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Destabilized Carbenium Ions: Secondary and Tertiary α-Carbomethoxybenzyl Cations

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The secondary α-carbomethoxybenzyl cations *a* and the tertiary α-carbomethoxybenzyl cations *d* have been generated by electron impact-induced fragmentation from appropriately α-substituted methyl phenylacetate and 2-phenylpropionates 1–4. The ions *a* and *d* are further examples of destabilized carbenium ions with a push–pull substitution at the carbenium ion centre. The characteristic reaction of these ions is a rearrangement by a 1,2-shift of the methoxy group concomitant to the elimination of CO. This rearrangement reaction is associated with a very large and non-statistical kinetic energy release (*a*: T_{50} = 570 meV; *d*: T_{50} = 760 meV), which is attributed to tight transition states along the reaction coordinates corresponding to the three-membered cyclic oxonium ions *b* and *h*, respectively. The tertiary ion *d* can be distinguished from its more stable isomers *f* and *g* by the mass-analysed ion kinetic energy and collisional activation spectra. The investigation of specifically deuterated analogues of ions *d* and *g* reveals an isomerization of *d* to *g* via a species protonated at the phenyl group but no equilibration between *d* and *g*. This isomerization exhibits a large isotope effect for the hydrogen transfer, indicating similar energy barriers for the isomerization and for the CO elimination of *d*.

INTRODUCTION

α-Acyl carbenium ions represent an important subgroup of the interesting class of destabilized carbenium ions, which carry an electron-withdrawing acyl group COR, carbalkoxy group COOR and carbamoyl group $CONR_2$, respectively, at the positive centre. The destabilized carbenium ions are reactive intermediates of organic reactions and it is known that these ions exhibit a distinct tendency for rearrangement reactions.[1] We have therefore started a systematic study of the properties of these ions in the gas phase by mass spectrometric techniques.[2] It is known[3] that the most simple α-acyl carbenium ion, the α-formylmethyl cation, is not a stable species and this is probably true also for other primary α-acyl carbenium ions.[2b,d] Our results show, however, that α-acyl carbenium ions behave as stable species sitting in a potential energy well if the electron-withdrawing effect of the acyl substituent is opposed by an additional electron-donating group at the carbenium ion centre.[2e,f] Examples of this 'push–pull' substitution are the α-acyl benzyl cations[2e] and the tertiary α-acyl dimethylmethyl cations.[2f] These α-acyl carbenium ions can be generated in a mass spectrometer by electron impact ionization (EI) or chemical ionization (CI) from suitable precursors carrying an appropriate leaving group X at the α-position to the carbonyl group. The characteristic fragmentation reaction of α-acetyl and α-benzoyl carbenium ions is a 1,2-shift of the methyl and phenyl group, respectively, and a concomitant loss of a CO molecule, which is accompanied by a large kinetic energy release (KER).

In this paper we report our results about the generation and the reactions of secondary and tertiary α-carboxymethylbenzyl ions. It is known from the literature that methyl 2-bromophenylacetate (**1**) and related esters decompose in their 70-eV mass spectra by consecutive losses of Br˙ and CO,[4] which would correspond to the typical reaction of α-acyl carbenium ions. Similar reactions are to be expected in the mass spectrum of methyl 2-bromo-2-phenylpropionate (**2**). However, in the latter case rearrangement reactions may interfere with the generation and the further reactions of the tertiary α-carboxymethyl methylbenzyl ions. H. Schwarz[5] has shown that the loss of a substituent at the α-position of an ester molecular ion occurs by preceding hydrogen migration and skeletal rearrangement, but it is clear from the investigations of Burgers *et al.*[6] and from our work[2f] that it depends on the nature of the substituent lost whether or not a rearrangement of the molecular ions will precede the bond cleavage. Hydrogen migrations have also been observed for tertiary α-acetyl and α-benzoyl carbenium ions[2e] which interconvert into more stable protonated α,β-unsaturated carbonyl structures by a 1,4-H shift.[2e,f,7] Hence we have investigated the generation and the reactions of secondary and tertiary α-carboxymethylbenzyl ions and isomeric ions in the EI and CI mass spectra of compounds **1**–**6** by deuterium labelling and metastable ion techniques.

