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Destabilized Carbenium Ions

Secondary and Tertiary α-Acetylbenzyl Cations and α-Benzoylbenzyl Cations

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The secondary α-acetylbenzyl and α-benzoylbenzyl cations, as well as their tertiary analogues, have been generated in a mass spectrometer by electron impact induced fragmentation of the corresponding α-bromoketones. These ions belong to the interesting family of destabilized α-acylcarbenium ions. While primary α-acylcarbenium ions appear to be unstable, the secondary and tertiary ions exhibit the usual behaviour of stable entities in a potential energy well. This can be attributed to a 'push–pull' substitution at the carbenium ion centre by an electron-releasing phenyl group and an electron-withdrawing acyl substituent. The characteristic unimolecular reaction of the metastable secondary and tertiary α-acylbenzyl cations is the elimination of CO by a rearrangement reaction involving a 1,2-shift of a methyl group and a phenyl group, respectively. The loss of CO is accompanied by a very large kinetic energy release, which gives rise to broad and dish-topped peaks for this process in the mass-analysed ion kinetic energy spectra of the corresponding ions. This behaviour is attributed to the rigid critical configuration of a corner-protonated cyclopropanone derivative and a bridged phenonium ion derivative, respectively, for this reaction. For the tertiary α-acetyl-α-methylbenzyl cations, it has been shown by deuterium labelling and by comparison of collisional activation spectra that these ions equilibrate prior to decomposition with their 'protomer' derivatives formed by proton migration from the α-methyl substituent to the carbonyl group and to the benzene ring.

INTRODUCTION

Destabilized carbenium ions are carbocations with an electron-withdrawing substituent (e.g. $-CF_3$, $-CN$, $-COR$, $-SO_2R$) attached to the positive centre. It has been shown that these carbocations are important intermediates of organic reactions, as are their counterparts, the carbenium ions stabilized by electron donors, and their chemistry in solution has been recently reviewed.[1] An interesting subgroup of the destabilized carbenium ions are α-acylcarbenium ions which carry an acyl group $-COR$, a carbohydroxy or carbalkoxy group $-COOR$, and a carbamoyl group $-CONR_2$, respectively, at the carbenium centre. These species are intermediates during the solvolysis of appropriately substituted carbonyl compounds and, besides the normal substitution, one also observes rearrangement reactions of these ions,[2,3] indicating a special reactivity. However, it is not clear whether charge delocalization according to an oxaallyl system occurs in these ions as suggested by theoretical calculations.[4]

There has been up to now no systematic investigation of destabilized carbenium ions in the gas phase. Recently, we have shown that α-acetylcarbenium ions[5] and α-benzoylcarbenium ions[6] can be generated in a mass spectrometer by electron impact (EI) and chemical ionization (CI) from suitable precursors. It appears from these studies that the primary α-acylcarbenium ions are not stable species but rearrange immediately into an isomer which is probably an oxiranylium ion.[7] Similarly, the α-formylmethyl cation is also known to be unstable against a rearrangement into the acetyl cation.[8] However, the tertiary α-acetyl- and α-benzoylcarbenium ions are discrete entities in a potential energy well.[5] Some confusion has arisen[9] because of an interconversion of these tertiary α-acylcarbenium ions and the isomeric protonated α,β-unsaturated ketones by a 1,4-hydrogen shift. However, the tertiary α-acetyl- and α-benzoyl-α,α-dimethylmethyl cations are characterized by a rearrangement and loss of CO which is associated with a large kinetic energy release (KER) and which gives rise to broad and dish-topped peaks in the mass-analysed ion kinetic energy (MIKE) spectra of these ions.

It seems possible that α-acylcarbenium ions are discrete, stable species only if the electron-withdrawing effect of the acyl substituent is somewhat counterbalanced by the presence of electron-releasing groups at the carbenium ion centre. As a test of this hypothesis of a 'push-pull' substitution for α-acylcarbenium ions, we investigated the formation and reactions of α-acetylbenzyl ions and α-benzoylbenzyl ions. It is shown that these ions behave analogously to the tertiary α-acylcarbenium ions and, in particular, also rearrange by loss of CO associated with a large and non-statistical KER.

