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

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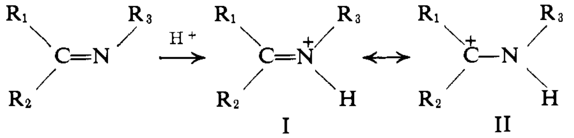
Abstract: Nuclear magnetic resonance study of protonated aldimines and ketimines in fluorosulfonic acid, fluorosulfonic acid–antimony pentafluoride, and deuteriosulfuric acid–antimony pentafluoride solution indicates the predominance of immonium structure ($R_1R_2C{=}N^+HR_3$), with only limited contribution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

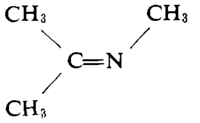
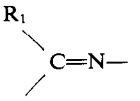
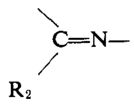
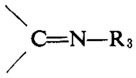
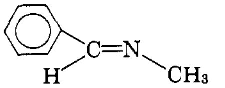
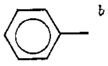
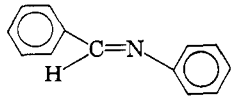
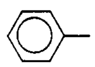
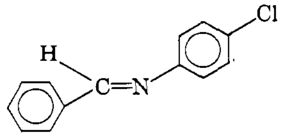
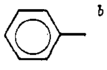
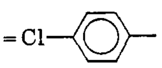
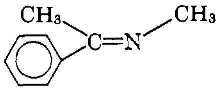
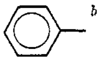
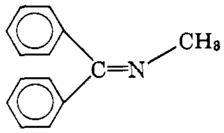
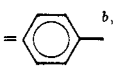
(7) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1963).

(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).

Table I. Nmr Chemical Shifts and Coupling Constants of Protonated Imines[a]

	Temp, °C	 R_1 = CH_3 −δ, ppm	J, Hz	Δδ, ppm	 R_2 = CH_3 −δ, ppm	Δδ, ppm	 R_3 = CH_3 −δ, ppm	J, Hz	Δδ, ppm	NH −δ, ppm
Neat	−30	1.88 (4)	1.35	...	1.75 (4)	...	2.95 (cm)	...	...	...
HSO_3F-SbF_5-SO_2	−60	2.82 (1)	0	0.94	2.73 (1)	0.98	3.66 (2)	5.1	0.71	9.53
HSO_3F-SbF_5	−20	3.08 (1)	0	1.20	3.02 (1)	1.27	3.96 (2)	5	1.01	9.83
D_2SO_4-SbF_5-SO_2	−30	2.88 (1)	0	1.00	2.81 (1)	1.05	3.68 (1)	≈0	0.73	...
		R_1 = H			R_2 =  [b]		R_3 = CH_3			
Neat	38	8.04 (4)	1.6	...	7.54 (cm)	...	3.33 (2)	1.6	...	...
$CDCl_3$	−30	7.99 (4)	1.8	...	7.45 (cm)	...	3.36 (2)	1.8	...	...
HSO_3F	−30	8.81 (2)	17.3	−0.77	8.03 (cm)	−0.49	3.84 (2)	4.5	−0.51	10.0
HSO_3F-SbF_5-SO_2	−30	8.70 (2)	16.9	−0.72	7.83 (cm)	−0.38	3.72 (2)	4.0	−0.36	N.o.
D_2SO_4-SbF_5-SO_2	−20	8.91 (b)	≈0	−0.87	8.16 (cm)	−0.62	4.03 (b)	≈0	−0.70	...
		R_1 = H			R_2=R_3=  [b,c]					
SO_2	−20	8.17 (1)	...	...	7.27 (cm)	...				...
HSO_3F-SO_2	−20	9.15 (2)	18	−0.98	7.85 (cm)	−0.58				N.o.[d]
HSO_3F-SbF_5-SO_2	−40	9.35 (2)	18	−1.18	8.22 (cm)	−0.95				N.o.
D_2SO_4-SbF_5-SO_2	−20	9.08 (6)	...	−0.91	7.83 (cm)	−0.56				...
		R_1 = H			R_2=  [b]		R_3= 			
SO_2	−30	8.32 (1)	...	...	7.58 (cm)	...	7.13		...	...
HSO_3F-SO_2	−30	9.33 (2)	17.4	−1.01	7.90 (1)	−0.32	8.25		−1.12	N.o.
HSO_3F-SbF_5-SO_2	−30	9.27 (2)	17.2	−0.95	7.85 (1)	−0.27	8.18		−1.05	N.o.
D_2SO_4-SbF_5-SO_2	30	9.45 (1)	... (b)	−1.13	8.05 (1)	−0.47	8.40		−1.27	N.o.
		R_1 = CH_3			R_2=  [b]		R_3 = CH_3			
Neat	38	1.87 (4)	0.8	...	7.55 (cm)	...	3.16 (4)	0.8	...	...
HSO_3F-SO_2	−40	2.97 (1)	...	−1.10	7.92 (cm)	−0.37	3.70 (2)	5.1	−0.54	10.0
HSO_3F-SbF_5-SO_2	−40	3.00 (1)	...	−1.13	7.95 (cm)	−0.40	3.72 (2)	5.5	−0.56	N.o.
D_2SO_4-SbF_5-SO_2	−30	3.18 (1)	...	−1.31	8.18 (cm)	−0.63	3.92 (1)	... (6)	−0.76	N.o.
		R_1=R_2=  [b,c]					R_3 = CH_3			
$CDCl_3$	−20	7.32 (cm)	0.9	...			3.24 (1)	...	...	...
HSO_3F-SbF_5-SO_2	−30	8.00 (cm)	0.87	−0.68			3.79 (2)	5.5	−0.55	9.7
D_2SO_4-SbF_5-SO_2	−30	7.75 (cm)	0.68	−0.43			3.85 (1)	...	−0.61	...