RESULTS AND DISCUSSION

α-Carbomethoxybenzyl ion

The 70-eV mass spectrum of methyl 2-bromo-2-phenylacetate (**1**) contains prominent peaks of the $[M - Br]^+$ and $[M - Br - CO]^+$ ions besides peaks

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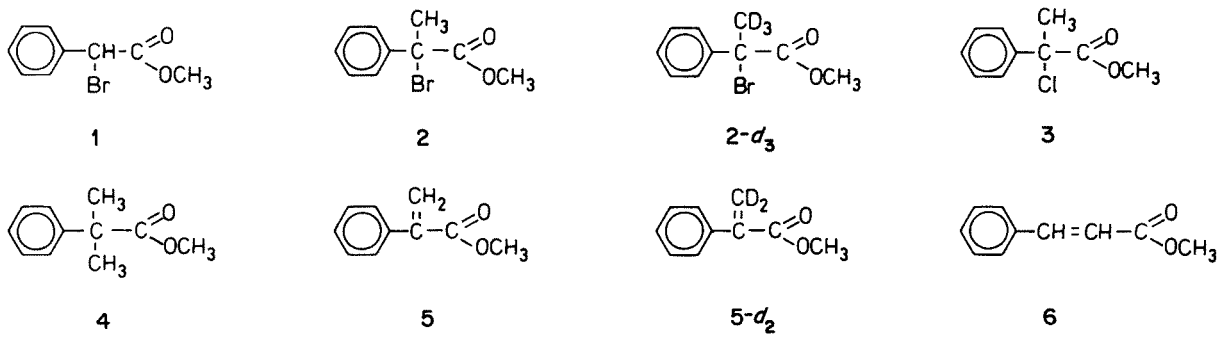


1 2 2-d_3 3

4 5 5-d_2 6

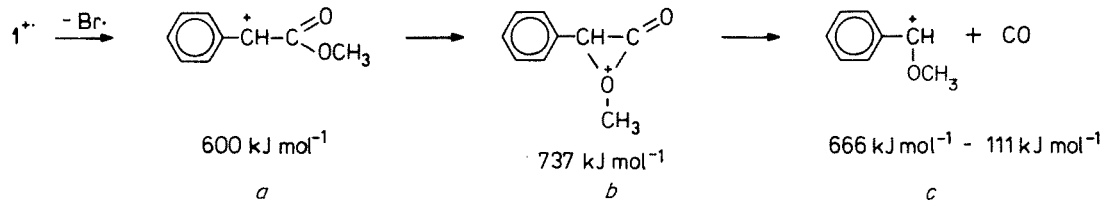
of those ions expected from the fragmentation via α-cleavage at the ester group and from further fragmentations of the aromatic group (Table 1). This has been noted before by Cooks and Williams.[4] The loss of Br· from $\mathbf{1}^{+\cdot}$ is the only reaction of the metastable ions in the second field-free region (2nd FFR) of the VG ZAB-2F mass spectrometer and a Gaussian-shaped peak (T_{50} = 10 meV) is observed for this process. Hence formation of the α-carbomethoxybenzyl ions *a* by a direct bond cleavage[8] is the energetically most favourable fragmentation pathway of $\mathbf{1}^{+\cdot}$. The metastable ions *a* thus formed fragment in the 2nd FFR only by the loss of CO and the peak for this reaction is very broad and dish-topped. A T_{50} = 570 meV has been calculated from the width of the peak at 50% intensity, exceeding even the KER observed during the CO loss from α-acetyl and α-benzoylbenzyl ions[2e] and indicating a rearrangement of ion *a* via an energy-rich and tight critical configuration to a very stable product ion. This agrees with the mechanism depicted in Scheme 1 and the three-membered cyclic oxonium structure *b* as a critical configuration. The heats of formation of the ions *a* and *b* and of the α-methoxybenzyl product ion *c* have been calculated by MNDO and the corresponding values are shown in Scheme 1 below the formulae. These values lead to a large reverse activation energy of 182 kJ mol^{-1}, corroborating the observed KER of 55 kJ mol^{-1} (570 meV). Thus the behaviour of the α-carbomethoxybenzyl ions *a* is very similar to that of the other push–pull substituted α-acyl carbenium ions studied before.[2]