RESULTS AND DISCUSSION

Secondary α-acylbenzyl cations

α-Bromoketones have been shown to be suitable precursors for the generation of α-acylcarbenium ions by EI induced fragmentation.[5b] In this study, 1-bromo-1-phenylpropan-2-one (**1**) and 2-bromo-1,2-diphenylethanone (**2**) have been used to prepare α-acetylbenzyl ions (*a*) and α-benzoylbenzyl ions (*b*) as shown in

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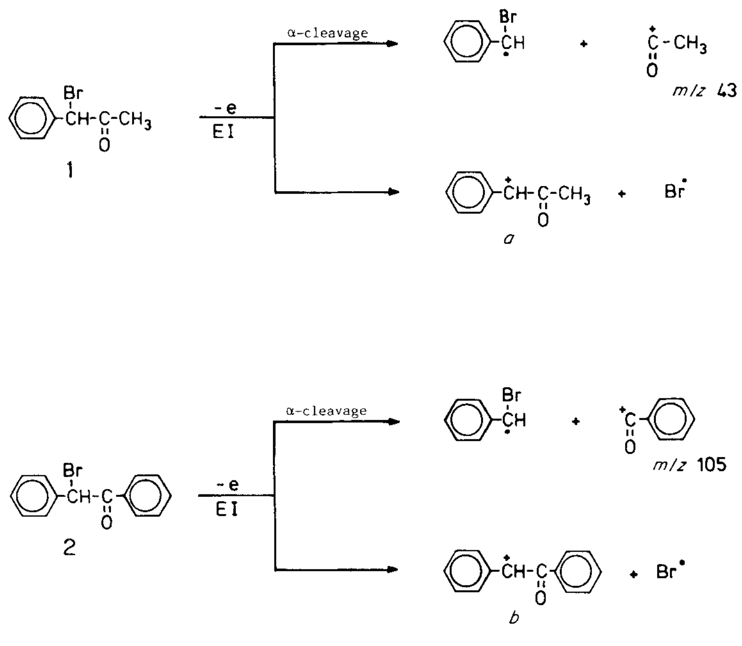
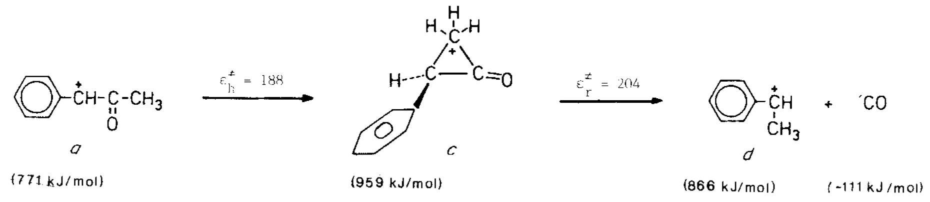


Scheme 1



Scheme 2

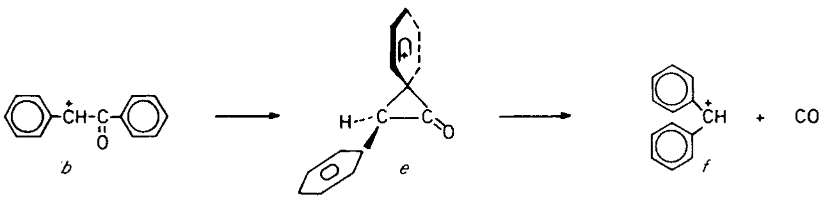
Scheme 1. The 70 eV mass spectra of **1** and **2** exhibit the signal of the acylium ions $[CH_3CO]^+$ and $[C_6H_5CO]^+$, respectively, as the base peaks, and the ions *a* and *b* are observed with only 23 and 28% relative abundance, respectively. The metastable molecular ions of **1** and **2**, however, decompose only by loss of Br$^\bullet$; thus, the formation of the α-acylcarbenium ions by this process is energetically favourable. A Gaussian peak with $T_{50} =$ 10 meV is observed for this process in the MIKE spectra, indicating Br$^\bullet$ loss without a rearrangement. It is not known whether the ions *a* and *b* formed by loss of Br$^\bullet$ from **1** and **2** are indeed α-acylbenzyl ions or whether a rearrangement to a tropylium structure has occurred before or after the fragmentation. An α-acyltropylium ion also corresponds to a 'push-pull' substituted destabilized carbenium ion, however, because of a destabilizing acyl substituent at the stable tropylium structure. Hence, this question is therefore not relevant to the present discussion.

