the methylene protons α, β, and γ to the oxocarbonium center in both series.

Succinic acid cleaves to the extent of *ca.* 50% in $FSO_3H-SbF_5-SO_2$, indicating that an equilibrium is reached between the diprotonated acid and the monooxocarbonium ion, as is observed with protonated monocarboxylic acids in H_2SO_4–oleum[10] or in $HF-BF_3$.[11] Increasing the strength of the acid by using neat FSO_3H-SbF_5 permitted the reaction to go to completion.

Malonic (and probably oxalic) acid did not give an oxocarbonium ion under experimental conditions, thus setting a limit on the strength of the acid system.

Chemical shifts and coupling constants of the alkylenemonooxocarbonium–monocarboxonium ions are tabulated in Table II and spectra of the ions are shown in Figures 5 and 6.

Table II. Nmr Chemical Shifts and Coupling Constants of Alkylenemonooxocarbonium–Monocarboxonium Ions

$$[O{=}\overset{+}{C}\overset{\alpha}{C}H_2\overset{\beta}{C}H_2(\overset{\gamma}{C}H_2)_nCO_2H_2^+]$$

Acid precursor	Temp, °C	OH	CH_2 (α)	CH_2 (β)	CH_2 (γ)
$(CH_2)_2(COOH)_2$	−90	−14.43 −14.27	-5.15^a	−4.47	...
$(CH_2)_3(COOH)_2$	−70	−13.47 −13.37	-4.70^b	-3.80^b	-3.2^c
$(CH_2)_4(COOH)_2$	−60	−13.15 −12.92	-4.60^b	-3.62^b	-2.8^d
$(CH_2)_5(COOH)_2$	−60	−12.85 −12.58	-4.48^b	-3.47^b	-2.8^d

[a] Broad triplet. [b] Triplet, J = 7 Hz. [c] Pentuplet, J = 7 Hz. [d] Multiplet.

Formation of Alkylenedioxocarbonium Ions. Loss of a second water molecule from protonated glutaric, adipic, and pimelic acids occurs between −20 and 10°. In the cases of adipic and pimelic acids, the acid functions are sufficiently well separated for the loss of the second water molecule to occur at a similar rate to that of the first, giving generally a mixture of the mono- and dioxocarbonium ions. Assignments for these species given in Table II are based on observations of the changes of the spectra with time. Glutaric acid could only be taken to a 50% equilibrium mixture of the dioxo- and monooxocarbonium ions in neat FSO_3H-SbF_5 at 0°. Increasing the temperature to +50° caused no significant change in the equilibrium position.

Table III. Nmr Chemical Shifts (in ppm) and Coupling Constants (in Hz) of Alkylenedioxocarbonium Ions in FSO_3H-SbF_5 at 0°

Dioxocarbonium ion	CH_2 (α)	CH_2 (β)	CH_2 (γ)
$O\overset{+}{C}(CH_2)_3C\overset{+}{O}$	-4.90^a	-4.17^b	...
$O\overset{+}{C}(CH_2)_4C\overset{+}{O}$	-4.72^b	-3.02^b	...
$O\overset{+}{C}(CH_2)_5C\overset{+}{O}$	-4.55^a	-2.82^b	-2.20^b

[a] Triplet, J = 7 Hz. [b] Multiplet.

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(10) N. C. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *J. Am. Chem. Soc.*, **86**, 4370 (1964).

(11) H. Hogeveen, *Rec. Trav. Chim.*, **86**, 289 (1967).

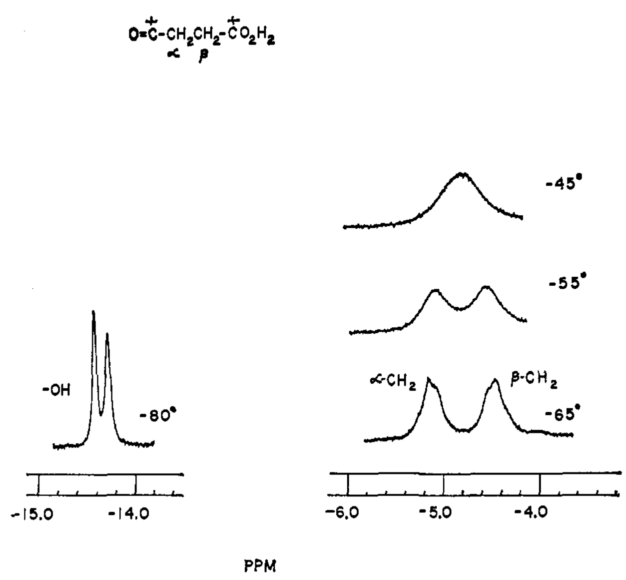


Figure 5.