α-Carbomethoxy-α-methylbenzyl ions and isomeric $[C_{10}H_{11}O_2]^+$ ions

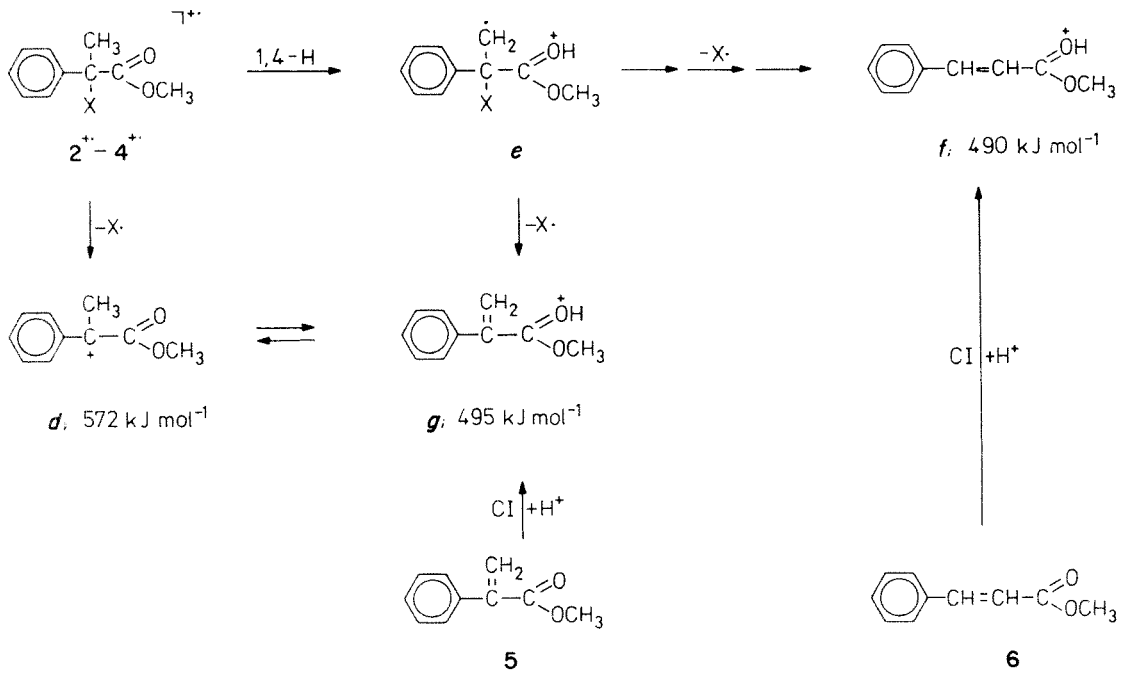
The loss of the substituent X from the molecular ions of the 2-substituted methyl 2-phenylpropionates **2**–**4** gives rise to $[C_{10}H_{11}O_2]^+$ ions, and a direct bond cleavage would result in the tertiary α-carbomethoxy-α-methylbenzyl ions *d* (Scheme 2). As mentioned above, however, the molecular ions $\mathbf{2}^{+\cdot}$–$\mathbf{4}^{+\cdot}$ possibly rearrange by a 1,4-hydrogen migration to the distonic ion *e* followed by a 1,2-shift of the protonated carbomethoxy group, hydrogen rearrangement and loss of X· to give eventually the ion *f* (Scheme 2). In addition, the loss of X may occur from the distonic ion *e* to give rise to ion *g*. Finally, ions *d* and *g* may interconvert mutually by a reversible 1,4-H shift (Scheme 2). The ions *f* and *g* correspond to protonated α,β-unsaturated ester molecules which are expected to be much more stable than ion *d*. This is corroborated by the relevant heats of formation calculated by MNDO which are given in Scheme 2 below the formulae.

The 70-eV mass spectra of **2**–**4** (Table 1) contain a large peak of the $[C_{10}H_{11}O_2]^+$ ions only in the case of the bromo derivative **2**, while the intensity of these ions in the mass spectrum of **4** (X = CH_3) is only 0.1%. The α-cleavage at the ester group is the most important fragmentation of **3** and **4** and the base peak in the mass spectrum of **2** corresponds to $[C_8H_7]^+$ ions at *m/z* 103. The metastable molecular ions of **2**–**4** lose the α-substituent X, giving rise to narrow and Gaussian-shaped peaks (T_{50} = 15–30 meV) in their mass-analysed ion kinetic energy (MIKE) spectra (Table 2). This agrees with the loss of X by a direct bond cleavage in all cases. However, the loss of X is an important reaction only in the MIKE spectrum of **2** (X = Br) while the metastable molecular ions of **3** (X = Cl) and **4** (X = CH_3) fragment again predominantly by the α-cleavage. Thus the MIKE spectra of $\mathbf{2}^{+\cdot}$–$\mathbf{4}^{+\cdot}$ show that the formation of $[C_{10}H_{11}O_2]^+$ ions is energetically favourable only for X = Br and that the structure of these ions may differ from *d*.