Metastable α-acetylbenzyl cations *a* fragment in the second field-free region (2nd FFR) of a ZAB 2F mass spectrometer by loss of CO (83% of total fragmentation), loss of H_2O (9%) and elimination of ketene (8%), while only the loss of CO is observed for metastable α-benzoylbenzyl cations *b*. In both cases, the peak observed for the loss of CO in the MIKE spectrum is broad and dish-topped. Thus, both *a* and *b* react by the typical rearrangement of the α-acylcarbenium ions.[5,6,10] The amount of the KER has been calculated from the width of the respective peak in the 1st and 2nd FFR at 50% intensity and the corresponding T_{50} are presented in Table 1.

The T_{50} value found for the CO loss from ion *a* is very large and exceeds even that observed during the CO loss from α-acetyl-α,α-dimethylmethyl cations.[5b] In both cases, the elimination of CO is accompanied by a 1,2-shift of a methyl group and the critical configuration of the process corresponds to a corner-protonated cyclopropanone as depicted in Scheme 2 for ion *a*. Corner-protonated cyclopropanes are assumed as intermediates during the skeletal isomerization of carbenium ions in superacidic solutions.[11] The rigid structure of the critical configuration *c* (Scheme 2) is the reason for the large and non-statistical KER,[12] and the association of rigid transition states with the release of a large part of its potential energy has been often observed.[13] Finally, the heats of formation of *a*, *c* and the α-methylbenzyl product ion (*d*) have been calculated by MNDO and the values are given in Scheme 2 below the relevant

Table 1. T_{50} (in meV) for the CO loss from secondary α-acylbenzyl cations *a* and *b*

Ion	T_{50}	
	1st FFR	2nd FFR
a	435	305
b	465	375



Scheme 3

formulae. While MNDO is known to give rather large systematic errors for the calculations of the heats of formation,[5b] the relative values may be used with some confidence.[6] From these results, it is clear that the loss of CO from *a* via *c* has a large reverse critical energy which exceeds that for the analogous reaction of α-acetyl-α,α-dimethylmethyl cations,[5b] in agreement with the larger value of T_{50} for ion *a*.

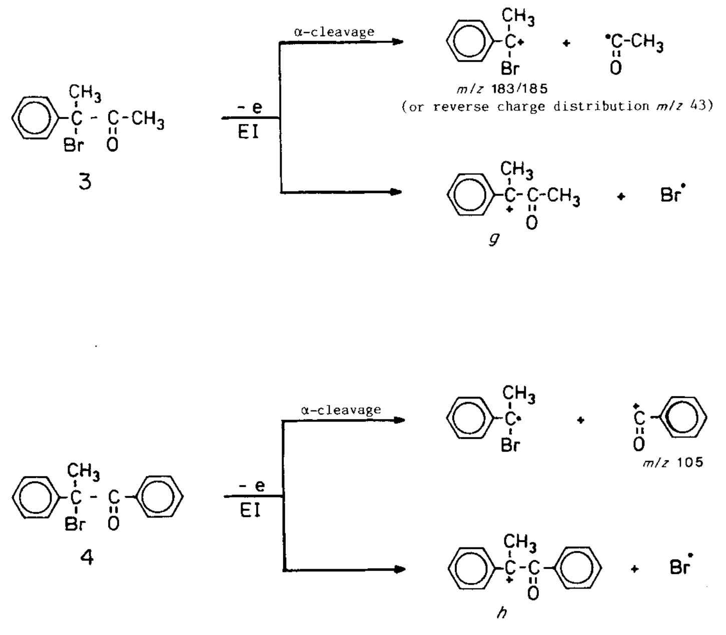
The loss of CO from ion *b* proceeds by a 1,2-shift of the phenyl group and the critical configuration of this process is the bridged phenonium ion *e* shown in Scheme 3 or a structure close to *e*. A similar transition state has been assumed for the CO elimination from α-benzoyl-α,α-dimethylmethyl cations.[5c] The value of T_{50} for this latter process is close to that observed for ions *b*, and again the rigid structure of the critical configuration *e* and the large reverse critical energy arising from its decomposition into very stable products, the benzhydryl cation (*f*) and the CO molecule, are responsible for the large KER and its non-statistical distribution.

