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DESTABILIZED CARBENIUM IONS : SECONDARY AND TERTIARY α-CARBAMOYL-BENZYL CATIONS

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RÉSUMÉ. — La formation et les réactions de cations α-carbamoyl benzyle secondaires **a** et **b** et α-carbomoyl α-méthyl benzyle tertiaires **l** et **m** ont été étudiés par spectrométrie de masse. Ces ions carbénium déstabilisés par une substitution « push-pull » proviennent d'ions moléculaires de phényl-2 acétamide substitués et de phényl-2 propionamide, respectivement, par perte du substituant. La perte de CO et l'élimination de NHR_2 (R = H, CH_3) sont les réactions caractéristiques des cations carbamoyl-2 benzyle. La perte de CO correspond à un réarrangement par déplacement 1,2 d'un NH_2 et d'un $N(CH_3)_2$, respectivement, elle est associée à une très importante libération de l'énergie cinétique (ions **a**/**b** : T_{50} = 720 meV ; ion **l** : T_{50} = 920 meV ; ion **m** : T_{50} = 870 meV). Les ions carbénium tertiaires α-carbamoyle **l** et **m** se réarrangent par un déplacement 1,4-H en phényl-2 acrylamide protonés **n** et **o** qui sont plus stables. Le réarrangement met en évidence un effet isotopique distinct ; les ions carbénium tertiaires α-carbamoyle **l** et **m** et phényl-2 acrylamide protonés isomères **n** et **o** se transforment mutuellement les uns dans les autres mais n'atteignent pas l'équilibre pendant leur temps de vie dans le spectromètre de masse. Un schéma du mécanisme expliquant ces observations expérimentales est discuté.

ABSTRACT. — The formation and reactions of secondary α-carbamoyl benzyl cations **a** and **b** and tertiary α-carbamoyl-α-methyl benzyl cations **l** and **m** have been investigated by mass spectrometric techniques. These destabilized carbeniumions with a « push-pull » substitution arise from the molecular ions of appropriately 2-substituted phenyl acetamides and 2-phenyl propionamides by loss of the substituent. The characteristic reactions of the α-carbamoyl benzyl cations are the loss of CO and the elimination of $NH(R)_2$ (R = H, CH_3). The loss of CO corresponds to a novel rearrangement reaction by a 1,2-shift of a NH_2- and a $N(CH_3)_2$-group, respectively, and is associated with a very large KER (ions **a**/**b** : T_{50} = 720 meV ; ions **l** : T_{50} = 929 meV ; ion **m** : T_{50} = 870 meV). The tertiary α-carbamoyl carbenium ions **l** and **m** rearrange by a 1,4-shift into the more stable protonated 2-phenyl acrylamides **n** and **o**. This rearrangement exhibits a distinct isotope effect, and the tertiary α-carbamoyl carbenium ions **l** and **m** and the isomeric protonated 2-phenyl acrylamides **n** and **o** interconvert mutually but do not equilibrate during their life time in the mass spectrometer. A mechanistic scheme explaining these experimental observations is discussed.

Carbocations destabilized by an electron withdrawing substituent at the positive center and in particular α-acyl carbenium ions are important intermediates of organic reactions [1]. These ions are very reactive and exhibit a definite tendency for rearrangements [2, 3]. We have recently shown that α-acetyl-, α-benzoyl, and α-carbomethoxy-carbenium ions can be investigated by mass spectrometric techniques if the destabilizing effect of the acyl substituents is counterbalanced by additional electron donating substituents in a « push-pull substitution » [4, 5, 6]. The characteristic reaction of these α-acyl carbenium ions is the elimination of CO which is associated with a large and non-statistical kinetic energy release (KER). A further reaction is the isomerization by a 1,4-shift of a hydrogen atom onto the carbonyl group yielding the much more stable isomeric protonated α-, β-unsaturated carbonyl compound if an appropriate alkyl group is present. In this paper we report the results of a study of the formation and reactions of secondary and tertiary α-carbamoyl-α-methyl benzyl cations with $-CONH_2$ and $-CON(CH_3)_2$ groups as the electron withdrawing (" pull ") substituents. It was of interest to see whether these destabilized carbenium ions rearrange also by elimination of CO corresponding to a 1,2-shift of the NR_2-group (R = H, CH_3).

Experimental

MASS SPECTROMETRY :

The EI mass spectra were obtained with a mass spectrometer Finnigan MAT 311A combined to a data system MAT SS200 using the following conditions : electron energy 70 eV, accelerating voltage 3 kV, ion source temperature *c.* 180 °C and sample inlet by direct insertion probe at low temperatures.

The metastable ions studies were performed with a mass spectrometer VG ZAB 2F using a combined EI/CI ion source at a temperature below 200 °C and an accelerating voltage of 6 kV. The ions under study were generated by EI at 70 eV or CI with methane (or

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tetra-deuteromethane) as reagent gas. The samples were introduced either by a direct insertion probe or by a direct inlet system with a variable leak valve at low temperatures. The MIKE spectra were obtained by focussing the relevant ions magnetically into the second field free region preceding the electrostatic analyzer and scanning the voltage at the electrostatic analyzer. The CA spectra were measured by the same technique but by introducing a stream of He into the collision cell of the second field free region at such a rate that the intensity of the main ion beam was reduced to less than 50 % of its original value. All intensity values given in the Tables are the mean values of at least three measurements.

COMPOUNDS:

All compounds have been purified by vacuum distillation or column chromatography, respectively, and their structures have been verified by ^{1}H-NMR spectroscopy and IR-spectroscopy [7].

