Nuclear Magnetic Resonance Investigations of Iminium Ion Intermediates. Part 9.† Multinuclear Study of the Reaction between Lewis Acids and Vinylogous Amides

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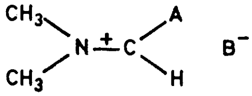
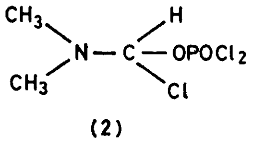
When treated with Lewis acids the vinylogous amides have analogous synthetic behaviour to that of amides. The structure and the electronic properties of the intermediate complexes formed in the course of the reactions between $COCl_2$ or $POCl_3$ and enaminoaldehydes, enaminoketones, or *p*-dimethylaminobenzaldehyde have been investigated. These complexes are identified and the mechanism is compared with that of the Vilsmeier reaction. The stereochemistry of the products is elucidated and examined in the light of the possible exchange processes. Electron delocalization in both the neutral compounds and cations of the type $(CH_3)_2N \overset{\cdots}{-} C \overset{\cdots}{-} C \overset{\cdots}{-} C \overset{\cdots}{-} A$ are discussed on the basis of nitrogen chemical shifts and rotational barriers.

THE reaction of amides with a Lewis acid such as $POCl_3$, $POBr_3$, $SOCl_2$, or $COCl_2$ provides an important method of formylation. Treatment of dimethylformamide gives an intermediate (1), which has been the subject of conflicting interpretations [1] but which is now unambiguously identified; [2] the mechanism of the reaction has been clarified.[2] Vinylogous amides, $(CH_3)_2N{-}(\overset{|}{C}{=}\overset{|}{C})_n{-}COR$, which are species of lower basicity than amides, are also utilized in various syntheses [3] and it was interesting to investigate the mechanism of their reaction with Lewis acids. Thus covalent or ionic species of types (2) and (3), which were postulated as intermediates, but not observed in detectable amounts, in the reactions involving amides, possibly exist with their vinylogues.

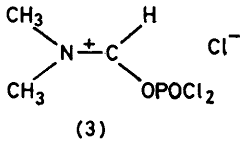


(1)

A = Cl, Br
B = Cl, Br, $OPOCl_2$, $OPOBr_2$



(2)



(3)

We have thus examined to what extent the mechanisms identified for the reactions of amides, acetamides, *etc.* can be transposed to the compounds in which either one or several double bonds or an aromatic ring is incorporated between the nitrogen and the carbonyl of the amide fragment. Our aim was therefore to identify the structure, and to specify the stereochemistry of the complexes eventually formed in the course of the reactions. Moreover, since the reactivity may depend on the delocalization of the nitrogen lone pair along the $>N \overset{\cdots}{-} C \overset{\cdots}{-} C \overset{\cdots}{-} C \overset{\cdots}{-} A$ framework, we have investigated this problem by examining the behaviour of the nitrogen chemical shift as a function of the rotational barrier, according to a methodology which has already been developed from a more general point of view.[4] This study was performed by ^1H, ^{13}C, ^{31}P, and ^{15}N n.m.r.

EXPERIMENTAL

Materials.—The vinylogous amides were synthesized as described previously.[5] *p*-Dimethylaminobenzaldehyde was a commercial sample. The reagents used were carefully dried and distilled. All reactions were performed using an air tight apparatus flushed with dry argon.[2]

In some cases, salts (particularly those obtained with $COCl_2$) were crystallized before dissolving in the appropriate solvent. The intermediate species which were observed at lower temperatures (263 K) were not isolated.

N.m.r. Measurements.—^1H Spectra were studied on Varian A 60 and XL100-12 spectrometers operating in the continuous wave mode. The ^{13}C chemical shifts at 25.18 MHz were measured at 305 K for $CDCl_3$ solutions using a Varian XL 100-12 spectrometer: spectral width 5 000 Hz, acquisition time 0.8 s. Chemical shifts are reported in p.p.m. from internal tetramethylsilane.

Proton noise-decoupled ^{15}N spectra were recorded at 9.117 MHz at the natural abundance level with a Brüker WH 90 DS spectrometer: spectral width 6 000 Hz, acquisition time 0.34 s, pulse angle 35°, temperature 300 K. $Cr(acac)_3$ (0.08M) was added to the samples. The shifts were referred to an external $D_2O–D^+$ (lock signal) solution of 30% ^{15}N enriched $NaNO_3$ contained in a coaxial 2 mm tube centred in a 10 mm sample tube. These shifts values have been converted to the nitromethane scale by applying the correction $\delta^{15}N/CH_3NO_2 = \delta^{15}N/NO_3^- - 1.5$.