Tertiary α-acylbenzyl cations

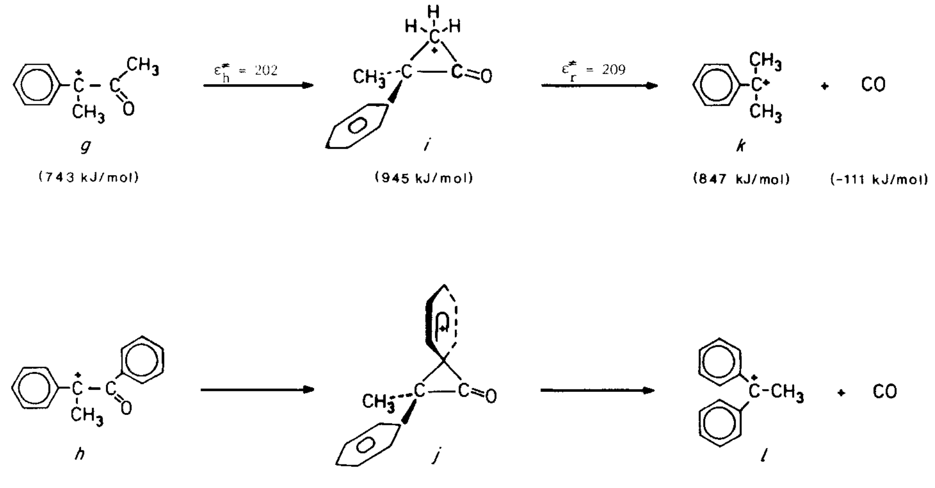
The tertiary α-acetyl-α-methylbenzyl cation (*g*) and α-benzoyl-α-methylbenzyl cation (*h*) have been generated by EI from 3-bromo-3-phenylbutan-2-one (**3**) and 2-bromo-1,2-diphenyl-propan-1-one (**4**) according to Scheme 4. Compared with ions *a* and *b*, the tertiary ions *g* and *h* are stabilized by the additional methyl group at the carbenium ion centre. However, this methyl group also facilitates α-cleavage in the molecular ions of **3** and **4**. Therefore, the most intense peaks in the 70 eV mass spectra of **3** and **4** are due to α-cleavage products, but the relative intensities of the peaks due to *g* and *h* (59 and 16%, respectively) are sufficient for a study of these ions. The metastable molecular ions of **3** and **4** show loss of Br$^\bullet$ as the only reaction and a narrow Gaussian-shaped peak ($T_{50} = 20$ meV) without any sign of a rearrangement in the MIKE spectra. Thus, the formation of ions *g* and *h* occurs via a simple bond cleavage.