The 2-substituted phenyl acetic acids, 2-substituted 2-phenyl propionic acids and their acyl chlorides have been prepared by standard procedures given in the literature [8]. The synthesis of the 2-substituted phenyl acetamides **2-4** was achieved by reaction of the corresponding phenyl actyl chlorides with 25 % NH_3/H_2O at − 10 °C [9]. The same method was used to prepare the 2-substituted 2-phenyl propionamides **15**, **17** and **22** from the corresponding 2-phenyl propionyl chlorides. Similarly, the N,N-dimethylamides **6-8**, **18**, **20** and **24** were obtained by the reaction of the acyl chlorides with a mixture of dimethylamine hydrochloride, 20 % NaOH and 1,2-dichloroethane at − 10 °C [10].

2-Iodo phenyl acetamide **1** crystallized from a reaction mixture of the bromo derivative **2** and NaI in acetone after 24 h at r.t. [11]. Similarly the N,N-dimethylamide **5** was obtained by the reaction of **7** with NaI in acetone and purified by column chromatography. A mixture of 2-chloro-2-phenyl propionamide **16** and 2-phenyl acrylamide **21** was obtained by a reaction of the acyl chloride generated from atrolactinic acid and $SOCl_2$ [12] with 25 % NH_3/H_2O at − 10 °C. The mixture was separated by column chromatography. The N,N-dimethyl-2-chloro-2-phenyl propionamide **19** was prepared by the same procedure using dimethylamine.

N,N-dimethyl-2-phenyl acrylamide **23** was obtained from the bromo derivative **18** via elimination of HBr by refluxing a solution in dioxane for 4 h DABCO.

3-Trideutero-2-phenyl propionic acid was prepared by reaction of phenyl malonic acid diethylester with NaH and CD_3I in DMF [13] followed by hydrolysis and decarboxylation. The 2-phenyl propionic acid-3-d_3 was used to synthesize the 2-bromo-2-phenyl propionamide **15-d₃** (D-content > 93 mol % d_3) and **18-d₃** (D-content > 93 mol % d_3) and the 2-phenylacrylamides **21-d₃** (D-content > 97 mol %) and **23-d₂** (D-content > 93 mol % d_2), respectively, by the methods used for the unlabelled compounds.

Results and Discussion

SECONDARY α-CARBAMOYL BENZYL CATION

The secondary α-carbamoyl benzyl cation $C_8H_8NO^+$ **a** and the N,N-dimethylcarbamoyl benzyl cation $C_{10}H_{12}NO^+$ **b** should arise by the loss of the substituent X from the molecular ions of the 2-substituted 2-phenyl acetamides **1-8** (*Fig.* 1).

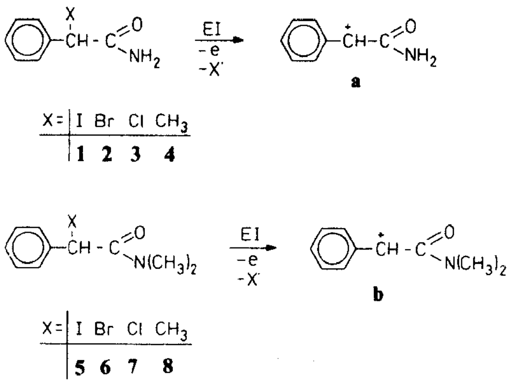


Figure 1. − Formation of ions **a** and **b** from **1-8**.

The 70 eV mass spectra (Table I) of **1**, **2**, **5** and **6** (X = I and Br) exhibit large peaks of these ions, while loss of X is only a minor process in the mass spectra of **3**, **4**, **7** and **6** (X = Cl and CH_3). The most important fragmentations in the ion source of the mass spectrometer are the α-cleavage and the formation of the ions R_2NCO^+ and $C_7H_6X^+$. However, the losses of X from metastable molecular ions are observed and give rise to narrow peaks (T_{50} = 15 ± 5 meV) in the MIKE spectra. This agrees well with a direct bond cleavage mechanism expected for the formation of the $[M\text{-}X]^+$ ions **a** and **b**. More information about the structure of the $[M\text{-}X]^+$ ions has been obtained from the MIKE spectra and collisional activation (CA) spectra of $C_8H_8NO^+$ ions from **1-3** and of some isomeric ions (*Fig.* 2).

The MIKE spectra of these $C_8H_8NO^+$ ions are given in Table II. The results demonstrate that the $[M\text{-}X]^+$ ions from **1-3** are identical but distinct from the ions **c**, **d** and **e**. The identical CA spectra of the $[M\text{-}X]^+$ ions (*Fig.* 3) prove that the small intensity variations in their MIKE spectra are due to different internal energies. Thus the α-carbamoyl benzyl structure **a** is the logical choice for a structure of the $[M\text{-}X]^+$ ions [14].

The structure of an α-carbamoyl benzyl cation **a** for the $[M\text{-}X]^+$ ions also agrees with the very predominant elimination of CO from metastable ions and the very large KER of T_{50} = 720 meV observed for this process (Table II). A loss of CO associated with a large KER has been observed previously for α-acetyl benzyl cations (T_{50} = 305 meV [5]), α-benzoyl benzyl cations (T_{50} = 375 meV [5]) and α-carbomethoxy benzyl cations (T_{50} = 570 meV [6]). The KER during the CO loss from ions **a** exceeds even that observed for the α-carbomethoxyl benzyl cations, in agreement with the mechanism of this reaction depicted in Figure 4. A very

Table I. − Characteristic ions in the 70 eV mass spectra of **1-8** (rel. intensity in % base peak)

	X	M^+	−X	−[X+CO]	$C_7H_7X^+$	$C_7H_6X^+$	$C_7H_7^+$	$C_8H_6O^+$	R_2NCO^+
1	I	−	100	43	−	3	19	5	6
2	Br	< 1	69	31	16	27	100	21	45
3	Cl	7	3	4	72	53	100	14	30
4	CH_3	16	< 1	−	66	100	53	−	11
5	I	−	60	100	−	3	14	4	100
6	Br	−	38	59	−	5	11	20	100
7	Cl	8	1	4	−	3	6	4	100
8	CH_3	24	< 1	< 1	−	20	< 1	< 1	100