RESULTS AND DISCUSSION

Structure and Stereochemistry of the Vinylogous Amides.—The n.m.r. parameters of the vinylogous amides are given in Tables 1 and 2. By taking into account the effect of the substituent electronegativities upon the coupling constants, *trans*-geometry can be assigned to compounds (5), (14), (22), and (24). In order to define the conformation about the =C(2)–C(1)=O bond we have determined the shifts induced by the lanthanide derivative $Eu(fod)_3$. Table 3 gives the values of the initial slopes of the curves which represent the variations of the induced shifts as a function of ρ,

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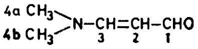
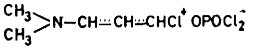
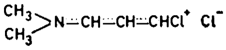
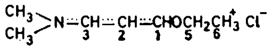
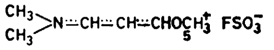
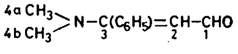
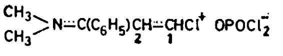
† Part 8, S. Poignant, J. R. Gauvreau, and G. J. Martin, *Can. J. Chem.*, 1980, **58**, 946.

TABLE 1

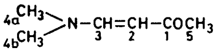
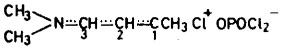
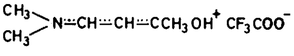
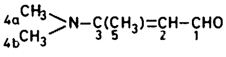
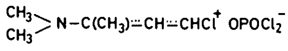
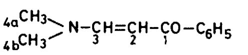
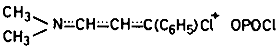
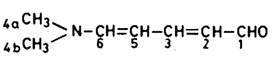
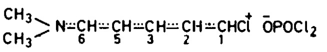
^{1}H and ^{13}C n.m.r. parameters for compounds (5), (11), and derivatives (2M solutions in $CDCl_3$). An intermediate species is evident in the mixture of these compounds and $POCl_3$. Recordings were carried out at 263 K for compounds (5′), (6), and (7)

Compound	No.	Nucleus	1	2	3	4a	4b	5	6	J_{1-2}/Hz	J_{2-3}/Hz
 $\mathrm{(\underset{4a,\,4b}{CH_3})_2N{-}\underset{3}{CH}{=}\underset{2}{CH}{-}\underset{1}{CHO}}$	(5)	δ_H	9.02	5.02	7.15	2.98	2.98			8.2	12.6
		δ_C	188	100.8	160.7	37	44.5				
		J_{C-H}/Hz	161	157	163.5	139	139				
	(5′)	δ_H	9.02	5.1	7.17	2.87	3.19			8.2	12.6
(5) + $POCl_3$ (1:1)	(6)	δ_H	8.47	6.05	8.16	3.33	3.58			≃11	≃11.2
		δ_C	168	100	177	39.6	47.7				
		J_{C-H}/Hz	194	164	178.6	145	145				
 $\mathrm{(CH_3)_2N{-}CH\stackrel{\cdots}{-}CH\stackrel{\cdots}{-}CHCl^{+}\ OPOCl_2^{-}}$	(7)	δ_H	8.25	7.3	9.18	3.68	3.83			12.8	10.6
		δ_C	155	125	169	42.1	49.7				
		J_{C-H}/Hz	204	174	181	146	146				
 $\mathrm{(CH_3)_2N\stackrel{\cdots}{-}CH\stackrel{\cdots}{-}CH\stackrel{\cdots}{-}CHCl^{+}\ Cl^{-}}$	(8)	δ_H	8.38	7.52	9.49	3.81	3.89			13	10.6
		δ_C	156	126	170	44	51				
 $\mathrm{(CH_3)_2N\stackrel{\cdots}{-}\underset{3}{CH}\stackrel{\cdots}{-}\underset{2}{CH}\stackrel{\cdots}{-}\underset{1}{C}HO\underset{5}{C}H_2\underset{6}{C}H_3^{+}\ Cl^{-}}$	(9)	δ_H	8.52	6.35	9.40	3.57	3.74	4.44	1.42	11	11
		δ_C	168.8 [a]	99.9	176.4 [a]	40.7	48.1				
 $\mathrm{(CH_3)_2N\stackrel{\cdots}{-}CH\stackrel{\cdots}{-}CH\stackrel{\cdots}{-}CHO\underset{5}{C}H_3^{+}\ FSO_3^{-}}$	(10)	δ_H	7.96	6.12	8.30	3.43	3.59	4.10		≃12	≃11
		δ_C	168.5 [a]	99	177 [a]	40	48	60			
		J_{C-H}/Hz	176	165.5	186	143	143	149			
 $\mathrm{(\underset{4a,\,4b}{CH_3})_2N{-}\underset{3}{C}(C_6H_5){=}\underset{2}{C}H{-}\underset{1}{C}HO}$	(11)	δ_H	8.6	5.19	[b]	2.83	2.83			8.3	
		δ_C	190	103	168	40.3	40.3				
		J_{C-H}/Hz	166	155.5		139	139				
(11) + $POCl_3$ (1:1)	(12)	δ_H	7.27	6.43	[b]	3.21	3.57			11.2	
		δ_C	131.5	103	177	42.6	44.8				
 $\mathrm{(CH_3)_2N\stackrel{\cdots}{-}C(C_6H_5)\underset{2}{C}H\stackrel{\cdots}{-}\underset{1}{C}HCl^{+}\ OPOCl_2^{-}}$	(13)	δ_H	7.58	6.84	[b]	3.58	3.98			13.2	
		δ_C	150.6	133	175.5	45.4	47.6				
		J_{C-H}/Hz	199	≃168		144	144				

[a] Tentative assignment. [b] Centre of the C_6H_5 pattern: δ 7.34 for (11), 7.50 for (12), 7.67 for (13).