The fragmentation pathways of ions *g* and *h* in the 2nd FFR of a ZAB 2F mass spectrometer consist of three reactions in each case. For the ion *g*, these are the loss of CO (60% of total fragmentation), loss of a methyl radical (36%) and elimination of H_2O (4%). The ion *h* fragments by elimination of CO (67%), elimination of C_6H_6 (27%) and elimination of C_8H_8 (6%). Hence, the loss of CO, which is the typical reaction of α-acylcarbenium ions,[5,10] is still the main pathway of the unimolecular reaction. The peaks for the corresponding process in the MIKE spectra of *g* and *h* are broad and dish-topped, and the values of T_{50} are shown in Table 2.

The elimination of CO from *g* and *h* occurs by a 1,2-shift of a methyl and phenyl group, respectively, via the corner-protonated cyclopropanone *i* and the bridged phenonium ion *j*, as depicted in Scheme 5. These reaction mechanisms are completely analogous to the corresponding fragmentation of the secondary α-acylbenzyl cations *a* and *b*, but in the tertiary ions *g* and *h*, T_{50} is



Scheme 4



Scheme 5

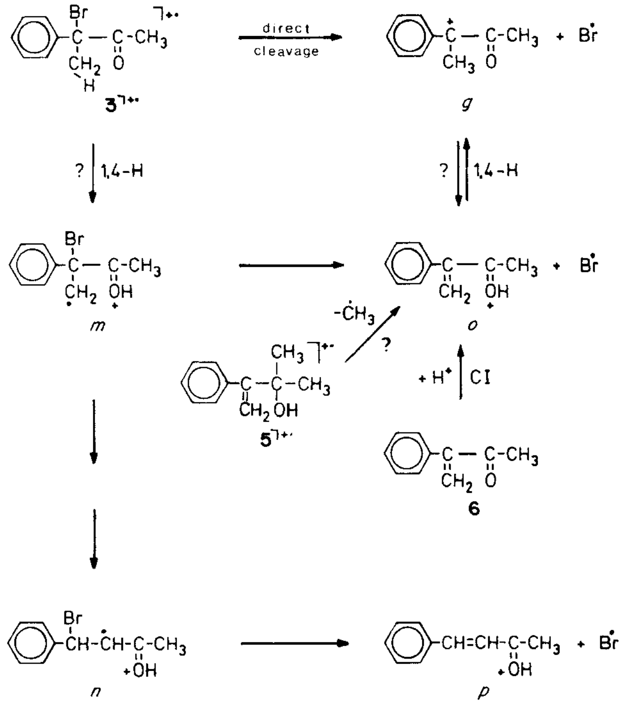
always distinctly larger. The heats of formation of the α-acetyl-α-methylbenzyl cation *g*, the corresponding critical configuration *i* and the product ion, 1,1-diphenylethyl cation *k*, have been calculated by MNDO and the values are given below the corresponding formulae in Scheme 5.[6] The magnitude of the reverse critical energy of the reaction sequence $g \rightarrow i \rightarrow k + \mathrm{CO}$ derived from these values is very similar to that for the reaction $a \rightarrow c \rightarrow d + \mathrm{CO}$; hence, the increase in T_{50} is probably due to some detail in the reaction coordinate channelling more potential energy into the kinetic energy.

The cleavage of substituents in the α-position of the molecular ions of carbonyl compounds may occur by an initial 1,4-hydrogen shift to the carbonyl group and leads eventually to a rearranged product ion.[14] This reaction mechanism has been formulated for the fragmentation of $[\mathbf{3}]^{+\cdot}$ in Scheme 6. It gives rise to the rearranged ion *p*, which is isomeric with *g*, via the distonic ions *m* and *n*. Another possible fragmentation would be a direct loss of Br$^{\cdot}$ *after* the 1,4-hydrogen shift, which leads eventually to the ion *o*, another isomer of ion *g*. The ions *o* and *p* correspond to protonated α,β-unsaturated ketones and are expected to be much more stable than *g*. This is corroborated by the heat of formation $\Delta H_f^0(o) = 695\ \mathrm{kJ\ mol^{-1}}$, which has been calculated by MNDO. It has been shown that the nature of the leaving group determines which of the routes in Scheme 6 is preferred,[15,16] and that Br$^{\cdot}$ as the leaving group is mostly lost by a direct bond cleavage in the molecular ions of α-bromoketones. Furthermore, it has been shown that ions with structures analogous to *g* and *o* equilibrate prior to fragmentation.[5b]