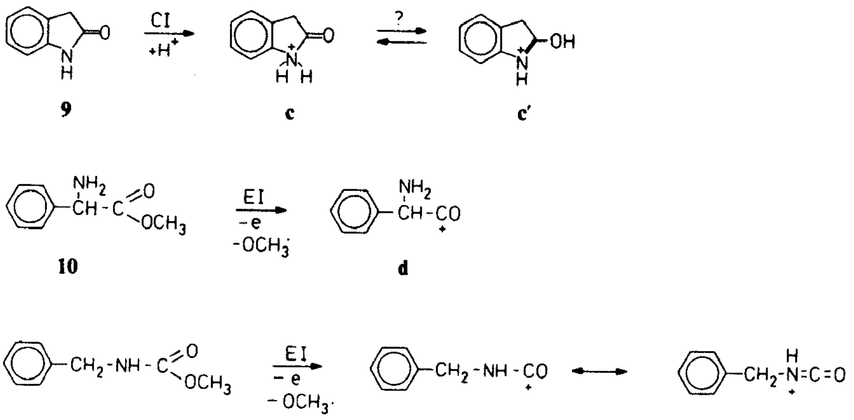


Figure 2. – Generation of isomeric $C_8H_8NO^+$ ions.

Table II. – MIKE spectra of isomeric $C_8H_8NO^+$ ions (rel. intensity in % base peak)

Precursor			m/z								
	X		133 –H	119 $-CH_3$	117	116	106 –CO	91	79	56	$T_{50}(-CO)$ [meV]
1	I	EI	–	–	–	5	100	–	–	–	740
2	Br	EI	–	–	–	3	100	–	–	–	700
3	Cl	EI	–	–	–	13	100	8	–	–	740
9		CI	> 200	–	–	–	100	–	–	–	450
10		EI	> 200	20	–	–	100	24	–	–	260
11		EI	33	5	12	21	100	7	9	10	100

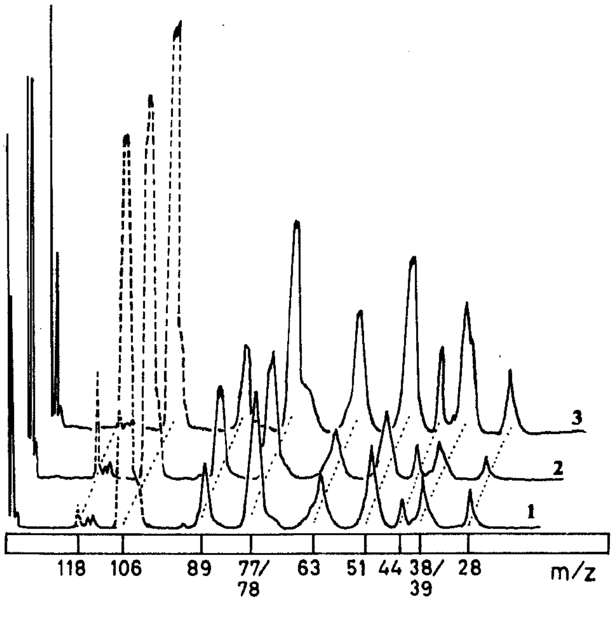


Figure 3. – CA spectra of the $[M-X]^+$ ions from 1-3.

Table III. – MIKE spectra of the $[M-X]^+$ ions from **5-7** (rel. intensity in % base peak)

Precursor		m/z		
	X	147 $-CH_3$	134 –CO	$T_{50}(-CO)$ [meV]
5	I	2	100	700
6	Br	3	100	730
7	Cl	9	100	720

stable α-amino benzyl cation **g** is formed according to this mechanism by a 1,2-shift of the H_2N-group via the rigid α-lactam structure **f**.

The MIKE spectra and the CA spectra of $C_{10}H_{12}NO^+$ ions $[M-X]^+$ from the N,N-dimethylamides **5-7** are reported in Table III and Figure 5, respectively. The Mike spectra and the CA spectra of the $[M-X]^+$ ions are identical and the main reaction is the elimination of CO accompanied again by a large KER (T_{50} = 720 ± 10 meV, Table III) as expected for ions of structure **b**.

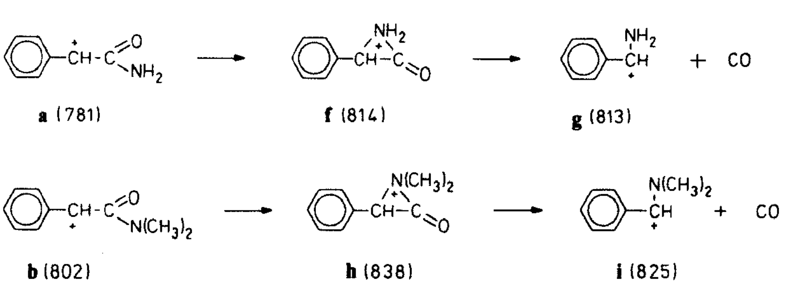


Figure 4. – Mechanism of the elimination of CO from **a** and **b** (in parenthesis ΔH_f [$kJmol^{-1}$] of the ions).

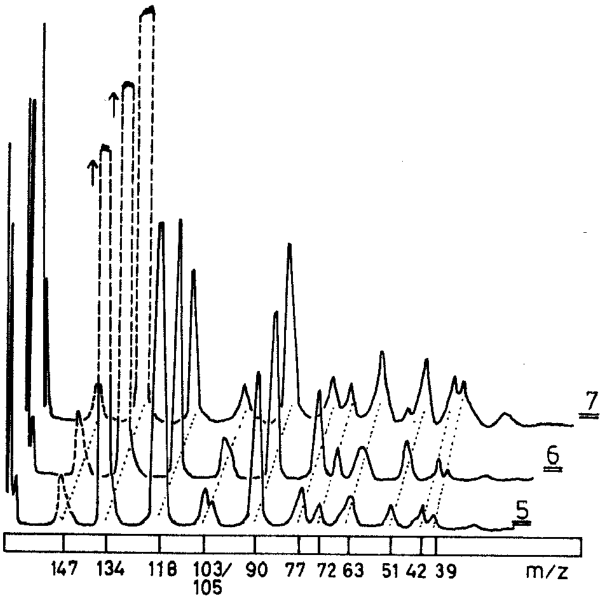


Figure 5. – CA spectra of the $[M-X]^+$ ions from **5-7**.