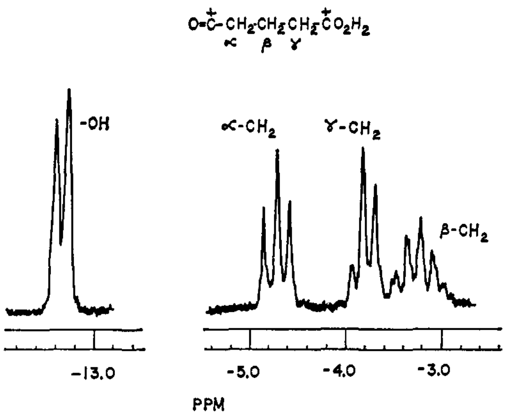


Figure 6.

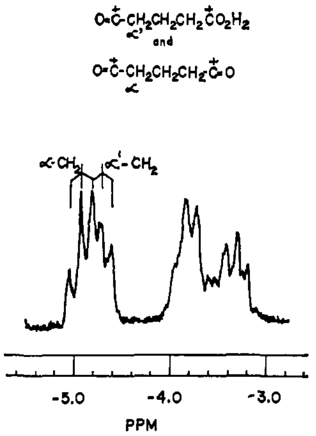


Figure 7.

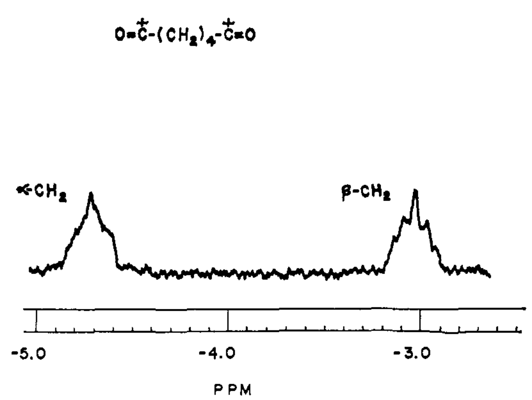


Figure 8.

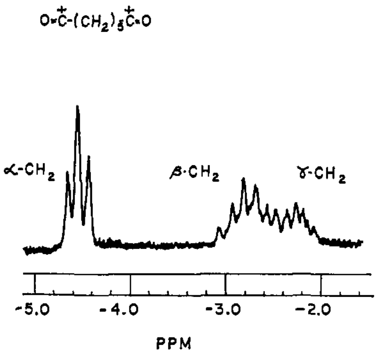
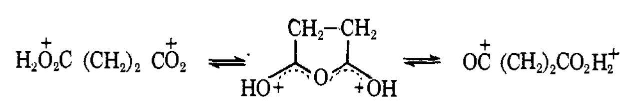


Figure 9.

The nmr spectra of the dioxocarbonium ions (see Table III and Figures 7-9) agree well with those previously reported for solutions of the SbF_6^- salts in SO_2 solution[4] though, as in the case of the formation of oxocarbonium ions from the protonated monocarboxylic acids, a downfield medium effect was noted. The fact that succinic acid would not give a dioxocarbonium ion is consistent with the observation that the diacid fluoride gives only a monooxocarbonium ion mono-donor-acceptor complex with SbF_5.[4]

Protonated Anhydrides and Their Cleavage. The anhydrides of succinic and glutaric acids were examined in FSO_3H-SbF_5-SO_2 solutions as an alternative route to the oxocarbonium ions. The protonated anhydrides could not be observed even when solutions were prepared and examined at −80°. In both cases the nmr spectra obtained corresponded to the alkylenemono-oxocarbonium-monocarboxonium ion formed from the protonated dicarboxylic acids. The existence of protonated anhydrides as intermediates was suggested by the observation that the two triplets in the mono-oxocarbonium ion from succinic acid collapsed reversibly to a single peak at −45°, suggesting an intramolecular rearrangement through a cyclic intermediate.



The observation that diprotonated cyclic anhydrides exist in the open-chain form led us to examine other anhydrides. Acetic and propionic anhydrides also show similar behavior and exist in FSO_3H-SbF_5-SO_2 as a 1:1 mixture of the oxocarbonium ion and the protonated acid.

$$(RCO)_2O \xrightarrow[-80°]{FSO_3H\text{-}SbF_5\text{-}SO_2} R\overset{+}{C}O + RCO_2H_2^+$$

This observation is in accord with the reported fourfold depression of freezing point by acetic anhydride in sulfuric acid.[12] Succinic anhydride was reported to be only partially protonated in sulfuric acid.[12]

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[12] R. J. Gillespie and J. A. Leisten, *Quart. Rev.* (London), **8**, 40 (1954).

Experimental Section

Materials. All dicarboxylic acids and anhydrides were reagent grade commercial chemicals. They were used without further purification except for glutaric anhydride which was found to be contaminated with the acid. Repeated recrystallizations from diethyl ether were used to purify this compound.