Table 2. T_{50} (in meV) for the CO loss from tertiary α-acylbenzyl cations *g* and *h*

Ion	T_{50} 2nd FFR
g	430
h	445
o	460
o'	450

To verify the analogous interconversion of ions *g* and *o*, the latter have been generated independently by EI induced $\mathrm{CH_3^{\cdot}}$ loss from 2-methyl-3-phenyl-3-buten-2-ol (**5**) and by protonation of 3-phenyl-3-buten-2-one (**6**) during CI (see Scheme 6). The MIKE spectra of the $[\mathrm{C_{10}H_{11}O}]^+$ ions of structure *g* from **3**, structure *o* from **6** and ions *o'* from **5** are shown in Fig. 1. These MIKE spectra are dominated by the large and broad peak due to the elimination of CO, and the KER associated with this process is identical within the limits of error (Table 2). However, the MIKE spectrum of the $[\mathrm{C_{10}H_{11}O}]^+$ ions *o'* derived from the allylic alcohol **5** by EI induced dissociation differs from those of the $[\mathrm{C_{10}H_{11}O}]^+$ ions *g* and *o* generated from **3** and **6**, respectively (Scheme 6) by a large peak for the elimination of $\mathrm{H_2O}$ and a small one for the loss of $\mathrm{CH_3^{\cdot}}$. Thus, the ions *o'* contain at least an admixture of $[\mathrm{C_{10}H_{11}O}]^+$ ions with



Scheme 6

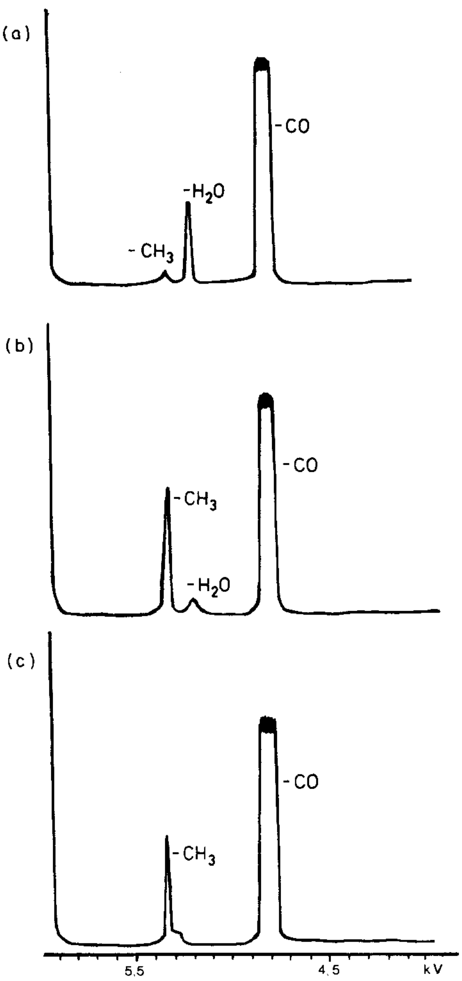


Figure 1. MIKE spectra of $[C_{10}H_{11}O]^+$ ions: (a) ion *o'* from **5**; (b) ion *g* from **3**; (c) ion *o* from **6**.

