[Arene$\cdot$Me$_3$C$^+$] non-covalent complexes in the gas-phase (trifluoro)methylation of *tert*-butyl-substituted diphenylalkanes

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Abstract

The reaction of Me_2F^+, Me_2Cl^+ and CF_3^+ with p-$Me_3CC_6H_4(CH_2)_nC_6D_5$ ($n = 2, 3$) initiates a reaction pattern whose major features are accounted for by the additional electrostatic stabilization afforded by the second (spectator) aromatic ring on ionic intermediates and ion–molecule complexes. The Me_3C loss following CX_3^+ (X = H, F) addition to the *tert*-butyl-substituted ring is significantly reduced with respect to a single-ring model substrate, p-$Me_3CC_6H_4Me$. [Arene$\cdot$Me$_3$C$^+$] non-covalent complexes mediate the observed interannular and intermolecular Me_3C^+ transfer. Unimolecular cleavage of Me_3CH from [arene$\cdot$Me$_3$C$^+$], following side-chain H^- abstraction, a major fragmentation pathway under mass spectrometric conditions, is instead largely inhibited in the reported radiolytic experiments. Such behavior is accounted for by the effective stabilization of ion–molecule non-covalent complexes ensured by unreactive collisions with about 1 atm bath gas.

Keywords: Arenium ions; Interannular carbenium ion migration; Ion–neutral complexes; Isomerization

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1. Introduction

The gas-phase behaviour of α,ω-diphenylalkanes (DPAs) has shown peculiar reactivity features related to the difunctional character of this class of compounds. Detailed studies have focused on the unimolecular decay of protonated DPAs by loss of neutral benzene [1]. This process follows a relatively fast interannular exchange between the hydrogens of the two terminal rings, which is complete within 10^{-5} s, whenever the linking methylene chain allows a suitable reciprocal interaction of the protonated phenyl ring with the second "spectator" ring. The detection of such processes by MIKE spectroscopy has recently found a counterpart in radiolytic studies of reactions of gaseous cations with DPAs at nearly atmospheric pressure [2]. In such a higher pressure environment, the arenium ions formed by alkylation of 1,2-diphenylethane selectively deuterated on one phenyl ring (DPE-d_5) by Me_3C^+ ions undergo a

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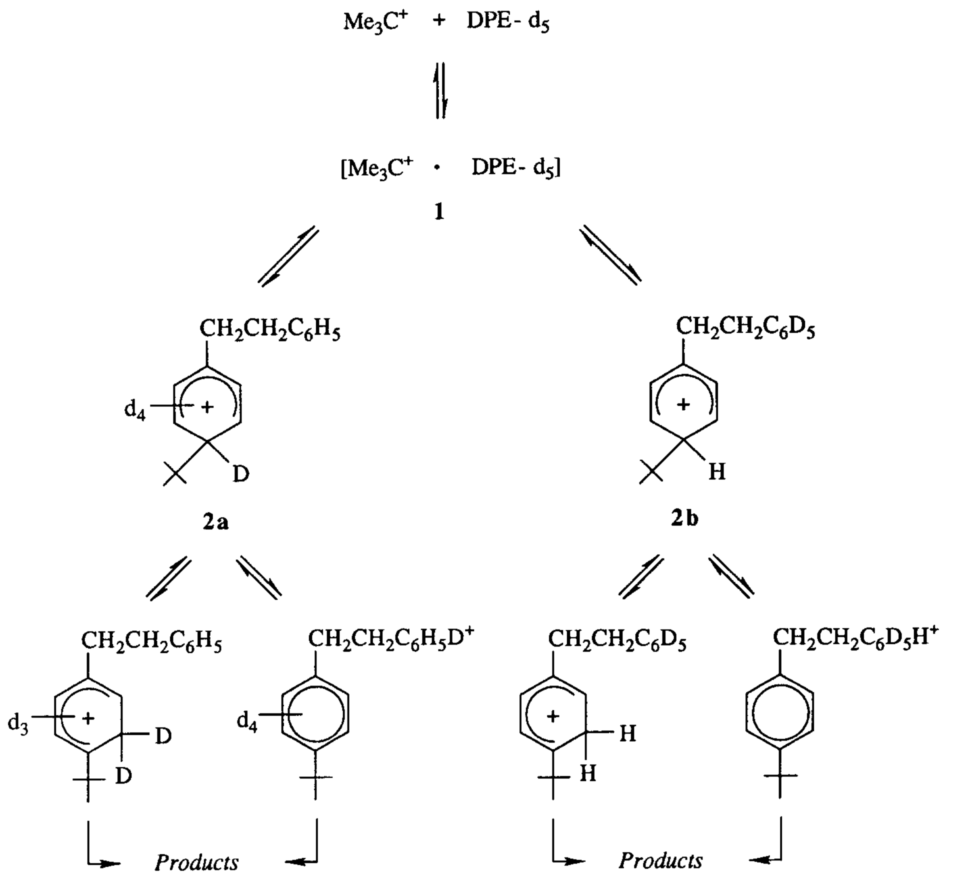
limited degree of interannular hydrogen migration whose temperature dependence affords an estimate of the activation parameters for the proton migration from the *tert*-buryl-substituted arenium ring to the spectator ring. The spectator ring then plays an active role, that is, it acts as a base, adding a novel feature within the pattern of the gas-phase aromatic substitution by Me_3C^+ ions [3]. The spectator ring behaves in much the same way as an arene solvent molecule (e.g. a toluene molecule) would behave in the neighbourhood of an arenium ion [4].

