Cyclization of α-Substituted α,ω-Diphenylalkyl Carbenium Ions: Reactivity of α-Trifluoromethylbenzyl Cations vs. α-Methylbenzyl Cations†

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1-(n-Phenylalkyl)-1-trifluoromethylbenzyl cations and the α-CH₃-substituted analogues were generated from the corresponding protonated benzyl alcohols by loss of H₂O during chemical ionization (CI). The unimolecular reactions of these ions and of their derivatives specifically deuterated at the 1-phenyl group were studied using the CI (methane) and CI (isobutane) mass spectra and the mass-analysed ion kinetic energy spectra. The characteristic reaction giving rise to abundant ions in all the spectra is the elimination of C_6H_6 initiated by an electrophilic attack of the benzyl cation on the remote phenyl group. The α-CH₃- and α-CF₃-substituted benzyl cations respond differently to the effect of internal excess energy on the intensity of the benzene elimination process and on the H–D exchange accompanying this process of the deuterated ions. This different reactivity of both series of ions demonstrates unambiguously that the α-CF₃-substituted benzyl cations correspond to destabilized benzyl cations exhibiting the particular reactivity of 'hot' carbenium ions in the gas phase.

INTRODUCTION

Carbenium ions are important intermediates in many organic reactions, and their stability has a dominating effect on the ease and course of the reaction and its potential in organic synthesis. The stability of carbenium ions is determined by the substituents at the positively charged carbon atom, and in most cases electron donors are used to stabilize the carbenium ion and to facilitate its formation during the progress of the reaction. In fact, the detection of a stable triphenylmethyl cation by Gomberg and Walden in 1902[1] was the beginning of the still fascinating carbocation chemistry.[2] However, it is now well known that there also exists a class of carbenium ions in solution[3] and in the gas phase[4] with an electron-withdrawing substituent attached to the carbenium centre. Typically, this electron-withdrawing substituent is an acyl, a nitro or a trifluoro group. The highly electron deficient centre of these destabilized carbenium ions creates a high reactivity, making these ions synthetically very effective intermediates.

Recently, it has been shown that certain n-aryl-1,1,1-trifluoro-2-alkyl triflates and 2,n-diaryl-1,1,1-trifluoroalkan-2-ols can be conveniently used to synthesize the corresponding trifluoromethyl-substituted benzocycloalkanes by a cyclization during solvolysis in CF₃COOH.[5] This cyclization occurs either by nucleophilic assistance of the ω-aryl group to the developing α-carbenium ion or via an intermediate α-trifluoromethyl-substituted carbenium ion. Specifically, this carbenium ion destabilized by the α-trifluoromethyl substituent is expected to be the reactive intermediate during the solvolysis of 2,5-diphenyl-1,1,1-trifluoropentan-2-ols and related compounds.

The reactions of ionized 1,n-diphenylalkanes in the gas phase both as radical cations[6] and as a protonated species[7] have been studied in detail by mass spectrometry, and recently Kuck[8] has shown that the [M − H]⁺ ions of α,ω-diphenylalkanes, generated by chemical ionization (CI) with methane and assumed to correspond to α-(ω-phenylalkyl)benzyl cations, fragment in the mass spectrometer by cyclization to the isomeric protonated 1-phenylbenzocycloalkanes prior to the loss of a benzene molecule. This cyclization reaction is a gas-phase analogue of the cyclization of the 2,n-diphenyl-1,1,1-trifluoroalkan-2-ols during solvolysis and allows the study of the reactivity of destabilized α-trifluoromethylcarbenium ions by an intramolecular process also in the gas phase.

It is much more convenient to generate the α-(ω-phenylalkyl)benzyl cations not by hydride abstraction in the CI (CH₄) plasma but by protonation and subsequent loss of H₂O from the corresponding α-(ω-phenylalkyl)benzyl alcohols. In this case the structure and the position of the carbenium centre of the resulting benzyl cation are unambiguously determined by the structure of the precursor alcohol. This is of special importance for benzyl cations carrying additional destabilizing substituents such as the trifluoromethyl group in one (α-)benzylic position. In this case hydride abstraction from an α,ω-diphenylalkane is expected to occur at the other (ω-)benzyl group to avoid the forma-

Scheme 1

$$\text{Ph}-(CH_2)_n-\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{C}}-\text{Ph}(d_5) \xrightarrow{\text{Cl}} \text{Ph}-(CH_2)_n-\overset{+}{\underset{\underset{R}{|}}{C}}-\text{Ph}(d_5)$$

R = CF₃, n = 3	1	1-d₅	a_F	a_F-d₅
R = CH₃, n = 3	2	2-d₅	a_H	a_H-d₅
R = CF₃, n = 2	3	3-d₅	b_F	b_F-d₅
R = CH₃, n = 2	4		b_H	
R = CF₃, n = 4	5	5-d₅	c_F	c_F-d₅
R = CH₃, n = 4	6		c_H	

$$\text{Ph}-\underset{\underset{CH_3}{|}}{CH}-(CH_2)_2-\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{C}}-\text{Ph}(d_5) \xrightarrow{\text{Cl}} \text{Ph}-\underset{\underset{CH_3}{|}}{CH}-(CH_2)_2-\overset{+}{\underset{\underset{R}{|}}{C}}-\text{Ph}(d_5)$$