TABLE 2

^{1}H and ^{13}C n.m.r. parameters for compounds (14)—(24) and derivatives (2M solutions in $CDCl_3$)

Compound		No.	Nucleus	1	2	3	4a	4b	5	6	J_{1-2}/Hz	J_{2-3}/Hz
 $\mathrm{(\underset{4a,\,4b}{CH_3})_2N{-}\underset{3}{C}H{=}\underset{2}{C}H{-}\underset{1}{C}O\underset{5}{C}H_3}$		(14)	δ_H		5.0	7.43	2.92	2.92	2.03			13.0
			δ_C	198	97.5	151	37	45	27.4			
			J_{C-H}/Hz		155.3	164	140	140	125.6			
 $\mathrm{(CH_3)_2N\stackrel{\cdots}{-}\underset{3}{C}H\stackrel{\cdots}{-}\underset{2}{C}H\stackrel{\cdots}{-}\underset{1}{C}CH_3Cl^{+}\ OPOCl_2^{-}}$		(15)	δ_H		7.12	8.75	3.72	3.90	2.65			10.2 [a]
			δ_C	167.4	119.3	165	41.8	49.9	24.6			
			J_{C-H}/Hz		169.5	≃180	144	144	132			
		(16)	δ_H		6.83	9.17	3.65	3.90	2.76			11 [a]
			δ_C	164.7	117.3	165.8	42.6	49.9	29.3			
			J_{C-H}/Hz		169	≃180	144	144	132			
 $\mathrm{(CH_3)_2N\stackrel{\cdots}{-}CH\stackrel{\cdots}{-}CH\stackrel{\cdots}{-}CCH_3OH^{+}\ CF_3COO^{-}}$	[b]	(17)	δ_H		5.85	8.19	3.29	3.29	2.40			12.5
			δ_C	189.4	98.1	166.1	39.7	48.4	18.6			
		(18)	δ_H		5.48	8.46	3.33	3.53	2.38			11.3
			δ_C	187.3	95.9	163.3	39.7	48.4	23.7			
 $\mathrm{(\underset{4a,\,4b}{CH_3})_2N{-}\underset{3}{C}(\underset{5}{C}H_3){=}\underset{2}{C}H{-}\underset{1}{C}HO}$	[c]	(19)	δ_H	9.47	5.07		2.99	2.99	2.26		8.0	
 $\mathrm{(CH_3)_2N{-}C(CH_3)\stackrel{\cdots}{-}CH\stackrel{\cdots}{-}CHCl^{+}\ OPOCl_2^{-}}$	[c]	(20)	δ_H	7.93	7.12		≃3.62	3.88	2.63		13.0	
		(21)	δ_H	8.5	6.53		≃3.62	3.88	2.75		14.5	.
 $\mathrm{(\underset{4a,\,4b}{CH_3})_2N{-}\underset{3}{C}H{=}\underset{2}{C}H{-}\underset{1}{C}O{-}C_6H_5}$		(22)	δ_H		5.7	7.77	2.91	2.91				12.0
			δ_C	188	92	155	37.3	44.9				
			J_{C-H}/Hz		156.5	165	140	140				
 $\mathrm{(CH_3)_2N\stackrel{\cdots}{-}CH\stackrel{\cdots}{-}CH\stackrel{\cdots}{-}C(C_6H_5)Cl^{+}\ OPOCl_2^{-}}$		(23)	δ_H		7.53	8.97	3.78	3.88				10.0
			δ_C	161.6	114.3	166	43	50.4				
			J_{C-H}/Hz		164	183	145	145				
 $\mathrm{(\underset{4a,\,4b}{CH_3})_2N{-}\underset{6}{C}H{=}\underset{5}{C}H{-}\underset{3}{C}H{=}\underset{2}{C}H{-}\underset{1}{C}HO}$		(24)	δ_H	9.17	5.63	7.0	3.0	3.0	5.17	6.83	8 [d]	14.4
			δ_C	191	118	158	40.3	40.3	97	154		
			J_{C-H}/Hz	163	156	146	139	139	155	163		
 $\mathrm{(CH_3)_2N\stackrel{\cdots}{-}\underset{6}{C}H\stackrel{\cdots}{-}\underset{5}{C}H\stackrel{\cdots}{-}\underset{3}{C}H\stackrel{\cdots}{-}\underset{2}{C}H\stackrel{\cdots}{-}\underset{1}{C}HCl^{+}\ {}^{-}OPOCl_2}$	[e]	(25)	δ_H	7.22	6.93	7.68	3.62	3.77	7.0	8.66	13.0 [d]	10.6
			δ_C	139	132.5 [f]	156.4 [f]	41.7	49.4	120.2 [f]	170		
			J_{C-H}/Hz	197	162	159	144	144	164	182		
		(26)	δ_H	7.22	6.9	7.95	3.65	3.81	6.88	8.78	13.0 [d]	7·6
			δ_C	135	128.5 [f]	152 [f]	41.6	49.3	122.5 [f]	170.5		
			J_{C-H}/Hz	201	160	156	144	144	160	182		