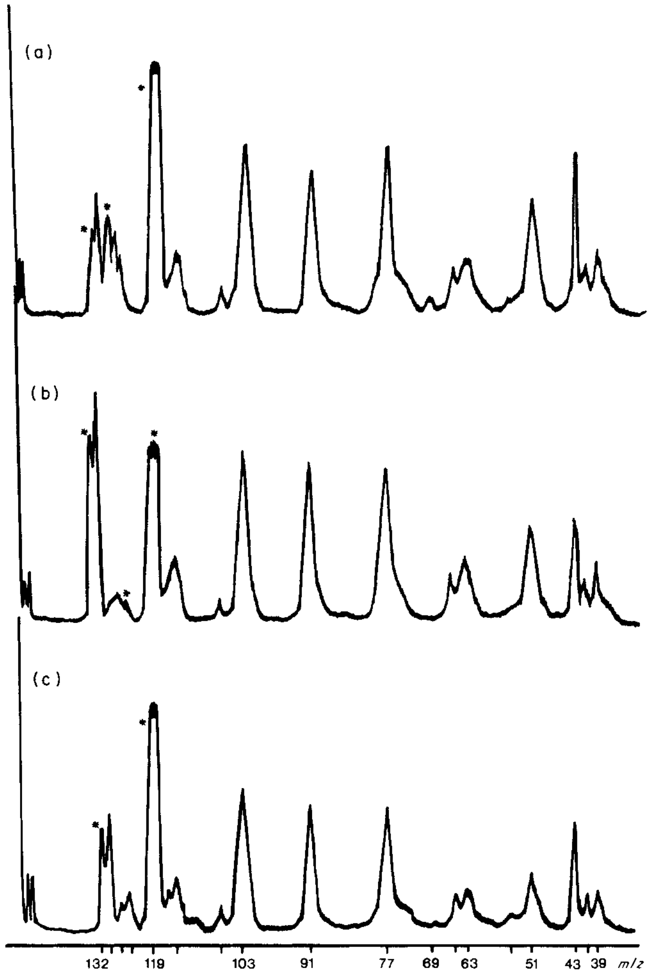
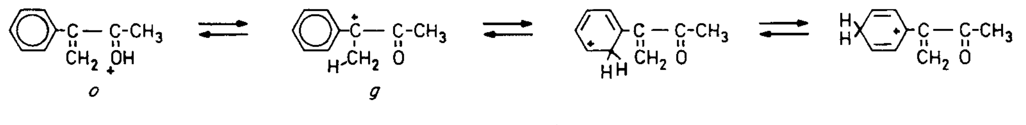


Figure 2. CA spectra of $[C_{10}H_{11}O]^+$ ions: (a) ion *o'* from **5**; (b) ion *g* from **3**; (c) ion *o* from **6** by CI (CH_4). Peaks indicated with an asterisk are also observed as a result of unimolecular reactions.

a structure different from *g* and *o*. This is corroborated by the collisional activation (CA) spectra shown in Fig. 2. Again the CA spectrum of ion *o'* is clearly different. It has been noticed[5b,7] that the loss of $CH_3^\cdot$ from the molecular ions of tertiary allylic alcohols is accompanied by skeletal rearrangements, but in the present case, the structure of the resulting ion is not known.

The CA spectra of the ions *g* and *o* are very similar, but differ in the intensities of some peaks, especially at *m/z* 103 and 43. Moreover, the intensities of these peaks depend on whether the ions *o* have been prepared from **6** by CI (methane) or CI (isobutane). The protonation of **6** can occur at the *ortho* and *para* positions of the phenyl group as well as at the methylene group and carbonyl group of the side-chain, and it is difficult to predict which is the most basic site of the molecule. The variation of the CA spectra of the ions *o* with the acidity of the reactant ions during CI indicates that the $[C_{10}H_{11}O]^+$ ions formed represent an equilibrium mixture of different structures as shown in Scheme 7. Protonation of **6** at the phenyl group or at least migration of a D^+ to this group prior to fragmentation is confirmed by the CA spectrum of the $[MD]^+$ ions of **6** in the CI (CD_4) mass spectrum. All peaks, apart from that of the $[CH_3CO]^+$ ions *m/z* 43 and the small ones due to loss of H_2O, are shifted by 1 u, showing that the D atom resides in the styryl moiety of the ion, but not in the acetyl group.