R = CF₃, n = 3	7	7-d₅	d_F	d_F-d₅
R = CH₃, n = 3	8		d_H	
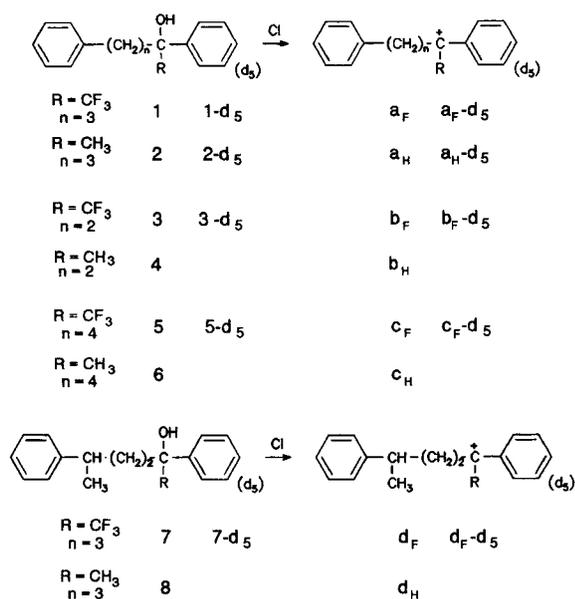
Scheme 1

tion of a destabilized carbenium ion. However, we have shown that α-trifluoromethylcarbenium ions are formed easily in a mass spectrometer from the corresponding alcohols by CI using methane or isobutane as the reagent gas.[9]

Thus, the tertiary α-trifluoromethylbenzyl alcohols 1, 3, 5 and 7 and their pentadeuterated derivatives 1-d_5, 3-d_5, 5-d_5 and 7-d_5 (Scheme 1) were synthesized to prepare α-(3-phenylpropyl)-α-trifluoromethylbenzyl cations a_F, 1-(2-phenylethyl)-1-trifluoromethylbenzyl cations b_F, 1-(3-phenylbutyl)-1-trifluoromethylbenzyl cations c_F, 1-(3-butylphenyl)-1-trifluoromethylbenzyl cations d_F and their pentadeuterated analogues a_F-d_5-d_F-d_5, by CI. The gas-phase reactions of ions a_F-d_F were studied and compared with those of the corresponding α-methyl substituted benzyl cations a_H—b_H, generated from the α-methylbenzyl alcohols 2, 4, 6 and 8 (Scheme 1). The results of these studies demonstrated convincingly the increased reactivity of the destabilized α-trifluoromethylbenzyl cations by comparing the CI mass spectra of the benzyl alcohols and the mass-analysed ion kinetic energy (MIKE) spectra of the corresponding benzyl cations.

EXPERIMENTAL

Mass spectrometry

The electron impact (EI) and CI mass spectra of the alcohols 1–6 and of their deuterated derivatives were obtained with a MAT CH5 mass spectrometer using methane and isobutane, respectively, as the CI reagent gas at a pressure of about 0.35 mbar in the ionization chamber and the following operating conditions: accelerating voltage 3 kV, electron energy 70 eV, emission current 0.1 mA (EI) or 0.6 mA (CI), ion source temperature 180–200 °C and sample inlet by an HTE system at 105 °C. The CI spectra also contained the molecular ion and fragment ions of the samples formed by EI ionization owing to imperfect CI and to charge-

transfer reactions under the conditions used. These peaks were omitted from the CI spectra.

The MIKE spectra and collisional activation (CA) spectra were obtained with a VG ZAB-2F mass spectrometer using a laboratory-built CI source and methane and isobutane, respectively, as reagent gas. The acceleration voltage was set at 6 kV and the electron energy and emission current at 100 eV and 0.2 mA, respectively. The ions studied were focused magnetically into the second field-free region following the magnet sector field of the instrument, and the MIKE spectra were obtained by scanning the voltage of the electrostatic analyser. The CA spectra were measured under the same conditions but introducing helium as a collision gas into the collision chamber of the second field-free region at a rate such that the main beam was attenuated to about 30% of the initial intensity.

Compounds

The full details of the synthesis of the benzyl alcohols 1–8 have been published elsewhere.[5,9] The general procedure for the synthesis was a Grignard reaction of phenylmagnesium bromide with the respective n-phenylalkan-2-one and n-phenyl-1,1,1-trifluoroalkan-2-one in diethyl ether. The substituted benzyl alcohol was isolated from the reaction mixture by the usual work-up techniques and purified by fractional distillation at reduced pressure. The product was identified by the ¹H NMR spectrum and 70 eV EI mass spectrum. The derivatives pentadeuterated at the n-phenyl group were synthesized by the same procedure but using pentadeuterophenylmagnesium bromide. The deuterium content of the pentadeuterobromobenzene used as the starting material was >99% and no loss of D during the synthesis was detected in the ¹H NMR spectra and EI mass spectra of the final products.