[a] Owing to coupling through the nitrogen atom the signals of H(3) are usually broadened in the salts. However the couplings are resolved for compounds (15) and (16); $^4J_{3-5}$ 1.15, $^4J_{3-4}\simeq$ 1,2 Hz. [b] Results from ref. 15. [c] As these products are obtained as mixtures with compounds (14) or (15),(16) the ^{13}C spectra are not easily assigned. [d] $^3J_{3-5}$ 11.5 in (24), 14.5 in (25), and 14 in (26); $^3J_{5-6}$ 12.5 in (24), 11 in (25), and 11 Hz in (26). [e] The ^{1}H spectra show the presence of two compounds (25) and (26) but the complexity makes the assignment uncertain. [f] Tentative assignment.

the ratio of the lanthanide concentration to the substrate concentration, for solutions containing 0.5M-substrate in $CDCl_3$. On the basis of the MacConnell–Robertson equation,[6] these results are satisfactorily interpreted by assuming that the lanthanide complex interacts with a lone pair on the oxygen atom, one situated towards the formyl hydrogen in compound (5) for example. Thus an important paramagnetic effect of the lanthanide is noted for the hydrogen in position 3 of compounds (14) and especially (22), but for compounds (5) and (11) the most important effect concerns the hydrogen in position 2. It can be concluded that enaminoaldehydes or enaminoketones adopt preferentially an *s-trans* conformation for compounds (5) and (11) and an *s-cis* conformation for compound (22) whereas an equilibrium between the *s-cis* and *s-trans* conformations is predicted for compound (14). This last result is in accordance with the observation of both the *s-cis* (30%) and *s-trans* forms in the ^1H and ^{13}C spectra obtained at low temperatures.[7] It should be noted however that a modification of the conformational equilibrium under the influence of an addition of the lanthanide reagent cannot be excluded.[8]

TABLE 3

Proton shifts $\Delta\delta[=\delta\ (\text{adduct}) - \delta\ (\text{substrate})]$ induced by $Eu(fod)_3$. These values were obtained by a linear extrapolation of the results to a unit value of the ratio $\rho = [Eu(fod)_3] : [\text{substrate}]$

Compound \ Proton	H(1)	H(2)	H(3)	$(CH_3)_2N$	Ar
$(CH_3)_2N{-}\underset{3}{C}H{=}\underset{2}{C}H{-}\underset{1}{C}HO$ (5)	$\simeq 0$	8.4	3.2	2.2	
$(CH_3)_2N{-}CH{=}CH{-}COCH_3$ (14)	8.2	4.4	11.1	1.82	
$(CH_3)_2N{-}CC_6H_5{=}CH{-}CHO$ (11)	-0.6	8.6		2.1	0
$(CH_3)_2N{-}CH{=}CH{-}COC_6H_5$ (22)		4.4	17.4	2.6	*ortho* 10 *meta* 1.9 *para* 1.9

Reaction of the Enaminoaldehydes with $COCl_2$.—The reaction of $COCl_2$ with the enaminoaldehyde (5) can be written as in equation (1). The formation of salts of type (8) is corroborated by the large paramagnetic shifts of the proton and carbon nuclei, with the exception of site 1 which has lost its ketone character (Table 1). The proton and carbon shifts are not affected by changing the anion in these salts [see (7) and (8)]. Thus the salts prepared with $COCl_2$ or $POCl_3$ are of similar structure. In addition the C–H coupling constants are noticeably enhanced. Thus $^1J_{C(4)-H}$ of the methyl groups [146 Hz in (7)] is the same order of magnitude as in salt (1) ($^1J_{C-H}$ *ca.* 146 Hz [2d]). This interpretation is also supported by the relatively large values of $^3J_{H(1)-H(2)}$ and the broadening of the H(3) signals due to coupling through nitrogen; thus $^4J_{H\text{-}C\text{-}N\text{-}CH_3}$ has been measured as 1.2 Hz in (15) for example. Moreover in contrast to the trend observed in enaminoaldehydes, $J_{H(1)H(2)}$ is larger than $J_{H(2)H(3)}$ in the salts. This behaviour which corresponds to the important double character of the N–C(3) and C(2)–C(1) bonds is related to the delocalization of the nitrogen lone pair of electrons which will be discussed later.