The relevant isomeric ions *f* and *g* (Scheme 2) should be formed by protonation of methyl cinnamate **6** and



Scheme 1



Scheme 2

methyl phenylacrylate **5**, respectively, in a CI experiment assuming protonation at the carbonyl group.[9] The MIKE spectra of the $[C_{10}H_{11}O_2]^+$ ions derived from **2–4** and from **5** (**5H**$^+$) and **6** (**6H**$^+$) are given in Table 3 and their collisional activation (CA) spectra are shown in Figs 1 and 2, respectively. Clearly the MIKE spectra and the CA spectra of the $[C_{10}H_{11}O_2]^+$ ions from **2–4** are identical. Thus in spite of the different reaction energies for different leaving groups X the same ion (or the same mixture of ions) is formed. The characteristic feature of these MIKE spectra is a broad and dish-topped peak for the loss of CO, which is in line with the expected behaviour of ions *d*. Identical T_{50} values of 760 ± 10 meV, within experimental error, have been calculated for this process for the ions derived from **2–4**, which is an additional proof for an identical structure *d* of these ions. The very large value of T_{50} indicates again a very large reversed activation energy for the CO elimination and a very rigid critical configuration, in agreement with the mechanism depicted in Scheme 3.

The MIKE spectra of the ions **5H**$^+$ and **6H**$^+$ differ from those of the ions *d* by the absence of a peak for the CO elimination and are distinguished from each other by an additional signal for the loss of C_2H_2O in the spectrum of **6H**$^+$. The elimination of ketene has been observed before for the fragmentation of the $[M - Br]^+$ ions from ethyl *β*-bromo-*β*-phenylpropionate.[4] These $[M - Br]^+$ ions contain the same unbranched carbon skeleton as ions *f* and the loss of ketene appears to be characteristic of this structure. The CA spectra of the $[C_{10}H_{11}O_2]^+$ ions derived from **5** and **6**, respectively, are also clearly different (Fig. 2). The CA spectrum of **5H**$^+$ exhibits a much more intense signal at *m/z* 103 and a small peak at *m/z* 135 due to loss of CO, which is absent in the CA spectrum of **6H**$^+$. The intensity of the CO elimination from **5H**$^+$ is much smaller than from the $[C_{10}H_{11}O_2]^+$ ions derived from

Table 1. Characteristic ions in the mass spectra (70 eV)[a] of 1–4

Ion	1 X = Br	2 X = Br	3 X = Cl	4 X = CH_3
$M^{+\cdot}$	10[b]	10[b]	18[b]	15
$-COOCH_3$	46[b]	22[b]	134[b]	100
$-X$	100	40	3	0.1
$-(X + CO)$	46	64	3	1.5
$-(X + OCH_3)$	16	5	2	–
$-(X + HOCH_3)$	–	14	2	–
$[C_8H_8]^+$	–	65	6	2
$[C_8H_7]^+$	–	100	37	10
$[C_7H_7]^+$	25	10	2	66
$[C_6H_5]^+$	11	66	15	15

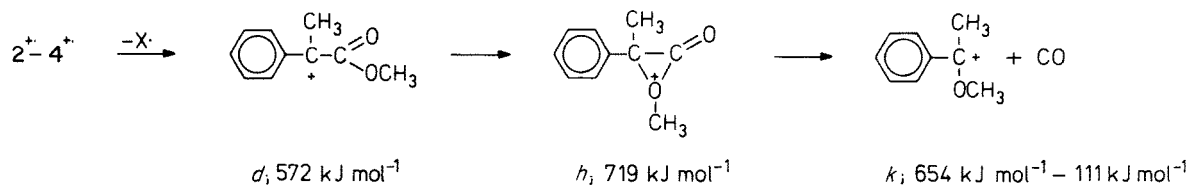
[a] The ions mentioned in the table correspond to >70% total ion current.
[b] Sum of the intensity of Br and Cl isotopes, respectively.

Table 2. MIKE spectra (70 eV) of the molecular ions of 1–4

X	$-X$	$-COOCH_3$	$-HCOOCH_3$	$-CH_3OH$
2 Br	100	–	–	–
3 Cl	11	100	–	1
4 CH_3	0.2	100	4	–

Table 3. MIKE spectra of $[C_{10}H_{11}O_2]^+$ ions

Ion	X		$-CO$	$-CH_3OH$	$-CH_2{=}C{=}O$
d (**2**)	Br	EI	4	100	–
d (**3**)	Cl	EI	3	100	–
d (**4**)	CH_3	EI	4	100	–
5H$^+$		CI	–	100	–
6H$^+$		CI	–	100	16



Scheme 3

2–4 (Fig. 1), however, and the peak at *m/z* 103 is much larger, so that one is obviously dealing with at least three different isomers of the $[C_{10}H_{11}O_2]^+$ ions. One should note that the MIKE and CA spectra of the $[C_{10}H_{11}O_2]^+$ ions from **2–4** and $\mathbf{5H}^+$, respectively, differ only by the intensities of the same fragment ions and hence both may represent mixtures of ions *d* and *g* with a different composition. It has been shown that α-acetyl-α,α-dimethylmethyl cations,[2f] α-acetyl-α-methylbenzyl cations[2e] and α-benzoyl-α-methylbenzyl cations[2e] equilibrate by reversible 1,4-H shifts with the corresponding protonated α,β-unsaturated ketones prior to decomposition. An analogous equilibration of metastable ions *d* and *g* can be excluded, however, because in this case their CA spectra should be identical. Nevertheless, an isomerization of the metastable α-carbomethoxy-α-methylbenzyl cations *d* into the more stable ions *g* competitive with CO elimination would be compatible with the experimental results discussed so far.