RESULTS AND DISCUSSION

The CI mass spectra of 1–8 are simple and show only small signals for the protonated molecules MH⁺, as expected for tertiary benzyl alcohols. The prominent peaks are due to ions formed by the loss of H_2O and by the combined losses of H_2O and C_6H_6 from MH⁺. Additionally, the CI mass spectra of the CF_3-substituted alcohols exhibit a peak for the loss of CHF_3 from the ions [MH⁺ − H_2O]. In particular, the relative abundances of the ions [MH⁺ − H_2O] and [MH⁺ − H_2O − C_6H_6] depend typically on the presence of a CH_3 and CF_3 substituent, respectively, at the benzylic position and on the reagent gas used for CI. The relevant data are summarized in Table 1. The effect of the substituent at the benzylic carbinol group is obvious. While the base peak in the spectra of the CH_3-substituted alcohols (2, 4, 6 and 8) corresponds to the ion [MH⁺ − H_2O], the protonated alcohols of the CF_3-substituted series (1, 3, 5 and 7) decompose quickly by the loss of H_2O and C_6H_6. As expected, the more acidic environment in the CI (methane) plasma induces more fragmentations of the protonated alcohols and, with the exception of the 2,4-diphenylbutan-2-ol (4), the

Table 1. Relative abundances (% of base peak) of characteristic ions in the CI (isobutane) and CI (methane) mass spectra of compounds 1–8

Mass spectrum	Ion	1	2	3	4	5	6	7	8
CI (isobutane)	MH^+	<1	1	<1	1	<1	<1	<1	<1
	$[MH^+ - H_2O]$	2	100	6	100	7	100	1	100
	$[MH^+ - H_2O - C_6H_6]$	100	60	100	15	100	40	100	30
CI (methane)	MH^+	<1	<1	<1	<1	<1	<1	—	—
	$[MH^+ - H_2O]$	1	45	2	100	3	67	—	—
	$[MH^+ - H_2O - C_6H_6]$	100	100	100	30	100	100	—	—

base peak in the CI (methane) mass spectra originates from the ions $[MH^+ - H_2O - C_6H_6]$. However, the different behaviour of the CH_3- and CF_3-substituted alcohols with respect to the relative abundances of the ions $[MH^+ - H_2O]$ is still apparent. Recognizing that the ions $[MH^+ - H_2O]$ of the benzyl alcohols 1–8 initially have the structures *a–d* shown in Scheme 1 and correspond to the ions $[M - H]^+$ in the CI mass spectra of α,ω-diphenylalkanes discussed by Kuck,[8] these observations corroborate the fragmentation mechanism suggested by Kuck and reveal further interesting details about the gas-phase reactivity of these ions.

Specifically, the mechanism for the fragmentation of the protonated 2,5-diphenylpentan-2-ols 1 and 2 and the 2,5-diphenylhexan-2-ols 7 and 8 is shown in Scheme 2. Protonation of the alcohols at the hydroxy group and loss of H_2O gives rise to the ions *a* and *d*, respectively. The important feature of this mechanism, however, is a cyclization of the ions *a* and *d* by an intramolecular electrophilic aromatic substitution of the remote phenyl group resulting in a protonated 1-phenyltetralin species *a′* and *a″*. It has been demonstrated convincingly by Kuck[7,8] that the typical gas-phase reaction of this species and other protonated α,ω-diphenylalkanes is the elimination of a C_6H_6 molecule, resulting in a cyclic product ion. In the present case the product ion is a substituted tetralyl cation.

No further fragmentation of metastable tetralyl cations generated from 1 or 2 is observed. The structure
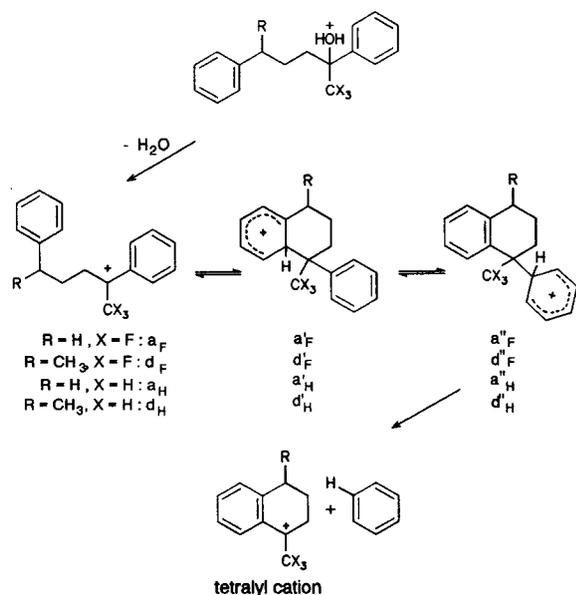
of the CF_3-substituted tetralyl ion from 1 was confirmed by comparing its CA spectrum with that of 1-trifluoromethyltetralyl cations generated from 1-bromo-1-trifluoromethyltetralin by EI-induced loss of Br. Good agreement between both spectra was observed; the main fragmentations induced by collisions are the loss of HF and of CHF_3, respectively.