In conclusion, the present results are consistent with the formation of α-acetylbenzyl cations *a* and α-benzoylbenzyl cations *b* and their tertiary analogues *g* and *h* by EI induced loss of $Br^\cdot$ from the corresponding α-bromoketones. These ions are further examples of destabilized α-acylcarbenium ions with a 'push-pull' substitution at the positive centre, which represent discrete species in a potential energy well. A common unimolecular reaction of metastable ions *a*, *b*, *g* and *h* is the elimination of a CO molecule. This rearrangement reaction is typical of all α-acyl ions studied so far,[5,6,10,16]



Scheme 7

and the process is associated with a large and non-statistical KER, if the α-acyl ion is a stable entity. The loss of CO occurs via a 1,2-shift of a methyl group (ions *a* and *g*) and a 1,2-shift of a phenyl group (ions *b* and *h*), respectively. In the former case, the critical configuration of the process is suggested to be a corner-protonated cyclopropanone (*c* or *i*); in the latter case, a bridged phenonium ion (*e* or *j*). Both configurations are rather rigid structures of high potential energy, decomposing into very stable products. This explains the non-statistical KER and the very large values of T_{50} of the CO elimination from these ions.

EXPERIMENTAL

The 70 eV mass spectra were obtained with the mass spectrometer/data system MAT 311A/SS 200 and the following conditions: electron emission, 2 mA; acceleration voltage, 3 kV; ion source temperature, ~180 °C; sample introduction via heated inlet system (180 °C, compounds **1**, **3**, **5**) or probe (compounds **2**, **4**).

The CI mass spectra were obtained with a VG ZAB 2F mass spectrometer equipped with a combined EI/CI ion source. The reagent gas (CH_4, CD_4, iso-C_4H_{10}) was introduced into the ion source at such a rate that the reading of the ion source pressure gauge was approximately at 0.5×10^{-5} Pa. The electron energy and electron emission current were 50 eV and 0.5 mA, respectively.

The MIKE spectra were measured with the same instrument in the EI (70 eV) or CI mode by focusing magnetically the ions of interest into the 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 ~30%.

The KER values for reactions in the 1st FFR were measured by scanning the acceleration voltage slowly across the appropriate signal. In the 2nd FFR, the electrostatic analyser voltage was scanned. The T_{50} values were calculated from the peak-width at half-height in the usual manner.[17]

The purity of all compounds used in this study was controlled by gas chromatography and structures were verified by ^1H NMR spectroscopy.

α-Bromoketones 1–4 were synthesized from the corresponding ketones by bromination with Br_2 in absolute diethyl ether, using a trace of $AlCl_3$ as catalyst, in 85–95% yields. The bromoketones were purified by vacuum destillation (**1**, **3**) or recrystallization from methanol (**2**, **4**).

3-Phenylpropan-2-one (for preparation of **1**) was synthesized by an ester condensation of ethyl acetate and benzyl cyanide.[18]

1,2-Diphenylethanone (for preparation of **2**) was obtained by a Friedel–Crafts acylation of benzene with phenylacetyl chloride $AlCl_3$.[19]

3-Phenylbutan-2-one (for preparation of **3**) was made by methylation of 3-phenylpropan-2-one with CH_3I/NaOH without any solvent and heating for 2 h at 25 °C, then 3 h to 100 °C, according to the method of Schultz *et al.*[20]

1,2-Diphenylpropan-1-one (for preparation of **4**) was prepared by the same method.[20]

2-Methyl-3-phenyl-3-buten-1-ol (5) was synthesized as described by Jacques *et al.*[21]

3-Phenyl-3-buten-2-one (6) was prepared via HBr elimination from **3** by refluxing for 24 h in dioxane with DABCO as base. The reaction mixture was filtered and evacuated, and the residue dissolved in *n*-hexane. After washing the hexane solution with 2N HCl, $NaHCO_3$ (5%) and H_2O, followed by evaporation, a fractional destillation of the residue resulted in pure **6**, with yield 48% and b.p. 80 °C at 1 Pa.

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