Isomerization of $[C_{10}H_{11}O_2]^+$ ions *d* and *g*

The possible isomerization of the destabilized α-carbomethoxybenzyl cation *d* into its stable isomer *g* prior to or in competition with the loss of CO is important for the question of whether *d* is really a distinct species in a potential energy well. This isomerization has been studied by observing the deuterium distribution in the reaction products of deuterated ions derived from **2**-d_3 by EI and CI and from deuterated ions obtained by CI(CH_4) of **5**-d_2 and by CI(CD) of **5**, respectively. The MIKE spectra of these ions are shown in Table 4 and the mechanism derived from these results is outlined in Scheme 4.

The metastable ions $\mathbf{5D}^+$ obtained by deuteronation of **5** eliminate both CH_3OH and CH_3OD in a ratio of

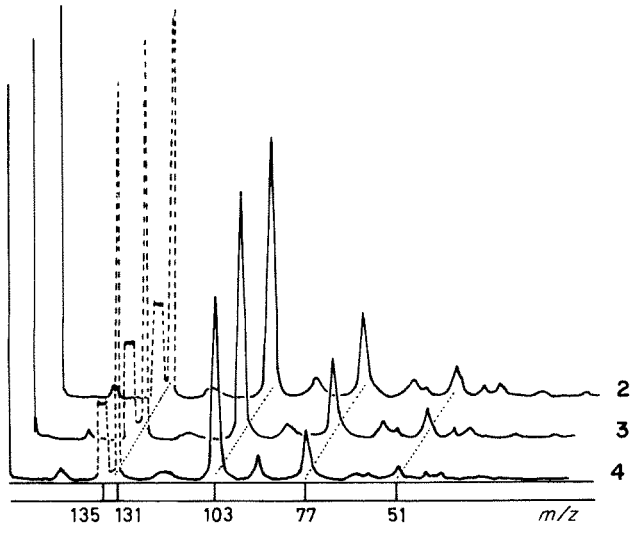


Figure 1. CA spectra of $[C_{10}H_{11}O_2]^+$ ions from **2–4**.

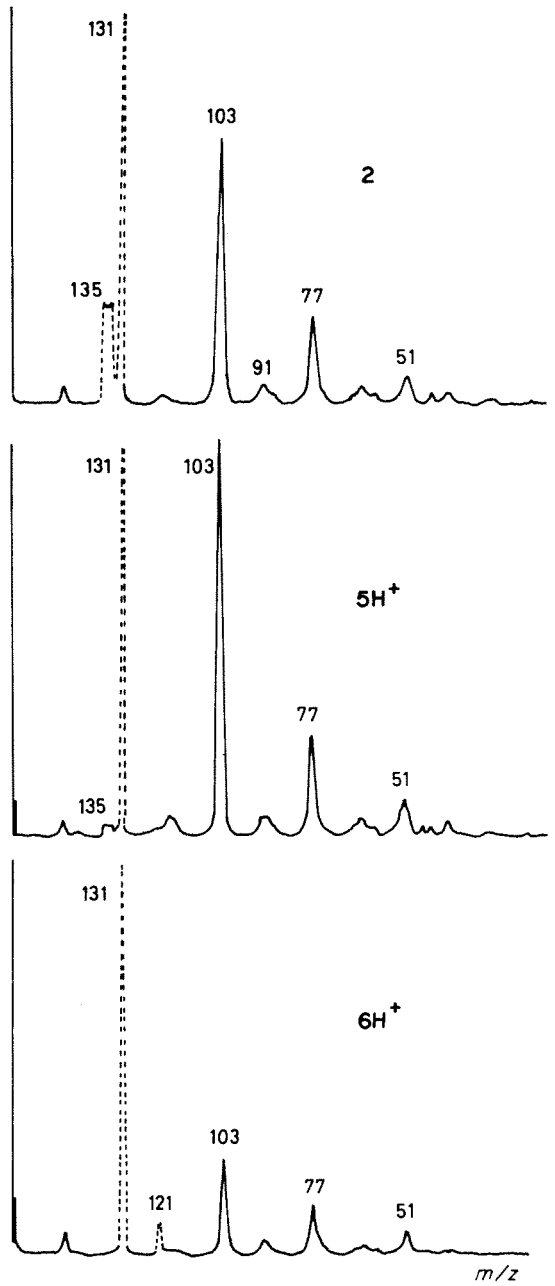


Figure 2. CA spectra of $[C_{10}H_{11}O_2]^+$ ions from (a) **2**, (b) **5** and (c) **6**.