The structure of the ions $[MH^+ - H_2O]$ is not unambiguously known *a priori*. First, the proton affinities (*PA*) of benzyl alcohol[10] ($PA = 788.7$ kJ mol^{-1}) and toluene[10] (794.1 kJ mol^{-1}) are not very different and protonation may occur at the hydroxy group in addition to the aromatic ring of 1 and 2. Nevertheless, no elimination of HDO or D_2O is observed in the CI mass spectra of the deuterated benzyl alcohols $1\text{-}d_5$ and $2\text{-}d_5$ which would arise from an initial protonation at the deuterated phenyl ring and a subsequent migration of H^+ and D^+, respectively, to the hydroxy group. Thus, a direct loss of H_2O from the protonated molecules occurs and the structure *a* is a reasonable choice for the incipient ions $[MH^+ - H_2O]$. Second, however, the loss of H_2O may be followed quickly by a cyclization yielding ions *a′* and *a″* (Scheme 2), or some other protomers. Further, the loss of H_2O and the cyclization may be concerted yielding ions *a′* directly. Certainly, the formation and lifetime of the ions *a* depend on their thermodynamic stability, on their excess energy acquired during the formation and on the activation barrier for the electrophilic attack at the remote phenyl group.

The relative abundances of the ions $[MH^+ - H_2O]$ (Table 1) derived from the CH_3-substituted benzyl alcohols decrease distinctly in favour of the subsequent C_6H_6 elimination if generated by a protonation with the very acidic ions CH_5^+ and $C_2H_5^+$ during CI (methane). Certainly, this is a clear effect of the free excess energy of the ions $[MH^+ - H_2O]$ on the subsequent C_6H_6 elimination and indicates that for these ions the elimination of C_6H_6 has to surmount an activation barrier. Indeed, the ions a_H, b_H, c_H and d_H (Scheme 1) are tertiary benzyl cations substituted by electron-releasing alkyl groups and correspond to stable carbenium ions. In contrast, the relative abundances of the ions $[MH^+ - H_2O]$ obtained from the CF_3-substituted benzyl alcohols are always small and more or less independent of the CI gas used. Thus, the elimination of C_6H_6 is already fast for these ions $[MH^+ - H_2O]$ of small excess energies. Indeed, the ions a_F, b_F, c_F and d_f correspond to destabilized carbenium ions because of the electron-withdrawing α-CF_3 substituent. The different behaviour of the ions $[MH^+ - H_2O]$ in the two series is clear evidence for the difference in the

R – H, X – F : a_F
R – CH_3, X – F : d_F
R – H, X – H : a_H
R – CH_3, X – H : d_H

tetralyl cation

Scheme 2

electrophilic reactivity between benzyl cation stabilized by a CH_3 substituent and destabilized by a CF_3 substituent in the gas phase. This is similar to the different reactivities of these species observed in solution.[5] A corollary of this different situation for both types of ions $[MH^+ - H_2O]$ is that the structures of the CH_3-substituted ions probably correspond to a_H–d_H whereas for the CF_3-substituted ions the cyclic structures of a_F'–d_F' (or protomers thereof) are more favoured.

An additional detail supporting the different energy requirements of the cyclization–elimination sequence of the ions a_F and a_H is the kinetic energy release (KER) associated with the elimination of C_6H_6 from metastable ions. For both ions Gaussian-shaped peaks are observed in the MIKE spectra for this reaction, but whereas the elimination of C_6H_6 from a_H gives rise to a KER of $T_{50} = 133$ meV (148 MeV for a_H-d_5), calculated from the width of the peak at 50% of its height, the KER of $T_{50} = 33$ meV (48 MeV for a_F-d_5) for the reaction of a_F is distinctly smaller. This increase in the KER for the stable ion a_H by a factor of four points to a rate-determining rearrangement step preceding the loss of C_6H_6, whereas in the case of a_F the small KER indicates, by a quantitative Hammond postulate, an early critical configuration of the total cyclization–elimination process.[11] The heats of formation, ΔH_f, of the ions a, a' and a'' and of the tetralyl cations were estimated by an AM1[12] calculation and used to construct the schematic reaction energy profiles shown in Fig. 1.