Such solvent-like behaviour of the spectator ring can be exerted also in less obvious ways. Gas-phase basicity (GB) measurements of selected DPAs have shown that the presence of the spectator ring affects the stability of the protonated molecule depending on the length of the methylene chain, which in turn affects the enthalpic and entropic parameters of the conformation of $DPAH^+$, allowing the best internal solvation [5]. Thus a higher GB value is found for 1,3-diphenylpropane (DPP) with respect to both its lower and higher homologues, which is explained by the fact that a parallel, sandwich-type arrangement between the protonated and neutral rings is allowed by an all-staggered conformation of the $(CH_2)_3$ chain, which cannot be attained by the $(CH_2)_2$ and $(CH_2)_4$ chains [5(a)]. In addition to the stabilizing relationship of the spectator ring with respect to the arenium ring, the presence of two aromatic rings in a DPA molecule affords an effective electrostatic stabilization to $[DPA \cdot R^+]$ non-covalent complexes, where the cation R^+ may benefit from the interaction with two π systems. Such species have been shown to play a kinetically determining role in the overall pattern of the Me_3C^+ reaction with DPAs of varying chain length [6]. Inter alia, this is inferred from the significant intramolecular selectivity displayed in the attack at the two aryl rings of 1-phenyl-2-(*m*-tolyl)ethane (PmTE), which contrasts with the equal relative reactivity between this substrate and DPE. In a similar way, the intramolecular kinetic isotope effect (KIE) observed in the *tert*-butylation of 1,2-diphenylethane selectively deuterated in one phenyl ring (DPE-d_5) has been ascribed to the reversible formation of arenium ions **2a** and **2b** (Scheme 1), which may revert to the electrostatically bound complex **1** before evolving to products by intraannular or interannular hydrogen shifts followed by a final deprotonation step.

To test the generality of this reaction pattern and check the range of conditions where the intermediacy of non-covalent complexes can be unambiguously proven, we have approached the same system from a different direction, namely by forming an arenium ion of type **2** by attack of a gaseous cation on a α,ω-diphenylalkane bearing a Me_3C group at a para ring position. It is expected that such ionic intermediates should display a certain tendency to revert to complexes **1**. Interannular Me_3C transfer and loss of *tert*-butyl following (tri-fluoro)methylation of $p\text{-}Me_3C{-}C_6H_4(CH_2)_n{-}C_6D_5$ (BDPE, $n = 2$; BDPP, $n = 3$) by Me_2F^+, Me_2Cl^+ and CF_3^+ ions provided a positive confirmation of a facile interconversion of ipso-protonated arenium ions and $[DPA \cdot Me_3C^+]$ non-covalent complexes as exemplified by the $\mathbf{1} \rightleftarrows \mathbf{2}$ process. Such a finding fits into the ever-growing body of evidence pointing to the relevant role played by ion–arene complexes both under radiolytic conditions [7] and in low pressure mass spectrometry [8]. Recently, the intermediacy of ion–neutral complexes of $[DPA \cdot Me_3C^+]$ type has clearly emerged from MIKES studies of the gas-phase protonolysis of *p*-(*tert*-butyl)-substituted DPAs, where the loss of isobutane involves, with equal probability, a hydride abstraction from both the adjacent and the remote benzylic methylene groups [9].



Scheme 1.

2. Experimental

2.1. Materials

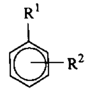
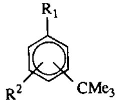
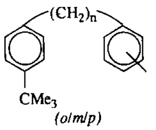
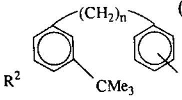
MeCl, CF_4, O_2, NO were research grade gases from UCAR with a stated purity exceeding 99.98 mol%. MeF, obtained from Fluorochem Ltd., was only 99.8 mol% pure, containing Me_2O as the major impurity.