$$(CH_3)_2N{-}CH{=}CHCHO + COCl_2 \longrightarrow (CH_3)_2N \overset{\cdots}{-} CH \overset{\cdots}{-} CH \overset{\cdots}{-} CHCl^+\ Cl^- + CO_2 \quad (1)$$

(5) (8)

Reaction of the Enaminoaldehydes or Enaminoketones with $POCl_3$.—We have shown that the reaction of $POCl_3$ with amides gives salts of structure (1). The existence in solution ($CHCl_3$, CH_2Cl_2, CH_3CN) at equilibrium of significant proportions of species of types (2) or (3) has been excluded.[2] It was therefore interesting to identify the species obtained with the vinylogous amides. When $POCl_3$ is added to an enaminoaldehyde or an enaminoketone two situations can be distinguished.

(a) With compounds (5) and (11) in $CDCl_3$ at 263 K the n.m.r. recording shows the superposition of two spectra of (6) and (7) or (12) and (13) (Table 1). For an equimolar mixture of (5) or (11) and $POCl_3$ the spectrum (6) or (12) irreversibly disappears to give slowly the spectrum of (7) or (13). As in the case of amides the species finally obtained, (7) or (13), can be identified as ionic structures with the anion $OPOCl_2^-$,$(CH_3)_2N \overset{\cdots}{-} \overset{|}{C} \overset{\cdots}{-} \overset{|}{C} \overset{\cdots}{-} CHCl^+$-$OPOCl_2^-$. Thus the n.m.r. parameters of (7) are very similar to those of (8) and no coupling with phosphorus is observed. Moreover a ^{31}P signal at *ca.* −5 p.p.m. with respect to H_3PO_4 can be attributed to the anion $OPOCl_2^-$.[2c] This interpretation is corroborated by the ^{15}N results (Table 5). Indeed the nitrogen chemical shifts of the complexes prepared from $POCl_3$ are very similar to those of the complexes prepared with $COCl_2$. Thus $\delta_{N/CH_3NO_2} = -174.4$ and -171.4 p.p.m. for the complexes of DMF with $POCl_3$ and $COCl_2$, respectively, and for the vinylogous amides $\delta_{N/CH_3NO_2} = -195.5$ in (7) and -194.4 p.p.m. in (8). In contrast δ_N is found in different ranges for the oxygenated cations of the salts $(CH_3)_2N{-}CHOCH_3^+$,OSO_2F^-(-236 p.p.m.) or $(CH_3)_2N \overset{\cdots}{-} CH \overset{\cdots}{-} CH \overset{\cdots}{-} CH \overset{\cdots}{-} OCH_3^+$,$OSO_2F^-$($-224$

p.p.m.). A structure of the type $(CH_3)_2N \cdots CH \cdots CH \cdots CHOPOCl_2{}^+,Cl^-$ may therefore be excluded.

For an equimolar mixture of (5) and $POCl_3$ the n.m.r. parameters of (6) are rather similar to those of the salt (9) obtained through the reaction of (1) with $CH_2=CHOEt$ and to those of the salt (10) which results from the reaction of FSO_3CH_3 with (5). However the parameters of the complex between (5) and $AlCl_3$, for example, are also found in analogous ranges. Moreover, if a large excess of amide (5) is added to compound (7), a species comparable to (6) appears again without noticeably modifying the quantity of (7). Thus when the salt (7) is formed, aggregates resulting from strong interactions of type (4) are likely to exist.

$$(CH_3)_2\overset{+}{N}\cdots CH\cdots CH\cdots CH-O^{-}\cdots\overset{+}{C}HCl\cdots CH\cdots CH\cdots N(CH_3)_2OPOCl_2^{-}\simeq(6)$$

(5) (4) (7)

It should also be noted that an exchange reaction between the enaminoaldehyde and the corresponding salt may occur. Thus an averaged spectrum is observed at room temperature when a small amount of salt (8) is added to (5). From this point of view the behaviour of the vinylogous compounds is again similar to that of the amides.[9]

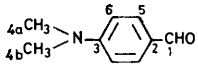
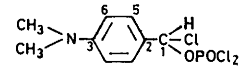
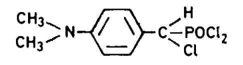
(b) When equimolar amounts of $POCl_3$ and of the enaminoketones (14) or (19) are reacted at room temperature we observe immediately the superposition of two spectra which can be assigned to geometrical isomers of the chlorinated cations (15),(16), and (20),(21) as discussed later.

