

Destabilized Carbenium Ions: α -Imidoyl Carbenium Ions and the Electron Impact Mass Spectra of α -Haloaldimines and α -Haloketimines

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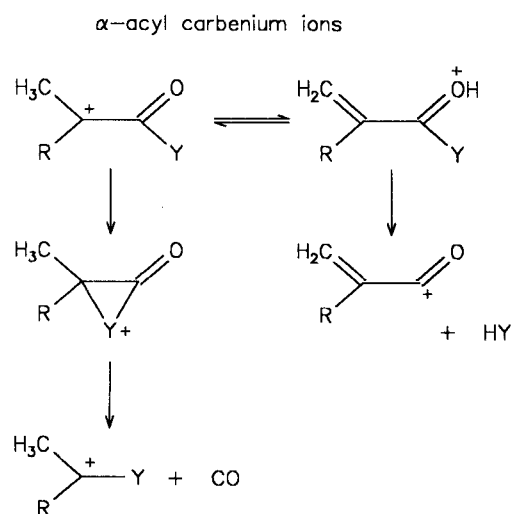
A series of α -chloro- and α -bromoketimines compounds (1-9) with different substituents at the α -position and at the imino group has been investigated by electron impact mass spectrometry as possible precursors of the correspondingly substituted α -imidoyl carbenium ion, an important class of destabilized carbenium ions. The main fragmentation of the molecular ions of compounds 1-9 in the ion source corresponds to an α -cleavage at the imino group; however, fragment ions are also formed by loss of the α -halo substituent. These fragment ions correspond at least formally to α -imidoyl carbenium ions. Their further reactions in dependence on the type of substituents at the imino group and at the α -C atom, were studied by mass-analysed ion kinetic energy and collisional activation mass spectrometry. The results agree with the initial formation of destabilized α -imidoyl carbenium ions but indicate an easy rearrangement of these ions in the presence of suitable alkyl substituents by 1,2- and 1,4-hydrogen shifts to more stable isomers.

INTRODUCTION

Carbenium ions carrying an electron-withdrawing α -substituent are characterized by a highly electron-deficient centre.¹ As a consequence, destabilized carbenium ions exhibit an especially large reactivity for electrophilic reactions and for rearrangements to more stable ions which makes them valuable intermediates in organic synthesis. Besides α -acyl carbenium ions, which have been studied in great detail by solvolytic reactions,² α -imidoyl carbenium ions arising from α -halogenoaldimines and α -halogenoketimines by reaction with Lewis acids have been shown to be important and useful intermediates for organic synthesis.³

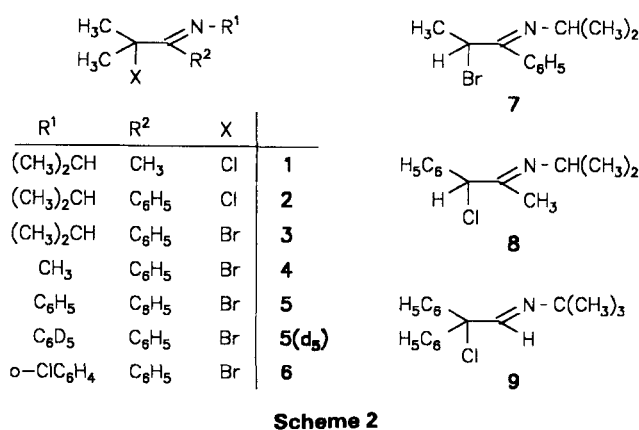
In view of the high reactivity of destabilized carbenium ions in solution it is of interest to study the behaviour of these species in the gas phase, where they are lacking any stabilization or interference from solvent effects. The problems addressed in these investigations are the detection of suitable precursors of the destabilized carbenium ions, the (kinetic) stability of the ions against spontaneous fragmentations, the possible interconversion into more stable isomers by hydrogen atom migrations and skeletal rearrangements, and their reactivity in bimolecular gas-phase ion-molecule reactions. In a series of studies we have investigated the structure and reactivity of the α -acyl carbenium ion carrying different types of acyl groups at the positive centre.⁴ The results demonstrate that these α -acyl carbenium ions are conveniently formed in the gas phase by electron-impact-induced fragmentation from α -halogenoacyl compounds if the destabilizing effect of the acyl substituent is offset somewhat by additional electron-releasing

groups at the α -position, i.e. alkyl or phenyl groups. The resulting tertiary or benzylic α -acyl carbenium ions exhibit a high reactivity towards isomerization and fragmentation. Typically, the unimolecular reactions observed correspond to 1,4-hydrogen shifts yielding much more stable protonated α, β -unsaturated carbonyl derivatives and to the loss of CO by a 1,2-shift of an alkyl group, an aryl group, a methoxy group, and an amino group, respectively (Scheme 1).⁴ Nevertheless, these 'push-pull' substituted carbenium ions represent 'normal' thermodynamically stable species in the gas phase.⁴