The mechanism of the CO loss from the α-N,N-dimethylcarbamoyl benzyl cations **b** is analogous to that for ions **a** (*Fig.* 4). This time the reaction proceeds by a 1,2-shift of a dimethylamino group via the quaternary ammonium ion **h** with a rigid α-lactam moiety as the critical configuration resulting eventually in the stable dimethylamino benzyl cation **i**. To our knowledge the rearrangement and fragmentation of even-electron ions in the gas phase by a 1,2-shift of an amino group and a dimethylamino group, respectively, have not been observed before although the migration of amino groups in radical cations has been studied in some detail [15].

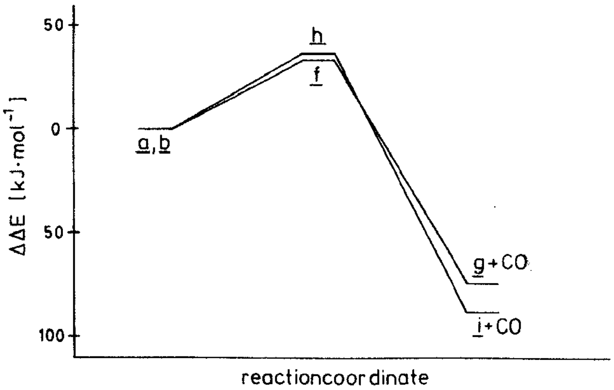


Figure 6. – Schematic reaction energy profiles for the loss of CO from the α-carbamoyl benzyl cations **a**.

The heats of formation ΔH_f of the ions of Figure 4 have been calculated by MNDO [16] and the resulting schematic reaction energy profile is shown in Figure 6. The energy profile shows that the fragmentation of the cyclic ions **f** and **h** into CO (ΔH_f = 111 kJ.mol^{-1} [17]) and the α-amino benzyl ions **g** and **i** is exothermic by 110 kJ.mol^{-1} and 120 kJ.mol^{-1}, respectively. This large exothermicity and the rigid nature of the three membered intermediates (or transition states) explains the large KER of c.67-70 kJ.mol^{-1} associated with this processes.

TERTIARY α-CARBAMOYL-α-METHYL BENZYL CATION

CO loss also expected for tertiary α-carbamoyl-α-methyl benzyl ions **l** and **m** formed by loss of the substituent X from the molecular ions of 2-substituted 2-phenyl propionamides **15-20** (*Fig.* 7). However, in the presence of additional methyl groups the loss of X from the molecular ions and the further reactions of the $[M-X]^+$ ions may be associated with rearrangements [6, 18] shown in Figure 8.

In competition to the formation of $[M-X]^+$ ions of structure **l** and **m**, respectively, by a direct bond cleavage, a 1,4-H-shift from the methyl group onto the amide group may occur followed by 1,2-migration of the protonated amide group [18]. This gives rise eventually to $[M-X]^+$ ions **p** and **q**, respectively, with the structure of protonated cinnamides. Another route could be the direct loss of X from the distonic ion formed by the 1,4-H-shift and the formation of $[M-X]^+$ ions **n** and **o** with the structures of protonated α-phenyl acrylamides. These latter ions may also be formed *after* elimination of X by a 1,4-H-shift within the initially formed tertiary α-carbamoyl benzyl cations **l** and **m**. Insight into this system of fragmentation and isomerization reactions is possible by an investigation of deuterated derivatives of the 2-substituted 2-phenyl propionamides and by comparing the $[M-X]^+$ ions from **15-20** with the isomeric ions **n** and **o** or **p** and **q**, respectively, generated from the amides **21-24** (see *Fig.* 7) in CI experiments.

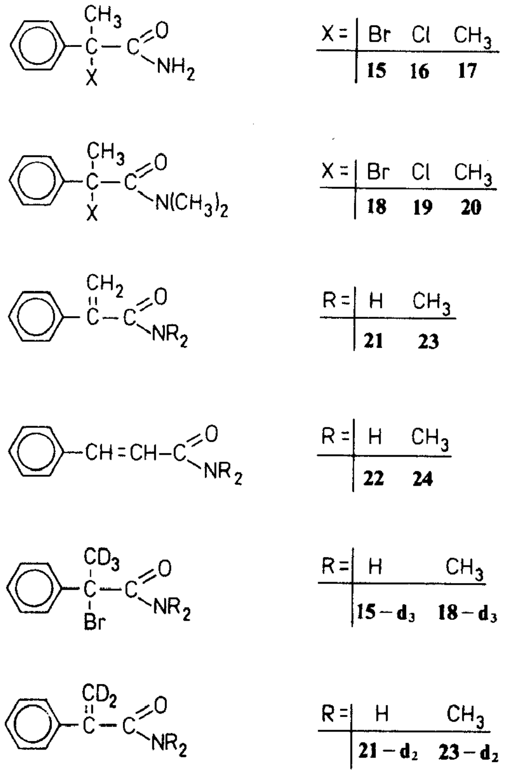


Figure 7. – Molecular structures of **15-22**.