Table 4. MIKE spectra of deuterated ions *d* and *g*

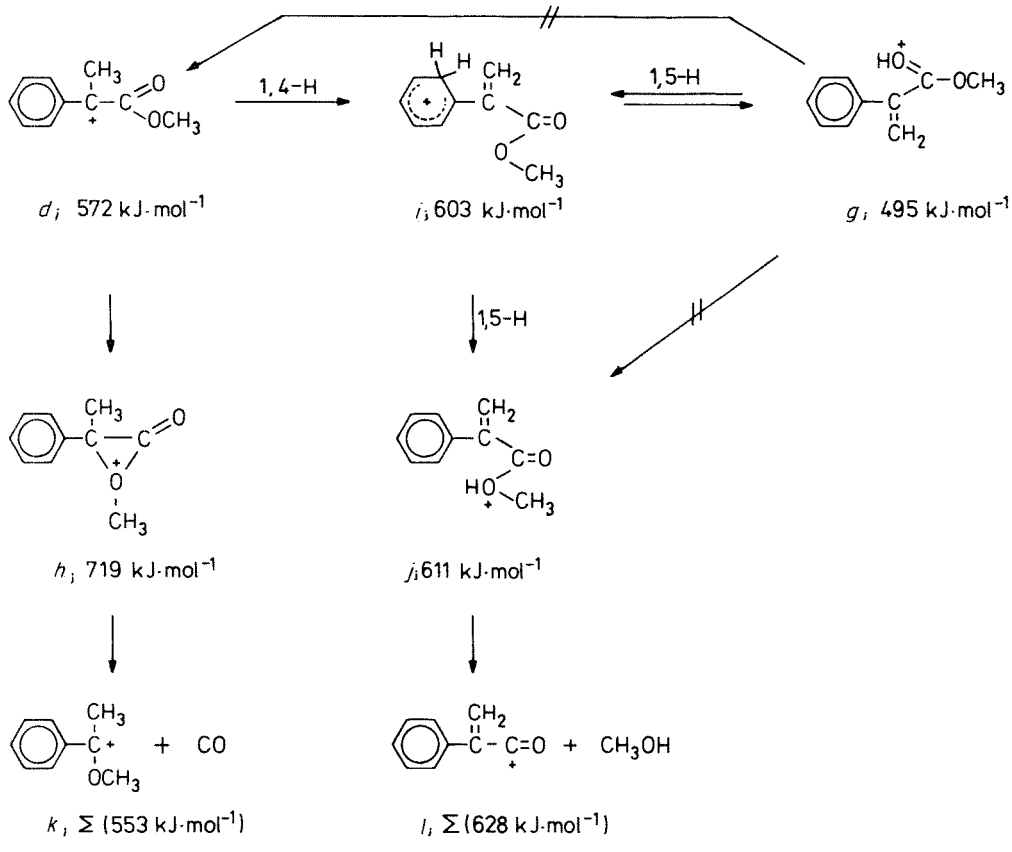
	Ion		$-CO$	$-CH_3OH$	$-CH_3OD$
2-d_3	*d*	EI	15	100	15
2-d_3	*d*	$CI(CH_4)$	12	100	15
5	*g*	$CI(C^2H_4)$	–	100	13
5-d_2	*g*	$CI(CH_4)$	–	100	–

100 : 13, but surprisingly the (**5**-d_2)$\mathbf{H}^+$ ions obtained by protonation of **5**-d_2 lose only CH_3OH. Thus any reversible H or D transfer from the protonated or deuteronated carbomethoxy group onto the terminal methene group of *g* and any equilibrium between metastable ions *d* and *g* can be excluded. Obviously the H/D exchange observed in metastable $\mathbf{5D}^+$ prior to the elimination of methanol occurs by an exchange of the D atom at the deuteronated ester group with the H atoms at the phenyl group. A scrambling of this type between 5 H and 1 D would give rise to an elimination of CH_3OH and CH_3OD in a ratio of 100:20 and the experimental values can be easily explained by an isotope effect $k_H/k_D = 1.54$ for the methanol elimination.