Scheme 1

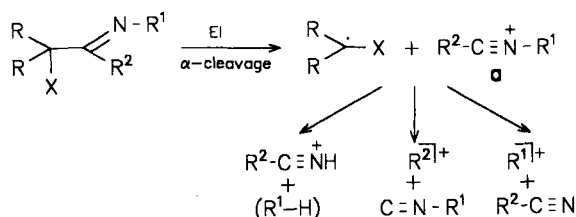
α -Imidoyl carbenium ions are the reactive essence of the synthetically important class of α -halogenoaldimines and α -halogenoketimines, and a theoretical study predicts that these ions are more stable than the related α -acyl carbenium ions.⁵ In view of the results of the mass spectral studies of α -acyl carbenium ions it was interesting to see whether α -imidoyl carbenium ions also can be generated and studied in the gas phase by mass spectrometric techniques. In this paper we report the results of an investigation of a series of α -chloro- and α -bromoaldimines and -ketimines (Scheme 2) by electron impact (EI) mass spectrometry and by mass-analysed ion kinetic energy (MIKE) spectrometry of some relevant fragment ions in the 70 eV mass spectra. Although it will become evident from the discussion that the formation of α -imidoyl carbenium ions is by no means the favoured fragmentation pathway in the mass spectra of the α -halogenoketimines, these ions are detected in the 70 eV mass spectra, and their further reactions reveal some interesting properties of these carbenium ions.



Scheme 2

RESULTS AND DISCUSSION

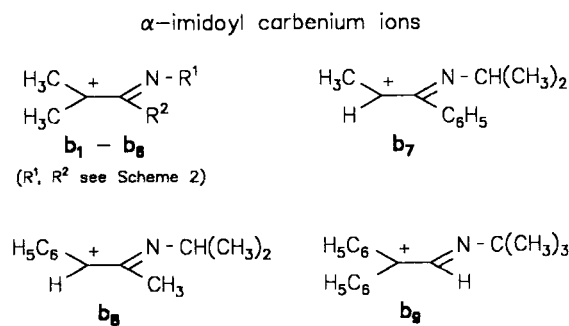
The 70 eV mass spectra (Table 1) of the α -halogenoketimines (1-9) show only rather small peaks of the molecular ions indicating a fast fragmentation of the ionized α -halogenoketimines. However, the preferred fragmentation is not the loss of the α -halogen substituent but the α -cleavage at the ketimino group giving rise to a stable nitrilium ion *a* and a stable α -halogenoalkyl radical (Scheme 3). The large peaks of the nitrilium ion *a* and their further fragmentation products dominate the EI mass spectra. Only in a few cases, and in particular for the 2,2-diphenylacetaldimine derivative (9), is the other ionized fragment of the α -cleavage also



Scheme 3

observed. This fragmentation behaviour of the molecular ions of 1-9 is in close analogy to the EI mass spectra of azomethines.⁶

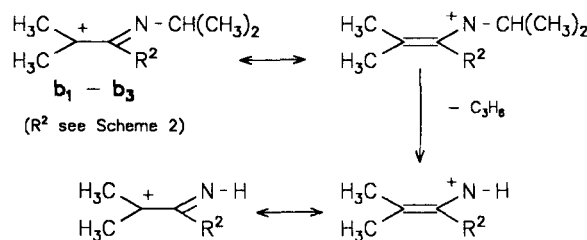
Nevertheless, small peaks of $[M - X]^+$ ($X = \text{Cl}, \text{Br}$) are observed in the EI mass spectra, and the spontaneous fragmentations of these ions from 1-9 were investigated by MIKE and collisional activation (CA) spectrometry (Tables 2 and 3). The $[M - X]^+$ ions of 1-6 correspond at least formally to the tertiary α -imidoyl- α , α -dimethyl carbenium ions (b_1 - b_6) (Scheme 4) with different substituents at the N and C atoms of the imidoyl group. The $[M - \text{Br}]^+$ ion from 7 is an example of a secondary α -imidoyl- α -methyl carbenium ion (b_7) whilst the $[M - \text{Cl}]^+$ ions of 8 and 9 are an α -imidoylbenzyl cation (b_8) and an α -imidoylbenzhydryl cation (b_9), respectively.