The characteristic ions in the 70 eV-mass spectra of the substituted 2-phenyl propionamides **15-20** are shown in Table 4 and abundant $[M-X]^+$ ions are observed for **15** and **18** (X = Br.). With X = Cl and CH_3, the intensity of these ions is small and the fragmentation of the molecular ions by α-cleavage competes effectively. Nevertheless, the loss of X is observed for metastable molecular ions **15, 16, 18** and **19**

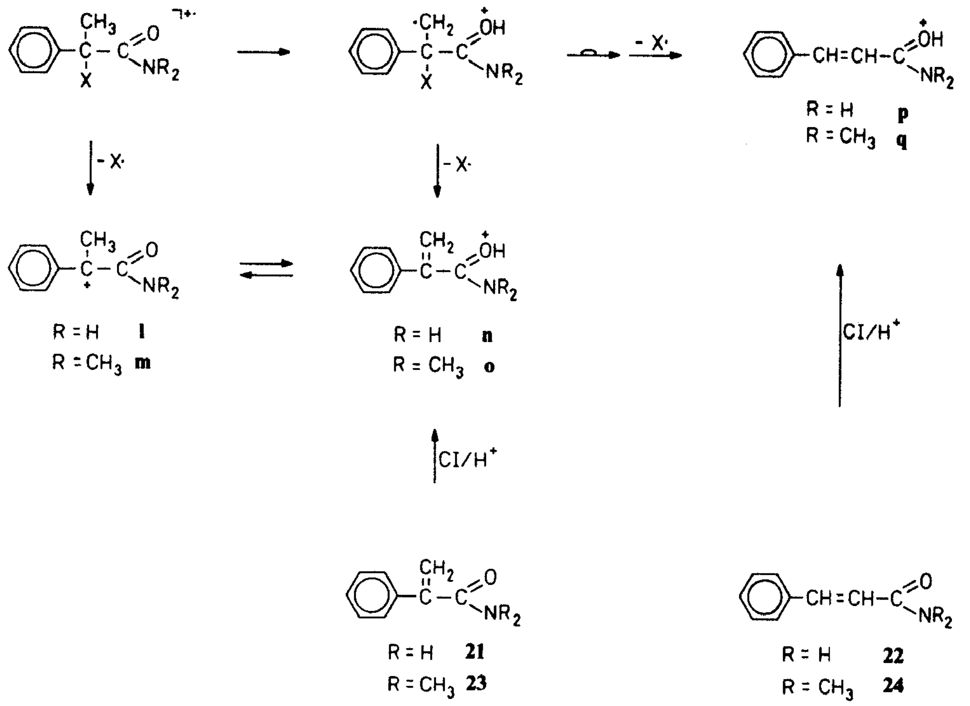


Figure 8. – Formation and rearrangements of ions **l** and **m**.

with narrow Gaussian peaks in the MIKE spectra (T_{50} = 30 ± 10 meV) agreeing with a direct bond cleavage.

More information about the structure of the $C_9H_{10}NO^+$ ions and of the $C_{11}H_{14}NO^+$ ions is obtained from the CA spectra (*Fig.* 9). The CA spectrum of the protonated cinnamide ions **p** is distinguished clearly from the other ones by the lack of signals for the loss of CO (*m*/*z* 120) and CH_3 (*m*/*z* 133), an abundant elimination of NH_3 (*m*/*z* 131) and an additional signal at *m*/*z* 105. In contrast, the CA spectrum of the $[M\text{-}Br]^+$ ions derived from **15** exhibits a large and broad signal for the CO elimination (*m*/*z* 120) and only a small one for the elimination of NH_3 (*m*/*z* 131). This and the absence of the peak *m*/*z* 105 proves clearly that no rearrangement into ions **p** occurs before or during the loss of Br from the molecular ions of **15**. A similar conclusion is drawn from the CA spectrum of the $C_9H_{10}NO^+$ ions derived from the chloro compound **16** [19] However, the rearrangement route from the molecular ions to the $[M\text{-}X]^+$ ions **p** (*Fig.* 8) happens if the substituent X is a « bad » leaving group CH_3 (**17** and **20**).

The CA spectra of the $C_9H_{10}NO^+$ ions obtained from **15**, **16** and **21** (*Fig.* 9) exhibit small differences in the intensities of certain fragment ions. In particular the intensity ratio of the peaks at *m*/*z* 120 (loss of CO) and *m*/*z* 103 (loss of $HCONH_2$) varies from about 1 : 1 in the spectrum of the ions from **15** to about 1 : 3 for the protonated 2-phenyl acrylamides formed from **21**. Obviously the CA spectra of these ions represent different mixtures of the structures **l** and **n** and abundant losses of CO are characteristic for the α-carbamoyl-α-methyl benzyl ions **l** while the protonated 2-phenyl acrylamides **n** exhibit a more abundant loss of $HCONH_2$. Note that a mixture of ions **l** and **n** arises also by protonation of **21** and not only by the loss of the substituent X from the molecular ion of **15** and **16**. Hence these mixtures are formed by a mutual interconversion of **l** and **n** and not by separate competing fragmentation routes of the precursor ions. However, the differences of the CA spectrum show clearly that **l** and **n** do not equilibrate to identical mixtures irrespectively of the origin of the $C_9H_{10}NO^+$ ions.