Formation of Ions and Their Nmr Spectra. A Varian A-56-60A nmr spectrometer with variable-temperature probe was used for all spectra. Solutions were prepared at −80° using a 1:1 *M* solution of HSO_3F–SbF_5 and SO_2 as a diluent according to procedures described previously.[4] Chemical shifts were referred to external capillary TMS.

Acknowledgment. Support of this work by a grant of the National Institutes of Health is gratefully acknowledged (GM 14082-01).

Stable Carbonium Ions. L.[1] Protonated Imines

George A. Olah and Paul Kreienbühl[2]

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

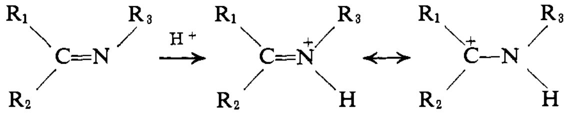
Abstract: Nuclear magnetic resonance study of protonated aldimines and ketimines in fluorosulfonic acid, fluorosulfonic acid–antimony pentafluoride, and deuteriosulfuric acid–antimony pentafluoride solution indicates the predominance of immonium structure ($R_1R_2C{=}N^+HR_3$), with only limited contribution of aminocarbonium ion forms ($R_1R_2C^+$–NHR_3).

The properties of the imine bond (>C=N) and the carbonyl bond (>C=O) are related and in some of their reactivity, imines and carbonyl compounds show similarity.[3]

In continuation of our previous work on protonated aldehydes,[4] ketones,[5] and esters,[6] we have now extended our investigation to protonated imines. We were particularly interested whether the contribution of aminocarbonium ion forms, as suggested by Deno,[7] could be substantiated.

Results and Discussion

Protonated aldimines and ketimines were observed by nmr spectroscopy in the extremely strong acid systems, FSO_3H, FSO_3H–SbF_5, or D_2SO_4–SbF_5 using SO_2 as diluent.


I II

The protonated imines give well-resolved nmr spectra. However, the N–H proton appears to broaden due to the quadrupole interaction of the nitrogen-14 and cannot always be observed. The failure to observe the N–H proton in some cases is not due to rapid exchange since splitting of adjacent protons by the N–H proton is always observed. Coupling contributes to N–H peak broadenings. Nuclear magnetic resonance spectroscopy offers a possibility of investigating whether the immonium salt structure I is the only contributing form of protonated imines or if there is evidence for some aminocarbonium ion character (II). The nmr data of protonated imines are summarized in Table I. Neat N-propylidenemethylamine shows a long-range coupling from the C-methyl to the N-methyl groups, $J_{H-H}trans$ = 1.35 Hz, $J_{H-H}cis$ = 0.7 Hz, which is analogous to homoallylic coupling. The most commonly observed examples of homoallylic coupling are interactions between vicinal vinylic protons in various butene derivatives,[8] and the size of such a coupling constant was proposed as a possible measure of the π character of a C=C double bond.[9] The nmr spectrum of the protonated N-propylidenemethylamine in SO_2 at −20° (Figure 1) shows a doublet for the N-methyl groups (J_{HNCH_3} = 5.0 Hz) at −3.96 ppm. The C-methyl group appears as two lines, at −3.08 and −3.02 ppm. There is no long-range coupling observable. The chemical shift of a methyl group adjacent to a positive carbon atom is expected at −4.5 ppm.[10] This is at substantially lower field than is observed in protonated N-propylidenemethylamine. However, the result could be understood in two ways: either as an immonium salt (I) where the two C-methyl groups are nonequivalent, or as an aminocarbonium ion (II), where the C-methyl groups are coupled to the NH proton through the positively charged C atom and split into a doublet. To distinguish between the two possibilities, we obtained the nmr spectrum in D_2SO_4–SbF_5 in SO_2. The two C-methyl groups remain unchanged. Therefore they are nonequivalent, clearly indicating that there is no free rotation around the carbon–nitrogen bond. Thus the aminocarbonium ion form can be eliminated.

The nmr spectra indicate that protonated N-propylidenemethylamine exists mainly as immonium salt

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(1) Part XLIX: G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **89**, 4752 (1967).

(2) National Science Foundation Postdoctoral Research Investigator, 1966–1967.

(3) For reviews, see M. M. Spring, *Chem. Rev.*, **26**, 297 (1940).

(4) G. A. Olah, D. H. O'Brien, and M. Calin, *J. Am. Chem. Soc.*, **89**, 3582 (1967).

(5) G. A. Olah, M. Calin, and D. H. O'Brien, *ibid.*, **89**, 3586 (1967).

(6) G. A. Olah, D. H. O'Brien, and A. M. White, *ibid.*, in press.

(7) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1963).

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

(9) G. O. Dudek, *J. Am. Chem. Soc.*, **85**, 694 (1963).

(10) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. Bastien, *ibid.*, **86**, 1360 (1964).