Scheme 4

The relative abundance of the $[M - X]^+$ ions from 1-6 is always small and varies between 2.5% (2) and 6.5% (5 and 6). A small leaving-group effect is seen from the mass spectra of 2 ($X = \text{Cl}$; $[M - \text{Cl}]^+$ 2.5%) and 3 ($X = \text{Br}$; $[M - \text{Br}]^+$ 5.0%). Similarly a small effect of the stabilizing α -methyl groups can be detected by comparing the intensity of the $[M - \text{Br}]^+$ ions of 3 and 7.

The predominant fragmentation of metastable ions b_1 - b_3 carrying an *N*-isopropyl group is the loss of C_3H_6 . This fragmentation is not observed for the metastable ions b_4 - b_6 lacking this group. Thus, it is clear that the C_3H_6 loss originates from the *N*-isopropyl group and not from the other isopropylidene moiety present in all of these ions (Scheme 5). Similarly, the loss of the *N*-alkyl group as an alkene molecule is also observed in the MIKE spectra of ions b_7 - b_9 . The exact mechanism of this alkene elimination is not known, but eliminations of *N*-alkyl groups to form even-electron ions are ubiquitous in the EI mass spectra of aliphatic amines and related compounds.⁷ Unfortunately, the product ion $[b - \text{C}_3\text{H}_6]^+$ coincides for 1-3 in mass and elemental composition with the α -cleavage ion *a*. Hence,



Scheme 5

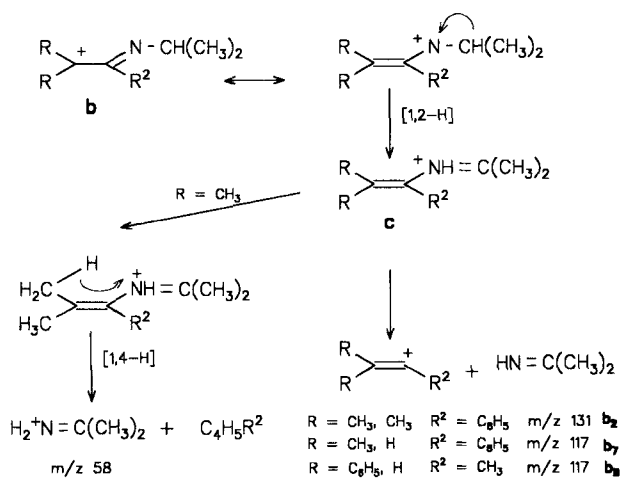
Table 1. Characteristic ions in the 70 eV mass spectra of α -chloroketimines compounds 1–9