[a] −δ = shift in parts per million from external capillary of TMS. Figures in parentheses represent multiplicity of peaks, cm = complex multiplex, b = broad single line. [b] For phenyl, we measured the shift of the middle of the complex multiplex. [c] The two phenyl patterns appear (especially in the starting material) in the same region and cannot be clearly distinguished. [d] Not observable due to quadruple broadening and coupling.

(I) with only minor contribution of the aminocarbonium form (II).

In aryl-conjugated systems it is expected that the aminocarbonium ion form should be stabilized. We prepared N-benzylidenemethylamine as a mixture of the two geometric isomers (see Experimental Section). The nmr spectrum in SO_2 shows two quadruplets for the methine proton at −8.38 ppm for the *anti* form IV and at 8.15 for the *syn* isomer V, and the two methyl doublets at −3.47 (IV) and −3.27 (V) ppm. The coupling constants J_{HCNCH_3} are 1.9 Hz (for IV) and 1.6 Hz (V). There was controversy over whether such isomers

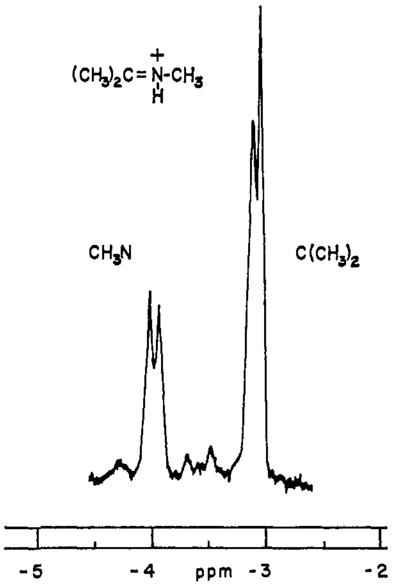


Figure 1.

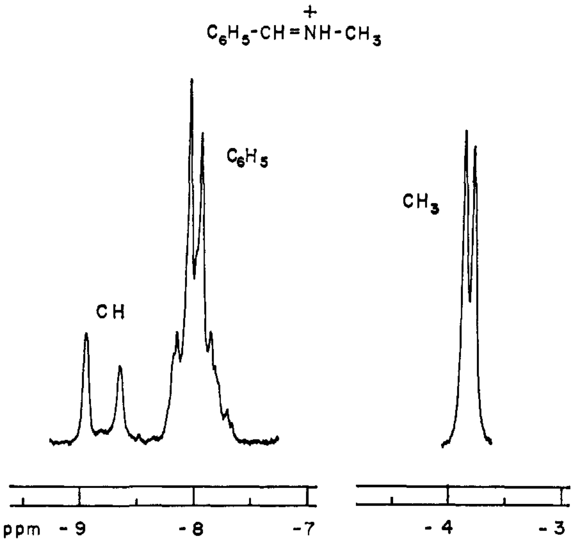
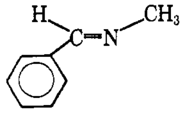
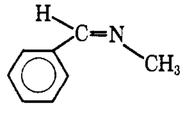


Figure 2.