Because of the limitations of the semi-empirical AM1 method, we did not try to calculate the complete reaction energy profile including transition states but only
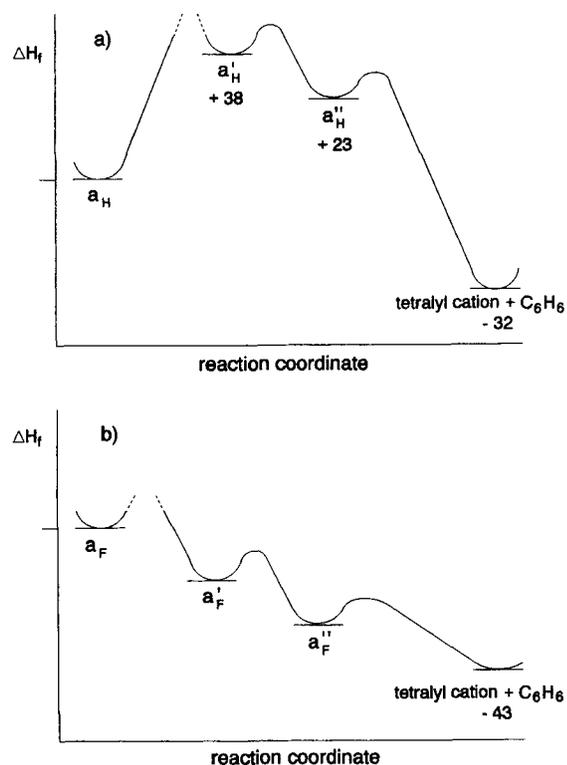
the ΔH_f of possible intermediates. However, fast proton shifts in benzenium ions exhibit a critical energy of ~ 40 kJ mol^{-1},[13] and this is certainly also true for a proton migration in the protonated 1-alkyl-1-phenyltetralins. Of these species the protomer a' (Scheme 2) carrying the proton at an angular position is the most unstable, and the ΔH_f of the $ipso$-protonated benzenium ion a'' exceeds that of the protomers with the proton in the $para$ or $ortho$ position of the phenyl group. Thus, a' and a'' are probably near to the potential energies of the transition states of the respective reaction steps. The elimination of C_6H_6 from a_F'' and a_H'' by a simple bond cleavage is exothermic by 7 and 55 kJ mol^{-1}, respectively. Hence, no large activation barrier is expected for this dissociation step, but an explicit energy barrier may be expected for the cyclization step $a \rightarrow a'$.

Interestingly, the AM1 reaction energy profile reveals comparable exothermicities of 43 and 32 kJ mol^{-1} for the complete elimination of C_6H_6 from a_F and a_H, respectively. However, the significant difference for the two reaction energy profiles is the order of the ΔH_f of the benzyl cations a_F and a_H relative to the reaction intermediates. In particular, whereas the stabilized carbenium ion a_H is more stable than the cyclization product a_H', the destabilized carbenium ion a_F' is higher in energy than a_F', and in the latter case the potential energy of the reaction system decreases step by step towards the reaction products. Thus, the AM1 calculation of the reaction energies fully corroborates the conclusions from the experimental observations of a different effect of the CI conditions on the relative abundances of the fragment ions and of the different KER during the C_6H_6 elimination from the CH_3- and CF_3-substituted benzyl cations a_H and a_F.

Similar reactivity differences of the benzyl cations stabilized by a CH_3 substituent and destabilized by a CF_3 substituent are also observed for the ions b, c and d (Table 1). Ions b and c differ from ion a by one group less and one group more, respectively, in the CH_2 chain to the remote phenyl group. The 3-phenylpropyl-substituted benzyl cations b give rise to indanyl cations via an electrophilic cyclization and C_6H_6 elimination, but the 4-phenylbutyl-substituted benzyl cations ions of type c have been suggested to eliminate C_6H_6 by a modified mechanism.[8] These ions are assumed to undergo a cyclization to protonated benzyltetralin derivatives after a 1,2-hydride shift rather than forming protonated benzocycloheptane derivatives directly by an electrophilic attack of the original benzyl ions on the remote phenyl group (Scheme 3).

No further attempts were made to determine the structures of the product ions b-C_6H_6 and c-C_6H_6, However, in the case of c_F, the 1,2-hydride shift converts the destabilized α-CF_3-substituted carbenium ion into a less electron-deficient carbenium ion substituted only in the β-position by CF_3. The reactivity of this ion should be similar to that of the rearranged ion derived from c_H, and one might expect that the mass spectral behaviour of 5 and 6 would be less different than for the other pairs of benzyl alcohols. The data in Table 1 show indeed that the elimination of C_6H_6 from the ions $[MH^+ - H_2O]$ generated from 4 and 6 is not as efficient as in the case of 2, but the elimination occurs most reluctantly from 4, not from 6, and no special effects are

Figure 1. Schematic reaction energy profile for the loss of benzene from ions a_F and a_H. Relative ΔH_f values in kJ mol^{-1} are shown, calculated by AM1.

X = F; b_F
X = H; b_H

indanyl cation

+

X = F; c_F
X = H; c_H

benzocycloheptyl cation
(or some isomer)

+

1,2-hydride shift

?