Stereochemistry of the Salts $(CH_3)_2N \cdots \overset{|}{C} \cdots \overset{|}{C} \cdots \overset{+}{C}Cl$,-$B^-$.—Owing to the delocalization of the nitrogen lone pair (see below) a mesomeric structure of type $(CH_3)_2\overset{+}{N}=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-Cl,B^-$ is important in the vinylogous Vilsmeier salts. Only one stereoisomer is observed for compounds (7)—(10) and (13) and the n.m.r. parameters are typical of a *trans,trans*-geometry of (7)—(10) and of a *trans*-geometry for (13) (Table 1). For the complex derived from the enaminoketone (14), the two spectra of (15) and (16) which are observed are assigned to the stereoisomers about the C(1)–C(2) bond (Table 2). This result further demonstrates that the exchange process involving the anion, which has been proved to intervene in various chlorinated iminium salts,[4c,9] is slower in the case of the vinylogous salts. Moreover since this exchange phenomenon is slow on the n.m.r. time scale the possibility that the spectrum is actually a weighted mean over ionic species [of types (1) and (3)] involving $OPOCl_2$ either in the cation or in the anion can be definitively excluded. Indeed in the case of the vinylogous salts such an exchange process, which would involve a covalent intermediate of type (2), would be expected to simultaneously average the spectra of the stereoisomers about the C(1)–C(2) bond.

It can be noted that the existence of the geometrical isomers (15),(16), or (17),(18) corresponds to the presence of both *s-cis-* and *s-trans*-conformations in the starting enaminoketone (14) and can be related to the substitution on the carbon of a methyl group which is likely to destabilize sterically the structures with the methyl *cis* to H(3) with respect to the corresponding *trans*-structures. On this basis a *cis*-geometry of the phenyl and CH(2) groups can be tentatively assigned to the unique salt of type (23). The stereoisomerism observed for complexes derived from (19) and (24) was attributed to the C(2)–C(3) bond. Thus coupling constants of 7.6 and 10.6 Hz for (25),(26) were observed. The ^1H chemical shifts of (20) and (21) are different and the stereoisomerism may arise on the C(2)–C(3) bond since the $J_{1,2}$ coupling constants are of similar magnitude.

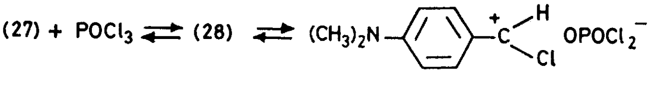
TABLE 4

^1H and ^{13}C n.m.r. parameters for *p*-dimethylaminobenzaldehyde and derivatives (2M solutions in $CDCl_3$)

		Nucleus	1	2	3	4a	4b	5	6
	(27)	δ_H	9.69			3.0	3.0	7.68	6.67
		δ_C	189.6	125.2	154.3	39.6	39.6	131.7	111
		J_{C-H}/Hz	168.5			136.4	136.4	160	160.5
	(28)	δ_H	6.66			3.18	3.18	7.83	7.83
		δ_C	70.3	142.9	144	47	47	129	122
		J_{C-H}/Hz	180			≃145	≃145	165	165
 a	(29)	δ_H	5.45			3.02	3.02	7.45	6.88
		δ_C	64	≃143	≃146	45	45	132	120
		J_{H-C}/Hz	159			≃145	≃145	≃163	≃163

[a] $^2J_{P-H(1)}$ 4.6, $^4J_{P-H(5)}$ 2.8, $^5J_{P-H(6)} \simeq 0.5$, $^1J_{P-C(1)}$ 118, $^3J_{P-C(5)}$ 8 Hz; δ_{P/H_3PO_4} 40.5 p.p.m.

Reaction of $POCl_3$ *with* p-*Dimethylaminobenzaldehyde*.—Different behaviour is observed when an aromatic ring instead of one or two double bonds is introduced between the carbonyl and the amino-groups as in (27). On the basis of the n.m.r. parameters (Table 4) the exclusive participation of a ionic complex (28′) analogous to the preceding ones can be excluded. The results are conveniently interpreted by assuming a fast dynamic equilibrium involving preferentially the covalent structure (28). Indeed the proton chemical shift of H(1) is very close to that of $C_6H_5CHCl_2$ (δ 6.61)[10] and the n.m.r. parameters are in satisfactory agreement with those of the

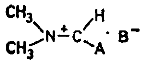
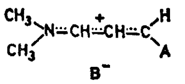
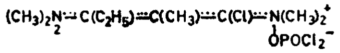
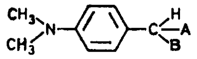


(28′)

covalent compound (29) which we have prepared through the reaction of PCl_3 with (27) (Table 4). Indeed it is known that the reaction of PCl_3 with carbonyl compounds may lead to covalent species[11] and for (29) it can be verified that the phosphorus chemical shifts, δ_{P/H_3PO_4} +40.5 p.p.m., is very close to the shift of $CH_2ClPOCl_2$ (+38 p.p.m.) or CH_3POCl_2 (+43.5 p.p.m.).[12] The ^{15}N parameters also illustrate the predominant occurrence of a covalent form (28) since δ_N of (28) is situated in the same range (δ_{N/CH_3NO_2} −338 p.p.m.) as that of the covalent species (29) (−328.8 p.p.m.) whereas δ_N of the ionic structures is found at higher frequencies (Table 5). This result is in accord with a relatively low delocalization of the nitrogen lone pair in (28) (see below).