The same result is obtained from the CA spectra of $C_{11}H_{14}NO^+$ ions derived from **18**, **19**, **23** and **24** (*Fig.* 10). Again the CA spectrum of the protonated N,N-dimethyl cinnamide **q** from **24** is distinguished from the other ones by the absence of a signal for the CO loss, by a very large peak due to the loss of $(CH_3)_2NH$ at *m*/*z* 131 and by a more intense peak at *m*/*z* 72 than at *m*/*z* 77. The other CA spectra exhibit a large and broad peak for the loss of CO and a distinct signal for the loss of the radical $(CH_3)_2N$ besides that for the loss of $(CH_3)_2NH$. The intensity differences between the CA spectra of the ions derived from **18**, **19** and **23** and in particular the variation of the intensity ratio *m*/*z* 148/*m*/*z* 103 are very likely due to different amounts of ions **m** and **o**. Again the especially intense loss of CO in the CA spectrum of the

Table IV. – Characteristic ions in the 70 eV-mass spectra of 2-substituted 2-phenyl propionamides **15-20** (rel. intensity in % base peak)

	X	M^+	−X	−[X+CO]	$C_8H_9X^+$	$C_8H_8X^+$	$C_8H_9^+$	$C_9H_8O^+$	R_2NCO^+
15	Br	0,2	100	23	10	23	56	3	21
16	Cl	9	3	4	98	76	100	2	18
17	CH_3	6	0,3	–	19	100	1	–	23
18	Br	< 0,5	69	10	–	9	1	46	100
19	Cl	4	1	3	–	4	–	7	100
20	CH_3	11	0,5	0,6	–	100	2	1	93

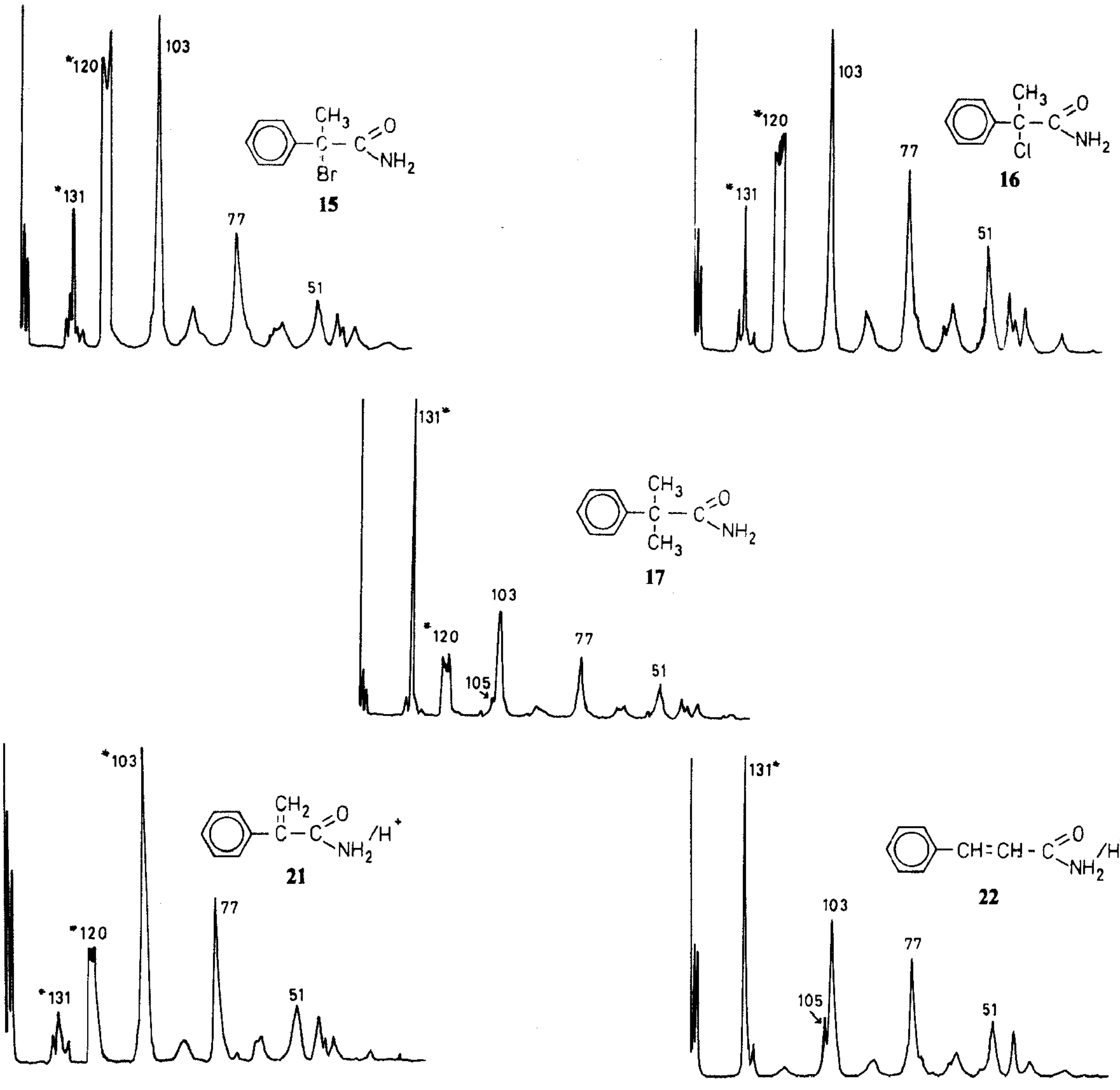


Figure 9. – CA spectra of $C_9H_{10}NO^+$ ions.