Scheme 3
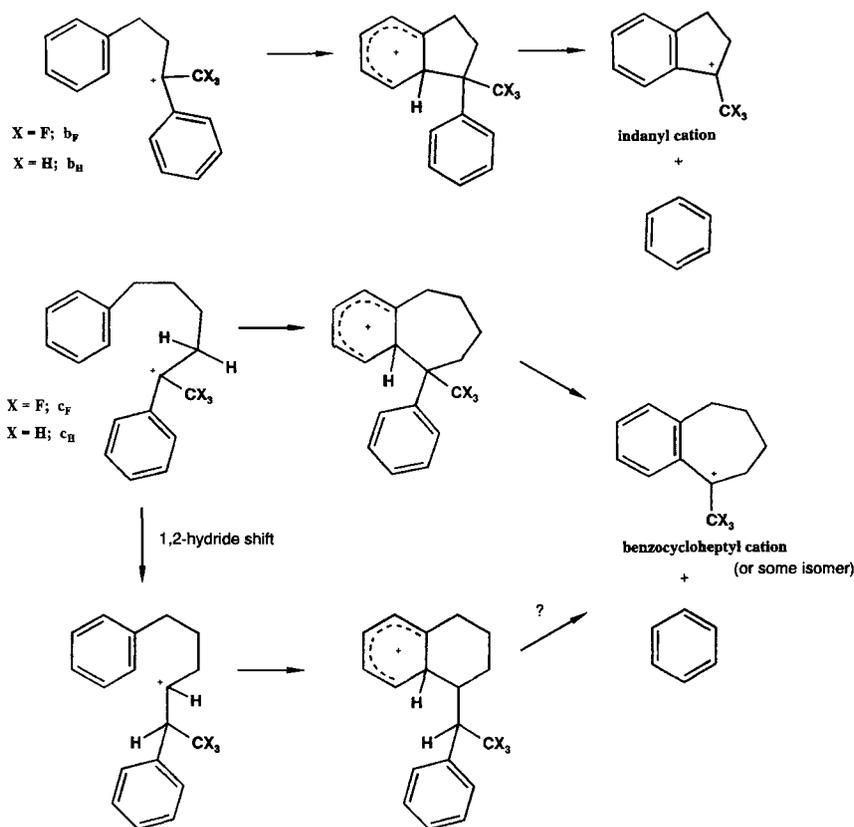
seen for the differences between the CH_3- and CF_3-substituted derivatives in the case of 5 and 6. Thus, a special mechanism for the elimination of C_6H_6 from the 4-phenylbutyl-substituted benzyl cations c cannot be deduced from the results discussed so far.

One most interesting phenomenon which constitutes also the main evidence for intermediate protonated benzocycloalkanes during the loss of C_6H_6 from the ions $[M - H]^+$ of α,ω-diphenylalkanes is the H–D exchange observed specifically for H and D atoms at the two phenyl groups.[8] In the present case this H–D exchange was examined for the ions a_F-d_5, a_H-d_5, b_F-d_5, c_F-d_5 and d_F-d_5 (Scheme 1) decomposing in the ion source under different CI conditions and in the second field-free region of the VG ZAB 2F mass spectrometer. In contrast to the ions $[M - H]^+$ generated by CI from α,ω-diphenylalkanes,[8] the ions studied here are tertiary benzyl cations carrying either a CF_3 or a CH_3 substituent at the carbenium ion centre and are formed specifically with the deuterated phenyl group next to the carbenium ion centre by the loss of H_2O form the corresponding protonated benzyl alcohols. Thus, unlike the 'concave' and 'convex' peak pattern observed by Kuck,[8] the intermediate ions a'-d' and a''-d'' give rise to a specific loss of C_6HD_5 in the absence of H–D exchange, and the occurrence of any H–D exchange is noticed by an increasing loss of $C_6H_nD_{6-n}$ until the 'convex' peak pattern due to a random distribution of all H and D between the two phenyl groups is reached. The results are presented in Table 2.

Generally, no extensive H–D exchange is observed in the CF_3-substituted benzyl cations a_F-d_5, b_F-d_5 and d_F-d_5. The exception is the 1-(4-phenylbutyl)-1-tri-

fluoromethylbenzyl cation c_F-d_5, which will be discussed below. The results obtained for the H–D exchange in the CH_3-substituted tertiary benzyl cation a_H represent a link to the secondary benzyl cations investigated previously.[8] Contrary to expectation, the CI mass spectra of 2-d_5 and the MIKE spectrum of the respective benzyl cation a_H-d_5 exhibit a 'concave' peak pattern for the loss of the benzene isotopomers $C_6H_{6-n}D_n$ similar to the same elimination process from the ions $[M - H]^+$ of 1-phenyl-4-pentadeuterophenylbutane.[8] However, the elimination of C_6H_6 is not observed, proving again that an H–D exchange occurs exclusively between the five H and five D atoms of the aromatic rings. In the case of the deuterated 1,4-diphenylbutane, two isomeric ions $[M - H]^+$ are formed by hydride abstraction from both benzylic positions and this, together with incomplete H–D exchange, results in a concave intensity distribution of the benzene isotopomers lost. From the benzyl alcohol 2-d_5, however, the benzyl cation a_H-d_5 is specifically formed by loss of H_2O under CI conditions. As a consequence, the preferred elimination of C_6H_5D besides C_6HD_5 requires the isomerization of the tertiary benzyl cation a_H-d_5 to the secondary ion $a_H{}^*$-d_5 by a 1,4-hydride shift prior to the cyclization process (Scheme 4). The data in Table 2 show that this isomerization depends on the excess energy of the benzyl cations and increases with decreasing internal energy of the ions, accompanied by a slight decrease in the H–D exchange. At first sight this effect is surprising because the secondary ion $a_H{}^*$-d_5 is less stable than the tertiary ion a_H-d_5. However, as discussed above, the C_6H_6 elimination probably requires a substantial activation energy, which may be larger than

Table 2. H–D exchange during elimination of benzene from unstable and metastable benzyl cations labelled with an α-pentadeuterophenyl group