TABLE 5

^{15}N Chemical shifts (2M solutions in $CDCl_3$)

	Compound	A	B	δ_{N/CH_3NO_2} (p.p.m.)
(30)	$(CH_3)_2N-CHO$			−274.9
(5)	$(CH_3)_2N-CH=CH-CHO$			−289.0
(27)	$p-(CH_3)_2N-C_6H_4-CHO$			−321.0
(31)		OCH_3	OSO_2F	−236[c]
(32)		Cl	$OPOCl_2$	−174.4
(33)		Cl	Cl	−171.4[a]
(34)		$N(CH_3)_2$	ClO_4	−257.7[b]
(35)		OCH_3	OSO_2F	−224.0
(9)		OC_2H_5	Cl	−220.1
(7)		Cl	$OPOCl_2$	−195.5
(8)		Cl	Cl	−194.4
(36)		SC_2H_5	Cl	−218.3
(37)	$(CH_3)_2\underset{2}{N}\overset{\cdots}{-}CH\overset{\cdots}{-}CH\overset{\cdots}{-}C(Cl)\overset{\cdots}{-}\underset{1}{N}(CH_3)_2+Cl^-$			−248.1 [N(1)][d] −258.3 [N(2)][d]
(38)	 $(CH_3)_2\underset{2}{N}\overset{\cdots}{-}C(C_2H_5)\overset{\cdots}{-}C(CH_3)\overset{\cdots}{-}C(Cl)\overset{\cdots}{-}N(CH_3)_2^+\ \ \underset{OPOCl_2^-}{}$			−191.4 [N(1)][d] −322.8 [N(2)][d]
		A	B	
(29)		Cl	$POCl_2$	−328.8
(28)		Cl	$OPOCl_2$	−338.0

[a] An erroneous report has been given for this compound in *J. Am. Chem. Soc.*, 1977, **99**, 1381. [b] Ref. 16. [c] Ref. 4*c*. [d] The assignment of δ[N(1)], δ[N(2)], δ[C(2)], δ[C(4)] is ambiguous.[4c]

Delocalization of the Nitrogen Lone Pairs of Electrons.—In conjugated systems nitrogen chemical shifts provide useful information about the delocalization of the nitrogen lone pair of electrons, especially when examined in conjunction with rotational barriers about N–X bonds.[4] In addition, deviations with respect to the linear relationship, $\delta_N = f(\Delta G^\ddagger)$, observed in certain series of compounds may enable particular properties of the chemical shift to be emphasized or special rotational mechanisms to be detected.[4c] In neutral enamines and enaminoketones satisfactory linear correlations between δ_N and $\Delta G^\ddagger$ are found.[4b,13] Moreover we observe that the ionic species $(CH_3)_2N \overset{\cdots}{-} CH \overset{\cdots}{-} CH \overset{\cdots}{-} CH \overset{\cdots}{-} N(CH_3)_2^+,B^-$, for which a rotational barrier of 90 kJ mol^{-1} has been determined,[14] can be included in the correlation relative to the neutral compounds of type $(CH_3)_2N \overset{\cdots}{-} CH \overset{\cdots}{-} CH \overset{\cdots}{-} A$ (A = CH=CH_2, C_6H_5, Ac, Bz, CHO, CH=CHCHO[4b]). The slope of the correlation is *ca.* 1.3 p.p.m. mol kJ^{-1}. Indeed a relation between δ_N and rotational barriers is likely to have a more general character in vinylogous compounds of the type $(CH_3)_2N \overset{\cdots}{-} C \overset{\cdots}{-} C \overset{\cdots}{-} C-A$ compared with structures of the type $(CH_3)_2N \overset{\cdots}{-} C \overset{\cdots}{-} X$[4c] since in the former the A fragment is not substituted directly on the carbon bound to the nitrogen atom. The ^{15}N chemical shift in particular is therefore expected to reflect electron delocalization more closely. As a consequence high rotational barriers around the C–N bond are expected in the vinylogous salts on the basis of the ^{15}N shifts (Table 5). In fact two *N*-methyl resonances are observed at room temperature for most salts (Tables 1 and 2) and a coalescence phenomenon appears at *ca.* 370 K (100 MHz) for the proton signals of (7) for example. In the hypothesis of a first-order process a free energy of activation of *ca.* 82 kJ mol^{-1} is estimated from these results. A higher rotational barrier would indeed be expected from the value of the ^{15}N shift and this behaviour suggests that a chlorine exchange process reminiscent of that which has been observed in various iminium salts,[4c] also occurs in the vinylogous compounds.