Compound	m/z M ⁺	Rel. int. [%] ^b	m/z b	Rel. int. [%]	m/z a	Rel. int. [%]	m/z (α -alkene)	Rel. int. [%]	Other abundant ions ^a m/z (%)
1	161/163	—	126	6.3	84	49.4	42	100.0	41 (9.6)
2	223/225	—	188	2.3	146	32.3	104	100.0	91 (5.3), 77 (7.1), 43 (6.2), 41 (7.0)
3	267/269	—	188	5.0	146	50.7	104	100.0	91 (7.6), 77 (5.0), 43 (7.0), 41 (7.3)
4	239/241	0.2/0.2	160	4.0	118	100.0	—	—	91 (12.0), 77 (20.4), 51 (8.8), 42 (10.4), 41 (10.2), 39 (6.8)
5	301/303	—	222	6.2	180	100.0	—	—	206 (5.0), 115 (7.0), 104 (6.2), 91 (13.3), 77 (51.3), 51 (19.8), 41 (8.5), 39 (7.1)
5(d_5)	306/308	8.3/8.1	227	9.8	185	100.0	—	—	211 (5.0), 184 (12.9), 119 (6.2), 115 (7.1), 109 (5.0), 91 (17.5), 82 (74.9), 77 (12.6), 54 (53.4), 51 (12.7), 41 (29.7), 39 (11.5)
6	335/337/339	1.0/3.9/2.9	256/258	4.8/1.6	214/216	100.0/33.9	—	—	115 (6.1), 111 (14.6), 91 (11.8), 77 (20.4), 75 (21.4), 51 (11.8), 41 (16.0), 39 (8.2)
7	253/255	0.8/0.7	174	3.1	146	51.1	104	100.0	117 (6.0), 115 (8.3), 91 (6.3), 77 (7.6), 43 (8.0), 41 (5.8)
8	209/211	1.9/1.8	174	2.0	84	63.9	42	100.0	125 (8.5), 117 (6.8), 115 (6.0), 104 (8.5), 91 (6.7), 89 (5.1), 41 (6.4)
9	285/287	0.7/0.2	250	3.0	84	8.6	28	4.0	203 (8.2), 201 (26.6), 194 (17.5), 193 (8.8), 178 (6.5), 165 (46.5), 139 (5.2), 105 (7.6), 84 (8.6), 77 (10.4), 57 (100.0), 51 (9.6), 41 (35.0), 39 (12.2)

^a Only peaks of $\geq 5\%$ relative intensity have been listed.^b Relative intensities in % of base peak.**Table 2. MIKE spectra of α -imidoyl carbenium ions b from compounds 1–9**

m/z^a	Ion m/z (b)									
	b_1 126	b_2 188	b_3 188	b_4 160	b_5 222	b_6 256	b_7 174	b_8 174	b_9 250	
Rel. int. [%] ^b	1.1	1.8	10.5	26.6	51.1	82.4	39.2	30.2	4.4	7.9
m/z	109	173	173	158	207	241	159	159	235	
Rel. int. [%]	15.4	2.1	2.1	0.9	6.6	11.2	6.7	4.3	2.0	
m/z	85	171	171	145	193	221	157	157	194	
Rel. int. [%]	12.9	1.3	1.1	11.8	1.0	25.1	6.4	34.7	90.1	
m/z	84	146	146	143	180	219	146	145		
Rel. int. [%]	46.4	22.3	18.4	1.1	0.8	11.0	0.8	3.0		
m/z	70	131	131	131	144	129	145	142		
Rel. int. [%]	1.0	57.2	41.8	26.4	1.0	5.8	2.7	1.0		
m/z	69	119	119	129	130	104	133	133		
Rel. int. [%]	1.9	2.1	1.8	4.4	2.7	4.2	6.2	6.2		
m/z	58	104	104	119	119	91	132	132		
Rel. int. [%]	11.2	1.5	1.1	3.5	0.8	3.5	16.1	31.9		
m/z	57	85	85	91	106		119	129		
Rel. int. [%]	1.7	0.7	0.7	0.9	2.4		1.3	1.8		
m/z	43	58	58		91		117	118		
Rel. int. [%]	2.2	2.3	1.0		1.9		4.8	1.7		
m/z	42						104	117		
Rel. int. [%]	5.2						10.2	2.0		
m/z							91	91		
Rel. int. [%]							1.8	3.5		
m/z							77	84		
Rel. int. [%]							3.0	0.8		
m/z							58	58		
Rel. int. [%]							10.0	1.0		

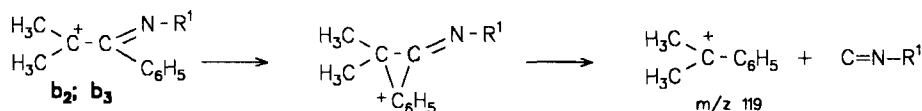
^a m/z values of fragment ions.^b Relative intensities in % total fragment ion current.



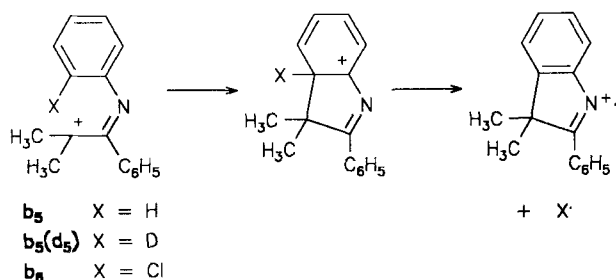
1,4-hydrogen shift (if possible) subsequent to the first 1,2-hydride shift and loss of an unsaturated hydrocarbon molecule from the iminium ion *c* yields the protonated acetone-imine *m/z* 58, and indeed, the formation of *m/z* 58 in the MIKE spectra is only observed concurrent to the loss of C_3H_7N .