could be observed until *cis-p*-chlorobenzophenone methylimine was obtained as a crystalline solid and found to rearrange to the *cis–trans* equilibrium mixture.[11,12] *anti*-Benzylidenemethylamine (neat) shows the methine proton as a quadruplet at −8.04 ppm (J_{H-H} = 1.6 Hz), the phenyl protons (main peak) at −7.54 ppm, and the methyl protons (doublet) at −3.33 ppm (J_{H-H} = 1.6 Hz).[13]



IV
anti



V
syn

In the protonated imine (Figure 2) the methine proton is shifted to −8.8 ppm (broad doublet, J_{H-H} = 17 Hz), the phenyl protons to −8.03 ppm, and the methyl protons to −3.84 ppm (J_{H-H} = 4.5 Hz). These data indicate the *trans*-immonium form VI, based on the 17-Hz coupling.

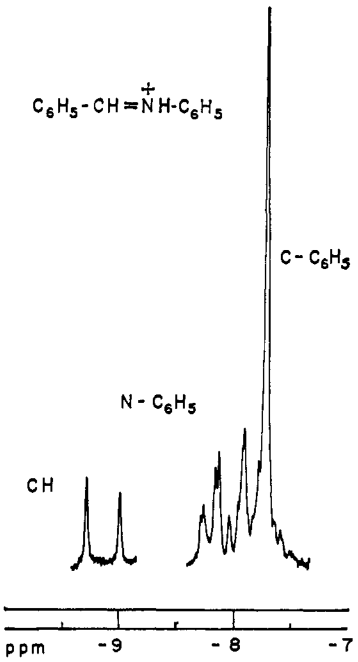
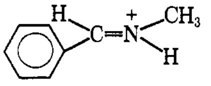
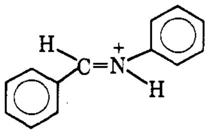


Figure 3.

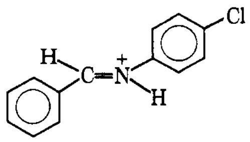


VI

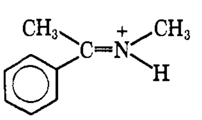
The size of the *trans* coupling constants through a double bond does not change much in isoelectronic molecules (see Table II). This close agreement shows that in proton spin–spin coupling, changes of geometry and bond character have much more effect upon the coupling constants than charge effects and the kind of atom bearing the hydrogen. The chemical shift and coupling data indicate that the immonium form is predominant over the aminocarbonium ion form, despite the fact that the latter should be stabilized by delocalization by the neighboring phenyl group. Similar conclusions were obtained from the investigation of protonated N-benzylideneaniline (VII) (Figure 3), N-benzylidene-*p*-chloroaniline (VIII) (Figure 4), N-α-methylbenzylidenemethylamine (IX) (Figure 5), and benzhydrylidenemethylamine (X) (Figure 6). In all these cases, the aminocarbonium ion form should be



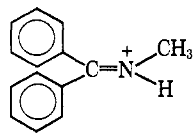
VII



VIII



IX



X

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[11] R. Kuhn and H. Schretzman, *Ber.*, **90**, 560 (1957).

[12] D. Y. Curtin and J. W. Hausser, *J. Am. Chem. Soc.*, **83**, 3474 (1961).

[13] R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **30**, 948 (1959).

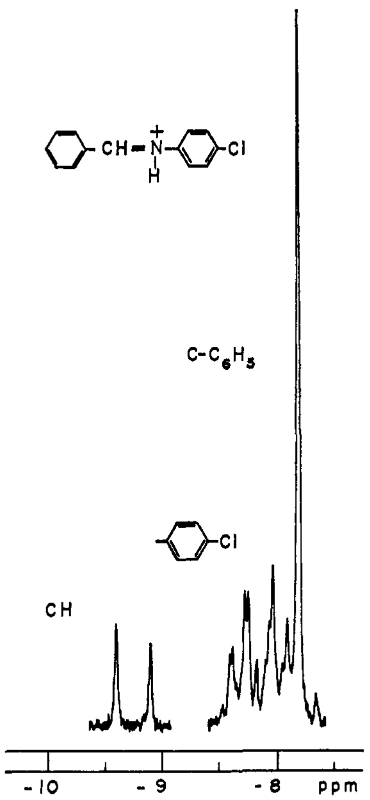

Figure 4.

stabilized by neighboring phenyl group(s). However, the nmr data still indicate the predominance of the immonium ion form.