Compound	Ion	Type[a]	$-C_6HD_5$	$-C_6H_2D_4$	$-C_6H_3D_3$	$-C_6H_4D_2$	$-C_6H_5D$
1-d_5	a_F-d_5	CI_M	71.4	13.6	3.6	4.3	7.1
		CI_B	86.2	9.5	1.7	0.9	1.7
		m^*	95.2	4.8	—	—	—
2-d_5	a_H-d_5	CI_M	58.5	11.1	7.0	8.2	15.2
		CI_B	56.2	5.6	5.0	5.1	28.1
		m^*	50.0	6.0	6.5	6.0	31.5
3-d_5	b_F-d_5	CI_B	92.6	4.6	0.9	0.8	0.9
		m^*	>95	<5	—	—	—
5-d_5	c_F-d_5	CI_M	4.1	16.0	41.0	28.7	10.2
		CI_B	2.9	19.7	41.8	27.2	8.4
		m^*	2.2	23.3	44.9	26.5	3.1
7-d_5	d_F-d_5	CI_B	87.7	7.9	1.8	0.8	1.8
		m^*	>90	<4	—	—	6.2
		Random exchange	2.4	23.8	47.6	23.8	2.4

[a] CI_M = CI (methane); CI_B = CI (isobutane); m^* = metastable ions, MIKE spectrum.

that of the hydride shift, thus admitting a competition by the 1,4-hydride shift for low-energy ions.

The CI (methane) mass spectrum of the CF_3-substituted benzyl alcohol **1**-d_5 shows only a small but nevertheless significant peak for the elimination of C_6H_5D form the cation a_F-d_5. Thus, in contrast to the CH_3-substituted analogue, the 1,4-hydride shift of the CF_3-substituted benzyl cation a_F-d_5 is preferred by ions of a higher excess energy, even though the hydride shift in this case converts a destabilized benzyl cation into a more stable cation and is exothermic by 74 kJ mol^{-1} ($\Delta H_f(a_F)$ = 353 kJ mol^{-1}, $\Delta H_f(a_F^*)$ = 279 kJ mol^{-1} by

AM1). Obviously, the electrophilic attack of the benzyl cation on the remote phenyl group is favoured over the 1,4-hydride shift. This must be due to a delicate balance between the energetic requirements of both processes as shown by the behaviour of the ion d_F-d_5. In this case an especially exothermic 1,4-hydride shift of the tertiary CF_3-substituted benzyl cation d_F results in a tertiary CH_3-substituted benzyl cation d_F^*, and the abundance of the 1,4-shift product ion increases for low-energy ions. Nevertheless, the amount of the H–D exchange in the ions a_F-d_5 and d_F-d_5 is very similar and is far from being random at all internal energies. This is also true

Scheme 4
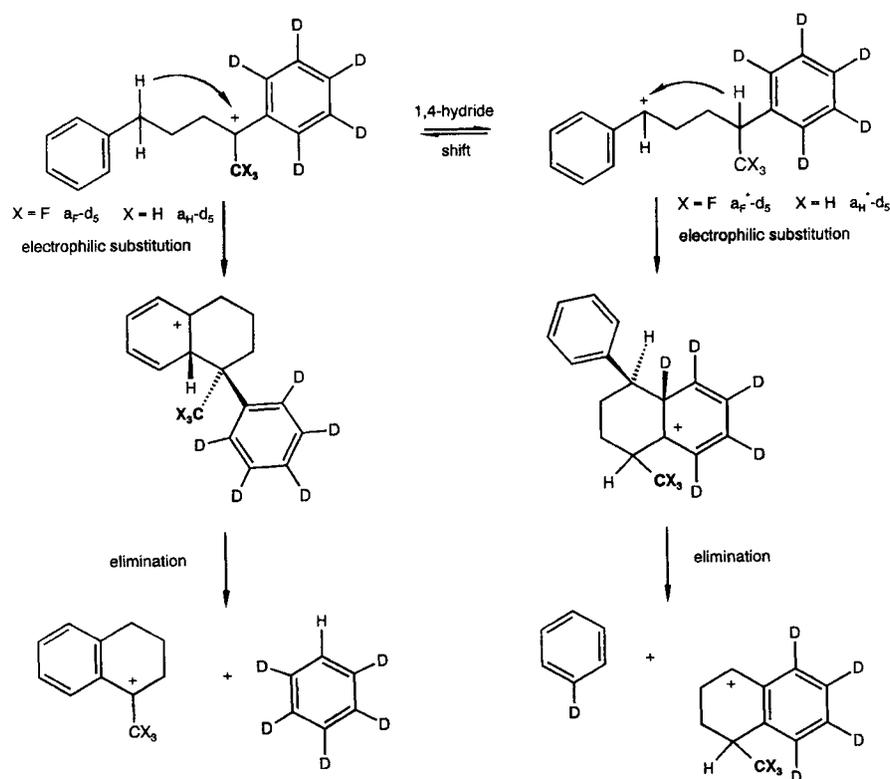
for the 1-(2-phenylethyl)-1-trifluorobenzyl cations b_F-d_5. Compared with the H–D exchange in the ions $[M - H]^+$ of the corresponding α,ω-diphenylalkanes,[8] however, the exchange in the α-CF_3-benzyl cations is significantly reduced. Summarizing so far the results for the reactions of the deuterated α-CF_3-benzyl cations, a picture of distinctly more reactive 'hot' carbenium ions evolves.