Winnik has suggested that the elimination of methanol from methyl ester ions requires protonation at the alkoxy oxygen and that the symmetry-forbidden 1,3-H shift from the carbonyl group to the alkoxy oxygen has a large critical energy.[10] Hence the transfer of the proton at the carbonyl group is catalysed intramolecularly by the presence of a second basic group at a suitable position to the ester group. In view of these observations[10] the methanol elimination of ions *g* via an intermediate ion *i* protonated at the aromatic ring and the ion *j* protonated at the alkoxy oxygen (Scheme 4) is clearly a further example of this intramolecular catalysis.

The metastable ions *d*-d_3 obtained from **2**-d_3 eliminate also CH_3OH and CH_3OD in the slightly different ratio of 100:15 irrespective of the origin and the mode of generation of these ions (Table 4). Thus the ions *d* do isomerize into ions *g*, although the reverse isomerization is not observed. The reason for this is certainly the large exothermicity of the hydrogen transfer reaction $d \rightarrow g$, and the excess energy of the ions *g* arising from this isomerization is probably reflected in the somewhat smaller isotope effect of $k_H/k_D = 1.33$. Of course it is not possible to decide whether the isomerization of *g* occurs by a direct 1,4-hydrogen migration or via ion *i* as an intermediate.

The most interesting and important observation, however, is a large increase of the relative intensity of the CO elimination in the MIKE spectrum of *d*-d_3 ions (13%, Table 4) compared to the MIKE spectrum of *d* (4%, Table 3). The only possible explanation for this large inverse isotope effect on the CO elimination is a corresponding primary isotope effect of about 3 on the hydrogen migration during the isomerization $d \rightarrow g$ which competes with the 1,2-methoxy group migration and subsequent CO elimination of *d*. In this case the activation energy of the isomerization $d \rightarrow g$ has to be nearly as large as the activation energy for the loss of CO and hence the destabilized α-carbomethoxy-α-methylbenzyl cation *d* is separated from its more stable



Scheme 4

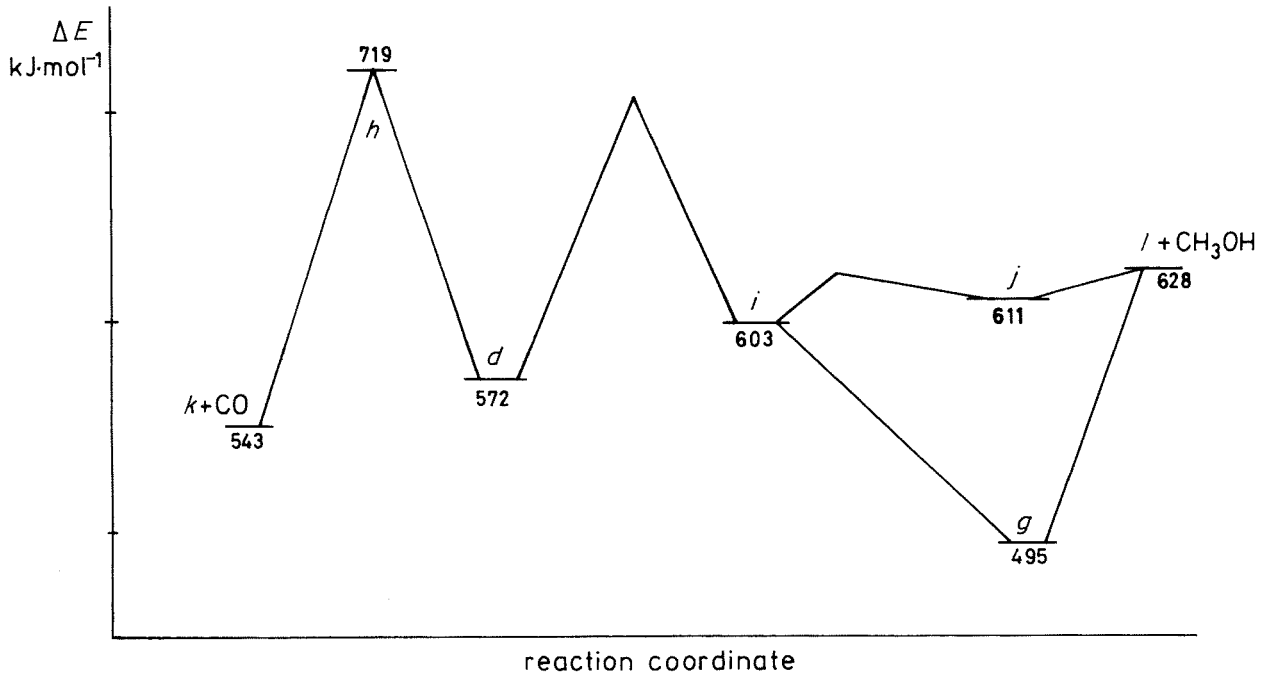


Figure 3. Reaction energy profile for the isomerization and fragmentation of ions *d* and *g*.

isomer *g* by a distinct energy barrier. Thus the observation of an inverse deuterium isotope effect on the CO elimination from *g* is the first direct experimental proof that α-acyl carbenium ions with a push–pull substitution are distinct species in a potential energy well.