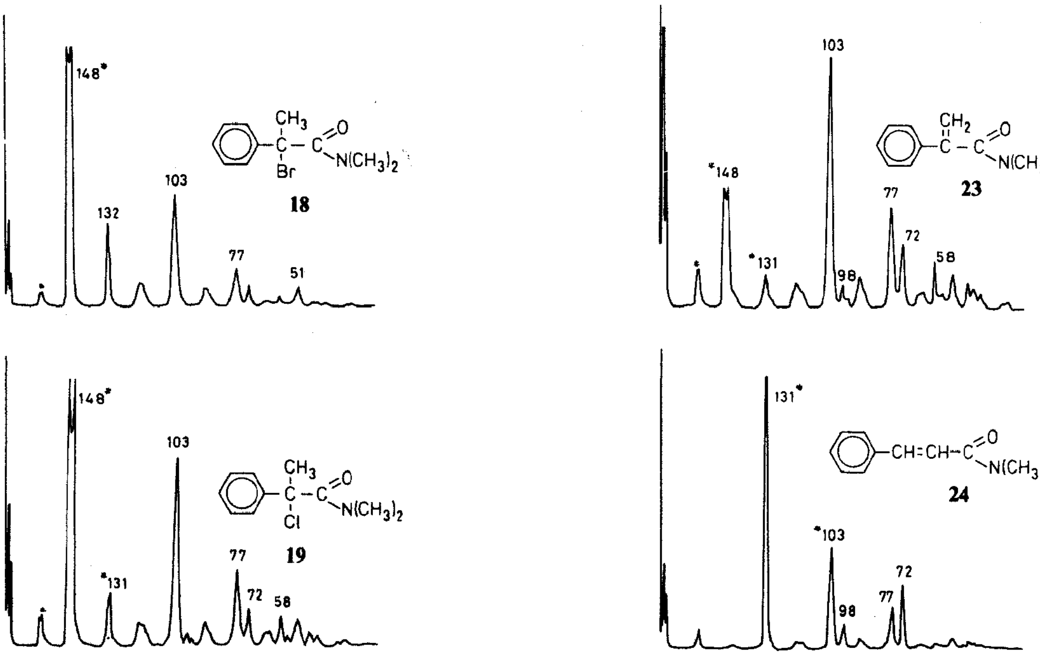


Figure 10. – CA spectra of $C_{11}H_{14}NO^+$ ions.

Table V. – MIKE spectra of $C_9H_{10}NO^+$ ions (rel. intensity in % base peak)

Precursor	X		m/z 147 −H	131 −NH_3	120 −CO	103 −$HCONH_2$	T_{50} (−CO) [meV]
15	Br	EI	–	100	31	4	940
16	Cl	EI	–	100	46	–	890
17	CH_3	EI	2	100	9	3	930
21		CI	–	100	36	13	940
22 [a]		CI	23	100	–	3	–

[a] Additional signals at m/z 105 (4 %) and m/z 104 (16 %).

Table VI. – MIKE spectra of $C_{11}H_{14}NO^+$ ions (rel. intensity in % base peak)

Precursor	X		m/z 161 −CH_3	138 −CO	135 −OCH_3	131 −$HN(CH_3)_3$	103 −$HCONH_2$	T^{50} (−CO) [meV]
18	Br	EI	10	100	–	24	–	820
19	Cl	EI	19	100	–	41	–	870
20	CH_3	EI	7	18	35	100	4	870
23		CI	26	100	–	26	–	
24		CI	–	–	–	100	19	–

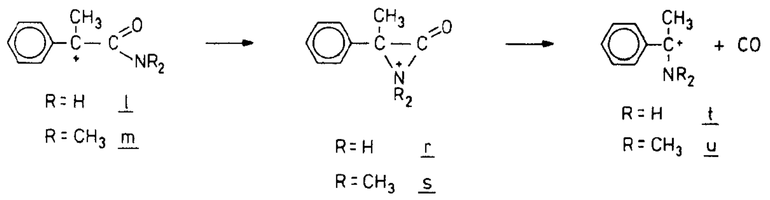


Figure 11. – Mechanism for the CO loss from **l** and **m**.

ions derived from the α-bromo amide **18** indicates an easy formation of these ions by a loss of the « good » leaving group Br.

The MIKE spectra of the metastable $C_9H_{10}NO^+$ ions obtained from **15**, **16**, **21** and **22** and those of the metastable ions $C_{11}H_{14}NO^+$ obtained from **18**, **19**, **23** and **24** by EI and CI, respectively, are reported in Table V and Table VI.

It is seen that the elimination of CO is again a characteristic rearrangement reaction of the destabilized tertiary α-carbamoyl benzyl cations **l** and **m**. The KER values are very large and are identical for the different precursors. This corroborates the mechanism of this reaction (*Fig.* 11) assuming the decomposition of the rigid α-lactam ions **r** and **s**, respectively, into the stable secondary benzyl amine ions **t** and **u**. The identical KER for CO loss is of special interest in the case of the ions formed by protonation of the 2-phenyl acrylamides **21** and **23**. An identical reactive configuration for the loss of CO from ions **l** and **n** or **m** and **o**, respectively, implies an isomerization of ions **n** and **o** into their isomers **l** and **m** by a 1,4-H-shift (see *Fig.* 8).

More information about the isomerization of $C_{11}H_{14}NO^+$ ions is obtained by an investigation of deuterated derivatives (*Fig.* 7). The isomerization reactions derived from this study are shown in Figure 14. Losses of NH_3 and NH_2D (or $(CH_3)_2NH$ and $(CH_3)_2ND$) are observed in the MIKE spectra (Table VII) of all deuterated derivatives indicating a preceding H/D exchange in every case. A very remarkable result, however, is the observation of an inverse isotope effect on the elimination of CO in the case of **15**-d_3 and **18**-d_3 which gives rise to an increase of the relative intensity of the CO loss by a factor of 2,2 and 3,1, respectively. The explanation

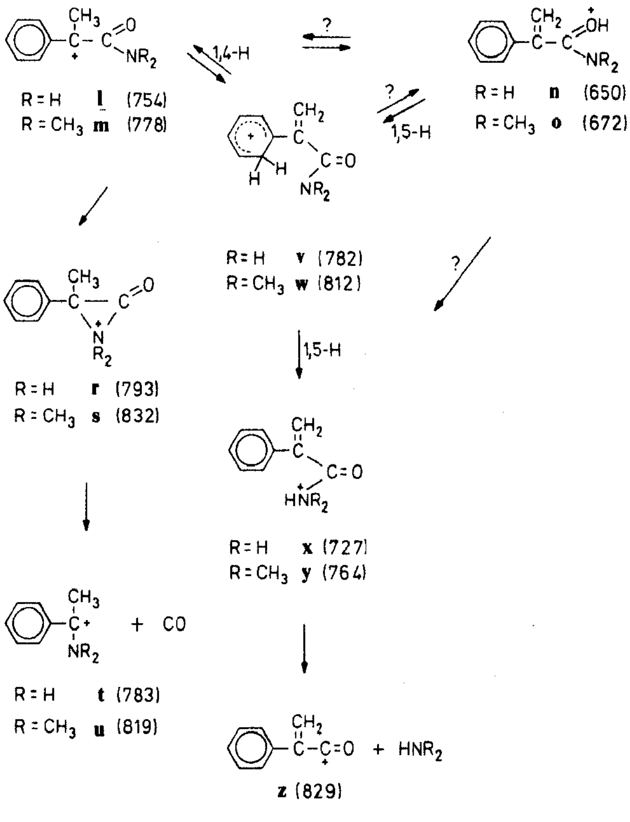
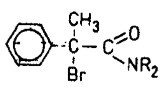
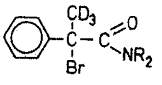
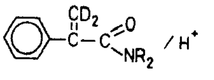
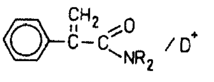