The pentadeuterated 1-(4-phenylbutyl)-1-trifluoromethylbenzyl cation c_F-d_5 deviates from the other α-CF_3-substituted benzyl cations by exhibiting an extensive H–D exchange. Metastable c_F-d_5 shows in the MIKE spectrum the symmetrical peak pattern for the loss of $C_6H_{6-n}D_n$ expected for a random distribution of the five H and five D atoms in the phenyl groups over all ten positions (Table 2). In fact, the label distribution is identical with that observed for the elimination of $C_6H_{6-n}D_n$ from metastable ions $[M - H]^+$ of 1-phenyl-5-pentadeuterophenylpentane.[8] Increasing the energy of the fragmention ions c_F-d_5 results in a distortion of the $C_6H_{6-n}D_n$ elimination pattern in favour of small n. Basically, this effect is again due to the competitive formation and fragmentation of an isomeric benzyl cation c_F^*-d_5 by a 1,5-hydride shift. The rearranged ion fragments initially via elimination of C_6H_5D, but extensive H–D exchange would result again in a 'concave' peak pattern for the loss of the $C_6H_{6-n}D_n$ isotopomers. This is not observed, however. To construct the peak pattern observed in the CI (methane) mass spectrum of 5-d_5 requires the superposition of the elimination of $C_6H_{6-n}D_n$ in a nearly random label distribution from the original ion c_F-d_5 and the elimination of $C_6H_{6-n}D_n$ with much less H–D exchange from the ion c_F^*-d_5 formed subsequently by a 1,5-hydride shift. There are at least two possible explanations for this phenomenon. First, it is possible that the C_6H_6 elimination from the ion c_F and the rearranged ion c_F^* occurs from ions of different internal energy. It is clear that only ion c_F with considerable excess energy rearranges by the 1,5-hydride shift and the lifetime of these excited ions may be too short for H–D scrambling. Second, a competitive formation of the intermediate protonated benzocycloheptane derivative and the protonated benzyltetralin derivative (see Scheme 3) may occur both in c_F and c_F^* but to different extents, because the CF_3-substituted benzyl cation c_F rearranges quickly by the 1,2-hydride shift necessary for the formation of the protonated benzyltetralin. It is assumed that protonated 1-benzyltetralins deuterated at one of the aromatic rings undergo an H–D exchange much faster than protonated 1-phenylbenzoalkanes.[8] This detail of the reactions of differently substituted benzyl cations derived from α,ω-diphenylalkanes needs further investigation for an unequivocal answer. However, this effect shows that the process leading eventually to the loss of C_6H_6 from 1-(n-phenylalkyl)benzyl cations may be more complex than expected.

CONCLUSION

The study of the gas-phase reactions of arenium ions and related ions[7] has given detailed information about the reactivity of these species important for so many synthetic reactions in solution. In this work, mass spectrometric techniques were used to identify the reactivity of benzyl cations destabilized by an α-CF_3 substituent for intramolecular aromatic substitution of the remote phenyl group of an ω-phenylalkyl substituent. A cyclization reaction producing CF_3-substituted benzoalkanes in high yields was found to be characteristic for such α-CF_3-benzyl cations.[5] It is known from previous work[8] that in the gas phase also 1-(n-phenylalkyl) benzyl cations undergo a cyclization to protonated 1-phenylbenzoalkanes. In contrast to the reaction in solution, these species are not eventually stabilized by deprotonation but by elimination of a benzene molecule via a protiolysis reaction. Adopting this fragmentation as an 'indicator reaction' to 1-(n-phenylalkyl)-1-trifluoromethylbenzyl cations a_F-d_F and 1-(phenylalkyl)-1-methylbenzyl cations a_H-d_F, clear differences in the reactivities of tertiary benzyl cations destabilized by an α-CF_3 group and stabilized by an α-CH_3 group are observed. In particular, the destabilized ions generated by CI from the corresponding benzyl alcohols always fragment rapidly by elimination of benzene, whereas the stabilized benzyl cations exhibit strong fragmentation by loss of benzene only if they are formed with excess energy by CI (methane). Further differences are observed by using the specifically deuterated derivatives, especially a_F-d_5 and a_H-d_5. The tertiary CH_3-substituted benzyl cations undergo a competing hydride shift yielding secondary benzyl cations in particular for metastable ions containing only a small amount of excess energy, whereas in the case of the tertiary CF_3-substituted benzyl cations a less intense hydride shift is only observed for energetically excited ions. In addition, the H–D exchange between the H and D atoms in the phenyl groups prior to the elimination of benzene is clearly less for the α-CF_3-benzyl cations. The rationale for these experimental observations is that the destabilized α-CF_3-substituted benzyl cations a_F-d_F represent 'hot' carbenium ions with a distinctly higher gas-phase reactivity towards the intramolecular electrophilic substitution, paralleling the behaviour of these ions in solution.

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