CONCLUSION

The present result demonstrates convincingly the formation of secondary and tertiary α-carbomethoxybenzyl cations *a* and *d* by EI-induced loss of a substituent X from the molecular ions of α-substituted methyl esters. However, this fragmentation route is only important if X is a good leaving group. The ions *a* and *d* are further examples of destabilized α-acyl carbenium ions with a push–pull substitution which exhibit the loss of CO as a typical reaction. In the case of ions *a* and *d* the elimination of CO gives rise to a very large and non-statistical KER, which is again a common feature of the reactions of α-acyl carbenium ions, and occurs via a 1,2-shift of a methoxy group and *O*-methylated α-lacton ions *b* and *h*, respectively, as the critical configuration.

The tertiary α-carbomethoxy-α-methylbenzyl cations *d* eliminate predominantly methanol, and loss of methanol is also observed as the main process of isomeric ions corresponding to protonated methyl cinnamate *f* and protonated methyl phenylacrylate *g*, respectively. However, the isomeric ions *d*, *f* and *g* can be differentiated by their MIKE and CA spectra. A deuterium-labelling study shows that reversible hydrogen transfers between the protonated ester group and the phenyl group of *g* precede the elimination of CH_3OH and that the formal 1,3-H shift from the ester carbonyl group onto the alkoxy oxygen prior to this elimination is intramolecularly catalysed by the phenyl group. The deuterium labelling also reveals an isomerization of *d* into *g*, but the reverse process is not observed. The isomerization $d \rightarrow g$ is associated with a deuterium isotope effect which results in an increase of the intensity of the CO loss from metastable *d* by a factor of ~3. Thus the isomerization to *g* and loss of CO are competitive and have a similar activation barrier. From these results the schematic reaction energy profile shown in Fig. 3 is derived for the interconversion and the reactions of *d* and *g*. Furthermore the experimental observation of competitive isomerization and fragmentation gives definite evidence that destabilized α-acyl carbenium ions with a push–pull substitution similar to *d* are distinct species in a potential energy well.

EXPERIMENTAL

The 70-eV mass spectra have been obtained with a mass spectrometer MAT 311 connected to a data system SS200 at an ion source temperature of ~180 °C and sample introduction via a heated inlet system at 180 °C.

The MIKE and CA spectra were measured with a VG ZAB-2F mass spectrometer equipped with a combined EI/CI ion source and an accelerating voltage of 6 kV. The ionization was performed either by 70-eV EI or by CI(CH_4) and CI(CD_4), respectively, at an ion source pressure corresponding to a reading of $\sim 0.5 \times 10^{-5}$ Pa. The ions under investigation were focused magnetically into the 2nd FFR of the mass spectrometer and the MIKE spectra were obtained by scanning the voltage across the electrostatic analyser. The CA spectra were obtained in an analogous manner but by introducing He as collision gas into the collision cell of the

2nd FFR at such a rate that the main beam intensity was reduced to ~30%.

The purity of all compounds used in this study has been controlled by gas chromatography and by thin-layer chromatography, respectively, and their structures have been verified by ^{1}H-NMR.

Methyl 2-bromophenylacetate (**1**) was obtained by bromination of methyl phenylacetate according to Ref. 11.

Methyl 2-bromo-2-phenylpropionate (**2**) was synthesized either by bromination of methyl 2-hydroxy-2-phenylpropionate[12] or via direct bromination of 2-phenylpropionylchloride followed by esterification.[13]

Methyl 2-bromo-2-phenylphenylacetate-3-d_3 **2**-d_3 and methyl 2-phenylacrylate-3-d_2 **5**-d_2 resulted as a mixture from a treatment of methyl 2-phenylpropinate-3-d_3 (from alkylation of dimethyl phenylmalonate with C^2H_3I) with NBS in CCl_4 at 100 °C for 24 h and have been investigated without separation.

Methyl 2-chloro-2-phenylacetate (**3**) was obtained by PCl_5 chlorination of methyl 2-hydroxy-2-phenylacetate.[12]

Methyl 2-methyl-2-phenylacetate (**4**) and methyl cinnamate (**6**) were obtained from the commercially available acid by treatment of the corresponding acid chlorides with CH_3OH.[12]

Methyl 2-phenylacrylate (**5**) was synthesized by HBr elimination of **2** using DABCO as a base.[14]

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