The ion *m/z* 119 in the MIKE spectra of *b*₂ and *b*₃ arises from a 1,2-shift of the phenyl group from the imidoyl-carbon atom to the carbenium centre and elimination of (formally) an isonitrile molecule $C=N-C_3H_7$ (Scheme 8). A similar reaction has been observed for protonated azirines,⁸ and this process is analogous to the loss of CO from the α -acyl carbenium ions⁴ (see Scheme 1). However, while the loss of CO in the MIKE spectra of most of the α -acyl carbenium ions is quite abundant and is associated with a large kinetic energy release (KER), the peaks due to the loss of $C=N-R^1$ are rather weak in the MIKE spectra of *b*₁–*b*₄ and show a normal Gaussian peak shape characteristic for a small KER. Obviously, this rearrangement is not as favoured as in the case of the α -acyl carbenium ions. There may be two reasons for this different behaviour of the two types of destabilized carbenium ions. Firstly, the α -imidoyl carbenium ions are more stable than their α -acyl analogues⁵ and the neutral fragment of the rearrangement is in the former case an isonitrile molecule which is less stable than CO eliminated from the latter ions. Hence, the rearrangement of the α -imidoyl carbenium ions is energetically less favoured. Secondly and more likely, the α -imidoyl carbenium ions *b* are predicted to collapse into their more stable cyclic isomers and furthermore rearrange by a 1,2-hydride shift within the *N*-alkyl moiety to the more stable iminium ions *c* (Scheme 7). Analogous isomerizations are not possible in the case of α -acyl carbenium ions.

The spontaneous fragmentations of metastable α -imidoyl carbenium ions *b*₅ were studied as an example where a stabilization of *b* by a 1,2-hydride shift is not

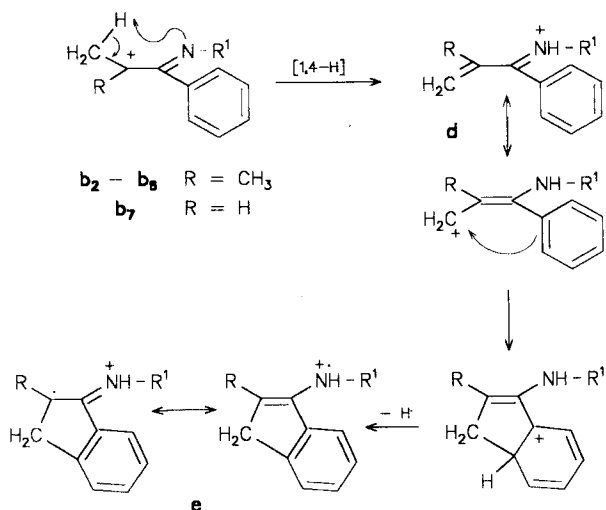


possible because of an *N*-phenyl substituent. It has been mentioned already that a peak due to the loss of C_6H_5N indicative of the 1,2-hydride shift is absent in the MIKE spectrum of *b*₅. Instead, a small peak at *m/z* 130 for the loss of $C_6H_5NH^+$ is observed. The only large signal in the MIKE spectrum besides a peak for the 'structurally not meaningful' loss of CH_3^+ arises from the loss of H^+ . In particular, no distinct signal at *m/z* 119 is observed, which would be due to a 1,2-shift of the *C*-phenyl group concomitant to an elimination of phenylisocyanide. The elimination of a hydrogen atom was also observed in the MIKE spectra of *b*₁–*b*₄ carrying a phenyl substituent at the imidoyl-carbon atom. However, in the case of *b*₅ the loss of H^+ is much more abundant, obviously because of the presence of the *N*-phenyl group. A rationalization of this effect is given by the mechanism shown in Scheme 9, which corresponds to an intramolecular electrophilic substitution of the destabilized α -imidoyl carbenium ion and formation of an ionized 3*H*-indole derivative.