Figure 12. – Isomerization of $C_9H_{10}NO^+$ ions and $C_{11}H_{14}NO^+$ ions. (in parenthesis ΔH_f [$kJmol^{-1}$] of the ions [20])

Table VII. – MIKE spectra of deuterated ions derived from **l**, **m**, **n** and **o** (rel. intensity in % total fragment ion current)

Precursor	R = H			R = CH_3		
	$-CO$	$-NH_3$	$-NH_2D$	$-CO$	$-HN(CH_3)_2$	$-DN(CH_3)_3$
	24	76	–	81	19	–
	41	44	15	93	5	2
	25	71	4	75	22	2
	36	55	9	75	17	8

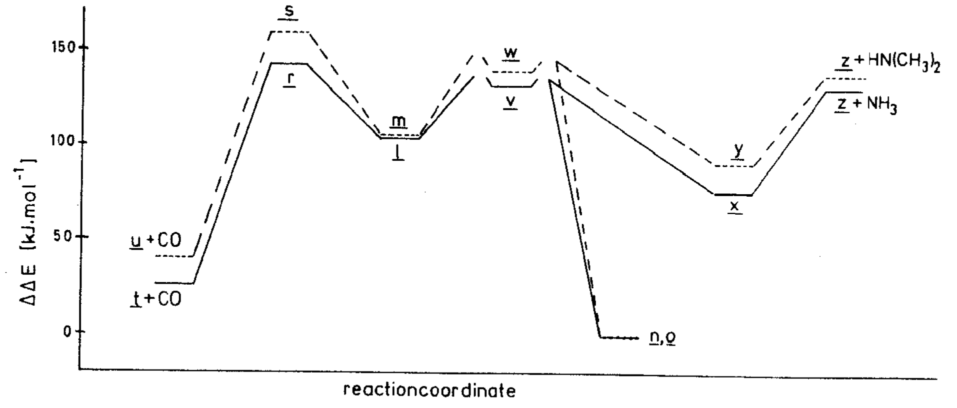


Figure 13. – Schematic reaction energy profile the loss of CO from the tertiary α-carbamoyl carbenium ions **i** and **m**

for this surprising effect is a (normal) isotope effect on the ammonia and amine elimination, respectively, which suppresses this reaction and enhances the CO elimination accordingly. The elimination of NH_3 and $(CH_3)_2NH$ from **l** and **m**, respectively, has to be preceded by a H-transfer onto the amide-N yielding ions **x** and **y** (*Fig.* 12). The observation of a large isotope effect for this H-transfer shows that this H-transfer is the rate determining step of the elimination process and proves unequivocally that the ions **l/m** and **x/y** are separated by an energy barrier. Thus, the destabilized α-carbamoyl benzyl cations **l** and **m** are very likely distinct species within potential energy wells.

Note that the $[M\text{-}Br]^+$ ions from **15-d₃** and **18-d₃** eliminate NH_3 and $(CH_3)_2NH$, respectively, besides the deuterated fragments. This proves that the hydrogen atoms at the phenyl group participate in the H/D-exchange and that the arenium ions **v** and **w**, respectively, are intermediates of the H(D) migration (*Fig.* 12). However, a statistical distribution of all D-labels over all accessible positions is not observed. Hence the isomeric ions **l/m** and **n/o** interconvert mutually but do not equilibrate by H-shifts. This result is expected if both isomers represent distinct species sitting in a potential energy well.

The conclusion, that the set of interconverting $C_9H_{10}NO^+$ ions are separated by energy barriers, is corroborated by a MNDO calculation of the heats of formation of the relevant ion structures. The results are presented as a schematic reaction energy profile in Figure 13. The O-protonated phenyl acrylamides **n** and **o** are more stable than the isomeric α-carbamoyl benzyl cations **l** and **m** by 104 kJmol⁻¹, as expected. The O-protonated ions **n** and **o** are also more stable than their N-protonated isomers **x** and **y** which are very likely the reactive configurations for the elimination of R_2NH. Furthermore, the heats of formation of the arenium ions **v** and **w**, which are intermediates of the hydrogen rearrangements, are larger than those of the destabilized ions **l** and **m**, respectively, and only slightly below the heats of formation of the α-lactam ions **r** and **s**. These latter ions are intermediates or transition states for the loss of CO from **l** and **m**. The arenium ions **v** and **w** are also intermediates for the hydrogen transfer between **n** and **x** or **o** and **y**, respectively, preceding the elimination of R_2NH, and this explains why the loss of CO competes with the elimination of R_2NH if the $C_9H_{10}NO^+$ ions and $C_{11}H_{14}NO^+$ ions are generated by Cl as protonated phenyl acrylamides **n** and **o**.

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[20] Additional heats of formation [19] : CO = − 111 kJ mol^{-1} ; NH_3 = − 46 kJ mol^{-1} ; $HN(CH_3)_2$ = − 18,5 kJ mol^{-1}.