Table II. *trans* Coupling Constants in Isoelectronic Molecules

	trans $J_{\mathrm{HC{=}CH}}$, Hz	Lit.
$\substack{\mathrm{C_6H_5}\\ \mathrm{H}}{>}\mathrm{C{=}C}{<}\substack{\mathrm{H}\\ \mathrm{CH_3}}$	15.6	
$\substack{\mathrm{CH_3}\\ \mathrm{H}}{>}\mathrm{C{=}O^{+}{-}H}$	19.5	4
$\substack{\mathrm{C_6H_5}\\ \mathrm{H}}{>}\mathrm{C{=}N^{+}}{<}\substack{\mathrm{H}\\ \mathrm{CH_3}}$	17.4	

Experimental Section

N-Benzylidenemethylamine, N-benzylideneaniline, and N-benzylidene-*p*-chloroaniline were reagent grade and were used without further purification.

N-Isopropylidenemethylamine. Acetone and methylamine (ratio 1:1.5) were condensed in a pressure tube. Solid KOH was added to bind the water which is formed during the reaction. The mixture was heated to 120° overnight. After distillation, N-isopropylidenemethylamine was obtained in about 45% yield, bp 65°.

N-Benzylidenemethylamine. To a large excess of liquid methylamine at −40° benzaldehyde was added dropwise, and the mixture was allowed to warm slowly to room temperature. The product was purified by vacuum distillation from KOH. The obtained material was found (nmr) to be a mixture of *syn*- and *anti*-N-benzylidenemethylamine.

α-Methylbenzylidenemethylamine. A mixture of 60 g of acetophenone, 31 g of methylamine, and 56 g of potassium hydroxide was heated for 6 hr at 140°. The crude product was vacuum distilled. Separation of the imine and acetophenone was accomplished by preparative gas chromatography (Airograph Autoprep, 20-ft silicon column at 180°).

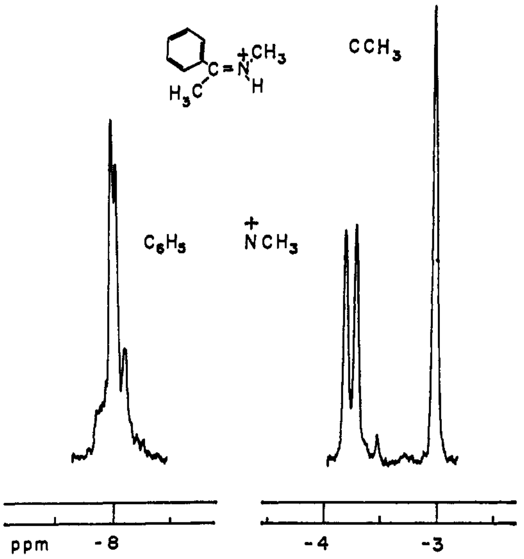

Figure 5.

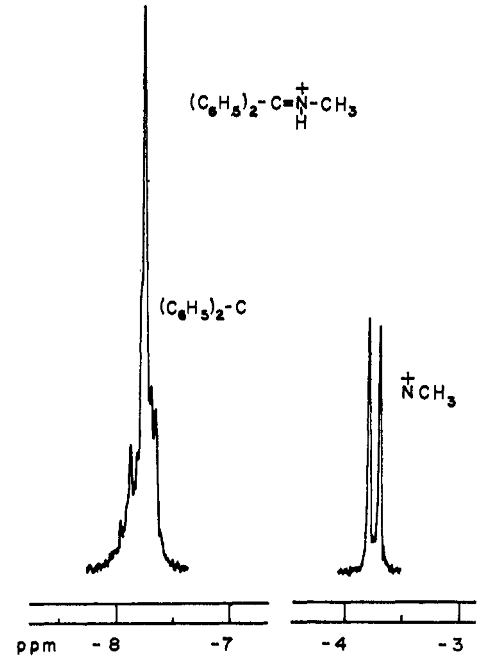

Figure 6.

Benzhydrilidenemethylamine was prepared from benzophenone and methylamine according to the method of Hauser, *et al.*[14]

Protonation of Imines. The protonated imines were observed by adding the corresponding imine in SO_2 to the stirred acid solution (FSO_3H, FSO_3H-SbF_5, D_2SO_4-SbF_5) diluted with SO_2 at temperatures indicated in Table I.

Nmr Spectra. A Varian Associates Model A-56-60-A nmr spectrometer with a variable-temperature probe was used for all nmr spectra. External capillary of TMS was used as reference.

Acknowledgment. Generous support of the work by a grant from the National Science Foundation is gratefully acknowledged.

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[14] C. R. Hauser, R. M. Manyik, W. R. Brasen, and P. L. Bayless, *J. Org. Chem.*, **20**, 1119 (1955).