To test this mechanism the deuterated ions *b*₅(*d*₅) were prepared by electron-impact-induced loss of Br^+ from *5*(*d*₅). The formation of the ionized 3*H*-indole derivative from *b*₅(*d*₅) would be indicated by a signal for the loss of D in the MIKE spectrum. In fact, the loss of D is observed, but the signal is rather small and the intensity ratio for the loss of D and H , respectively, is about 1:13. The ratio increases to 1:7 in the CA spectrum of *b*₅(*d*₅) but the loss of D is still not preferred. The low intensity for [*b*₅(*d*₅) – D] may be due to isotope effects and extensive H/D exchanges within the precursor ion. Hence, as a further test for the mechanism depicted in Scheme 9 the fragmentations of metastable *b*₆ were studied. The loss of an *ortho*-chloro substituent by an intramolecular aromatic substitution has been observed repeatedly,⁹ and the formation of the 3*H*-indole radical cation should be favoured in the case of *b*₆ by the loss of Cl^+ instead of H^+ . The MIKE spectrum of *b*₆ exhibits the expected large signal for the loss of Cl^+ , but again, also, an even larger peak for the loss of H^+ . These results show that the ionized 3*H*-indole derivative is formed, but that the mechanism of Scheme 9 is obviously not the main process for the elimination of H^+

from ions *b* containing an *N*-phenyl group. In fact, the loss of H⁺ from ions *b*₂–*b*₄ lacking this group has to occur by another mechanism. An abundant loss of H⁺ is observed only for metastable ions *b* carrying a phenyl substituent at the imidoil-carbon atom (*b*₂–*b*₇). This shows that in the second mechanism of the hydrogen elimination this *C*-phenyl group is involved as stated in Scheme 10.



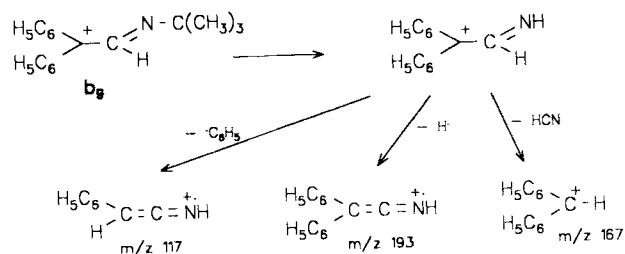
The key step of this mechanism is an isomerization of the ions *b* by a 1,4-H shift from a methyl group at the carbenium ion centre to the imino-N atom. The resulting *N*-protonated α, β -unsaturated ketimine *d* is a much more stable tautomer of *b*, and this tautomerization of the α -imidoil carbenium ions is entirely analogous to the stabilization of the α -acyl carbenium ions by a rearrangement to the *O*-protonated α, β -unsaturated carbonyl compounds⁴ (Scheme 1). The ion *d* has a partial positive charge at the terminal CH₂ group which enables an electrophilic ring closure to the *ortho*-position of the phenyl group. A subsequent loss of H⁺ gives rise to a stable radical cation of an indanone-enamine derivative *e*.

For destabilized α -imidoil carbenium ions *b* with suitable substituents, the 1,4-H shift *b* → *d* represents a second stabilization reaction besides the 1,2-H shift *b* → *c*. Both isomerizations compete with each other in the case of the ions *b*₁–*b*₄ and *b*₇, but ions *b*₅ and *b*₆ can rearrange only to *d*. This enhances the fragmentation route of Scheme 10 to the final product ion *e*. Furthermore, aniline forms more stable enamines than aliphatic amines, so that a reaction *b* → *d* → *e* is probably additionally assisted by the *N*-phenyl group of *b*₅ and *b*₆, explaining the increased intensities for the loss of H⁺ in the MIKE spectra of these ions.

The results discussed so far for the tertiary α -imidoil- α, α -dimethyl carbenium ions *b*₁–*b*₆ and the secondary α -imidoil- α -methyl carbenium ion *b*₇ reveal that all of the dominant fragmentations of metastable ions *b* can be explained by a preceding isomerization into the more stable tautomeric ions *c* and *d*. Only small peaks are observed in the MIKE spectra for a fragmentation by a 1,2-shift of the substituent at the imidoil-carbon atom followed by loss of an isonitrile molecule as expected by

the analogy with the CO elimination from the related α -acyl carbenium ions.⁴ Thus, it remains questionable whether the ions *b* persist as distinct species in the gas phase of a mass spectrometer after formation by electron-impact-induced fragmentations of the precursors 1–7. Theoretical studies have shown⁵ that α -imidoil carbenium ions are quite stable and easily interconvert with the isomeric cyclic iminium ions. However, isomerizations of even-electron cations by 1,2- and 1,4-H shifts are well documented in organic mass spectrometry¹⁰ and require only small critical energies for exothermic rearrangements as in the case of the ions *b* studied. Therefore, the ions *b* may be separated from their more stable tautomers *c* and *d* by only small energy barriers. This would explain why most of the reactions of fragmenting ions *b* with some excess energy occur via *c* or *d*.