We conclude, therefore, that in the salts considered δ_N offers an interesting probe of delocalization of the electron lone pair. The results then point out the great importance of a mesomeric structure of type $(CH_3)_2\overset{+}{N}=C-C=C-A$ in salts with A = Cl and to a somewhat lesser extent with A = OR. The higher values of δ_N observed when A = $(CH_3)_2N$ [compounds (34) and (37)] (Table 5) reflect the competition between delocalization of the lone pairs of both nitrogens. On this basis the surprisingly different values of δ_N measured for the two nitrogens of compound (38) can be explained by the importance of a mesomeric structure of type $(CH_3)_2\overset{+}{N}{=}C{-}C{=}C{-}N(CH_3)_2OPOCl_2^-$. Indeed the chemical shift of one nitrogen is relatively close to those of iminium salts (Table 5)[2c] whereas that of the other nitrogen is characteristic of a poorly delocalized lone pair and reaches a range of values typical of enamines [δ_N −324.5 p.p.m. in $(CH_3)_2NCH{=}CH{-}C_6H_5$ for example[4b]]. This particular behaviour is probably the result of a torsion around the C–C bond produced by steric hindrance between the chlorine and ethyl substituents. Hence it can be concluded that δ_N, which is more generally accessible than rotational barriers, may provide important information about electron delocalization in conjugated salts. Moreover examination of the nitrogen shifts in conjunction with dynamic parameters may enable particular exchange mechanisms to be detected.

[0/1821 *Received, 25th November*, 1980]

REFERENCES

[1] G. Hazebroucq, *Ann. Pharm. Fr.*, 1966, **24**, 793.

[2] (*a*) G. J. Martin and M. L. Martin, *Bull. Soc. Chim. Fr.*, 1963, 1637; (*b*) G. J. Martin and S. Poignant, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1964; (*c*) M. L. Martin, M. Helbert, and S. Poignant, *ibid.*, 1977, 1243; (*d*) M. L. Martin, G. Ricolleau, S. Poignant, and G. J. Martin, *ibid.*, 1976, 182.

[3] (*a*) Z. Arnold, *Collect. Czech. Chem. Commun.*, 1963, **28**, 869; (*b*) Z. Arnold and A. Holy, *ibid.*, 1962, **27**, 286; 1965, **30**, 47; (*c*) Z. Arnold and J. Zemlicka, *ibid.*, 1959, **24**, 2378.

[4] (*a*) G. J. Martin, J. P. Gouesnard, J. Dorie, C. Rabiller, and M. L. Martin, *J. Am. Chem. Soc.*, 1977, **99**, 1381; (*b*) J. Dorie, B. Mechin, and G. J. Martin, *Org. Magn. Reson.*, 1979, **12**, 229; (*c*) R. Rabiller, G. Ricolleau, M. L. Martin, and G. J. Martin, *Nouveau J. Chim.*, 1980, **4**, 35.

[5] (*a*) H. Normant and G. J. Martin, *Bull. Soc. Chim. Fr.*, 1963, 1646; (*b*) Z. Arnold and F. Sorn, *Chem. Listy*, 1957, **51**, 1082; (*c*) Z. Arnold and F. Sorn, *Collect. Czech. Chem. Commun.*, 1958, **23**, 452; (*d*) N. Kochetkow, *Izv. Akad. Nauk. SSSR Otd. Khim. Nauk.*, 1953, 991.

[6] H. M. MacConnell and R. E. Robertson, *J. Chem. Phys.*, 1958, **29**, 1361.

[7] (*a*) M. L. Filleux-Blanchard, H. Durand, and G. J. Martin, *Org. Magn. Reson.*, 1970, **2**, 539; (*b*) M. L. Filleux-Blanchard, F. Mabon, and G. J. Martin, *Tetrahedron Lett.*, 1974, 3907.

[8] M. L. Martin, J. J. Delpuech, and G. J. Martin, ' Practical NMR Spectroscopy,' Heyden, London, 1979, p. 391, and references quoted herein.

[9] G. J. Martin and S. Poignant, *J. Chem. Soc., Perkin Trans. 2*, 1974, 642.

[10] F. A. Bovey, ' Nuclear Magnetic Resonance Spectroscopy,' Academic Press, New York, 1969, 252.

[11] (*a*) J. B. Conant and A. A. Cook, *J. Am. Chem. Soc.*, 1920, **42**, 830; (*b*) K. L. Freeman and M. J. Gallagher, *Tetrahedron Lett.*, 1966, 121; *Aust. J. Chem.*, 1968, **21**, 2297.

[12] K. Moedritzer, *J. Am. Chem. Soc.*, 1961, **83**, 4381.

[13] W. Schwotzer and W. Von Philipsborn, *Helv. Chim. Acta*, 1977, **60**, 1501.

[14] M. L. Filleux-Blanchard, D. Lebotlan, A. Reliquet, and F. Reliquet-Clesse, *Org. Magn. Reson.*, 1974, **6**, 471.

[15] L. Kozerski, *Org. Magn. Reson.*, 1977, **9**, 395; L. Kozerski and J. Dabrowski, *ibid.*, 1972, **4**, 253.

[16] A. J. Jones, H. McNab, and P. Hanisch, *Aust. J. Chem.*, 1978, **31**, 1005.