In this connection the reactions of ions *b*₉ which cannot isomerize to ions of type *c* and *d* because of the *N*-*tert*-butyl group and of the phenyl substituents become important. As mentioned before, the only reaction observed for metastable *b*₉ is the loss of C₄H₈ yielding ions *m/z* 194. The additional signals in the CA spectrum of *b*₉ are only due to fragment ions expected for a benzhydryl group. However, the ion *m/z* 194 in the EI mass spectrum of **9** corresponds unambiguously to the ion [*b*₉ – C₄H₈], and its further fragmentation corresponds to that of an *N*-unsubstituted α -imidoil- α, α -diphenyl carbenium ion, which occurs mainly by the loss of H and of HCN, respectively, and slightly by the loss of C₆H₅⁺. These reactions agree with the proposed structure of a destabilized α -imidoil-benzhydryl cation as shown in Scheme 11.



EXPERIMENTAL

The 70 eV mass spectra were obtained with the mass spectrometer/data system Varian MAT CH5D/SS200 and the following conditions: electron emission, 2 mA; acceleration voltage, 3 kV; ion-source temperature, ~180 °C; sample introduction via a direct inlet system.

The MIKE spectra were measured with the VG ZAB 2F mass spectrometer using an EI source. The experiments were performed under the following conditions: acceleration voltage, 6 kV; electron energy, 70 eV; trap

current, 100 μ A. The pressure at the ion-gauge head below the ion-source housing was approximately at 3×10^{-7} mbar. The MIKE spectra were obtained by magnetically focusing the ions of interest into the second field-free region (2nd FFR) and scanning the voltage across the electrostatic analyser. The CA spectra were obtained in an analogous manner by introducing He as the collision gas into the collision cell of the 2nd FFR at such a rate that the main beam intensity was reduced to $\sim 30\%$. The intensity values given for the MIKE and CA spectra (Tables 2 and 3) are the mean of three measurements; mean deviation $\pm 6\%$.

α -Halogenated ketimines (**1**,¹¹ **2**, **3**^{3c} and **4**) were prepared by condensation of the corresponding α -chloroketone or α -bromoketone with their appropriate primary amine in ether or benzene in the presence of stoichiometric amounts of titanium(IV) chloride, according to the general synthesis of α -haloimines.¹¹ Following this method α -chloroketimine (**2**) (b.p. 50–51°C/0.01 mmHg) was prepared in 91% yield (C_6H_6 , reflux 30 min.), while α -bromoketimine **4** (bp. 55–56°C/0.08 mmHg) was synthesized in 92% yield (C_6H_6 , reflux 2 h). α -Bromoketimine **5** was synthesized in 90% crude yield from the reaction of 2-bromo-2-methyl-1-phenyl-1-propanone with aniline and titanium(IV) chloride in

ether (reflux 1 h). However, compound **5** decomposed completely upon high-vacuum distillation. Hence, a better procedure involved bromination with NBS (1.1 equiv.; CCl_4 , reflux 5 min., then room temperature 1 h) of *N*-(2-methyl-1-phenyl-1-propylidene) aniline (partially occurring as enamine). Compound **5** obtained in 99% yield was used without further purification. The deuterated α -bromoketimine **5**(d_5) and the *o*-chloro derivative **6** were prepared by the condensation of 2-bromo-2-methyl-1-phenyl-1-propanone with aniline- d_5 and 2-chloroaniline, respectively, in the presence of titanium(IV) chloride as described for compound **5**. The crude oils (yield **5**(d_5) 70%; **6** 78%) contained small amounts of educts besides the expected α -bromoketimines (GC/MS analysis), but were used without further purification for the mass spectrometric experiments because of the decomposition during distillation.

Acknowledgements

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