BDPE and BDPP were prepared as previously described [9(b)]. Most other chemicals used, including p-$Me_3CC_6H_4Me$ (TBT) and cyclohexanone, were purchased from commercial sources and used without further purification.

2.2. Radiolytic reactions

The gaseous systems were prepared in sealed 250 ml Pyrex vessels using a greaseless vacuum line, according to standard procedures [7]. Owing to the low vapour tension of BDPE and BDPP, an equilibration time (at least 1 h at 120°C) was allowed for the complete vaporization of the substrate. The irradiations were performed in a 220 Gammacell (Nuclear Canada Ltd) at a total dose of 1×10^4 Gy, delivered at the rate of about 2×10^4 Gy h^{-1}. The radiolytic products were extracted by freezing the vessels at 77 K and then washing their inner walls by repeated freeze-thaw cycles with ethyl acetate as solvent. The products

Table 1
(Trifluoro)methylation of *tert*-butyl-substituted arenes, *p*-$Me_3CC_6H_4R^1$ (TBT, R^1 = Me; BDPE, $R^1 = (CH_2)C_6D_5$; BDPP, $R^1 = (CH_2)_3C_6D_5$

No.	System composition (Torr)		Reactant ion	Product distribution (%)				
	Substrate	Bulk gas[a]		 (o/m/p)	b 	b  (o/m/p)	b 	$[R^2C_6H_4R^1 - Y_2]$ (Y = H, D)
1	TBT (0.76)	MeF (640)[c]	Me_2F^+ (R^2 = Me)	30 (37/51/12)	70	—	—	—
2	BDPE (0.19)	MeF (660)[c]	Me_2F^+ (R^2 = Me)	10 (17/59/24)	55 (5%)	32 (10%) (18/34/487)	3 (>60%)	—
3	TBT (0.80)	MeCl (630)	Me_2Cl^+ (R^2 = Me)	38 (38/52/10)	62	—	—	—
4	BDPE (0.14)	MeCl (610)	Me_2Cl^+ (R^2 = Me)	13 (19/52/29)	63 (3%)	12 (23%) (23/40/37)	3 (>60%)	8[d]
5	BDPE (0.21)	MeCl (660)[e]	Me_2Cl^+ (R^2 = Me)	8 (16/80/4)	75 (0.3%)	14 (9%) (15/20/55)	2 (>75%)	1[d]
6	BDPE (0.18)	MeCl (680)[f]	Me_2Cl^+ (R^2 = Me)	8 (19/75/8)	74 (0.2%)	12 (8%) (20/34/46)	3 (>50%)	3[d]
7	BDPE (0.20)	MeCl (650)[g]	Me_2Cl^+ (R^2 = Me)	9 (16/73/11)	74 (2%)	12 (15%) (16/37/47)	3 (>75%)	2[d]
8	BDPE (0.19)	MeCl (650)[h]	Me_2Cl^+ (R^2 = Me)	7 (16/77/10)	70 (2%)	15 (10%) (19/42/39)	3 (>60%)	5[d]
9 5	BDPP (0.18)	MeCl (645)	Me_2Cl^+ (R^2 = Me)	15 (15/52/33)	71	9		
10	TBT (0.88)	CF_4 (680)	CF_3^+ ($R^2 = CF_3$)	90 (52/37/11)	10	—	—	—
11	BDPE (0.27)	CF_4 (680)	CF_3^+ ($R^2 = CF_3$)	65 (37/34/29)	16 (4%)	19 (<1%)		—
12 —	BDPP (0.28)	CF_4 (680)	CF_3^+ ($R^2 = CF_3$)	62 (43/34/22)	>29	<9		

[a] O_2 (10 Torr) was added in all experiments except those with CF_4 where NO (10 Torr) was used as CF_3 radical scavenger. Irradiation temperature, 120°C unless stated otherwise.

[b] In parentheses, fraction of products from BDPE bearing the Me_3C group on the deuterated ring. Data accessible only when $R^1 = (CH_2)_2C_6D_5$. The presence of D atoms on the aryl rings is not explicitly noted. Standard deviation of data ±10%.

[c] MeF contains about 1 Torr Me_2O.

[d] This product has ben identified as 2-Me-9,10-dihydrophenanthrene.

[e] Experiment run at 90°C.

[f] Cyclohexanone (0.50 Torr) was added.

Table 2
Energetics of representative processes

Reaction	ΔH° [a] (kcal mol^{-1})
(a) $Me_2F^+ + C_6H_6 \rightarrow MeF + p\text{-}MeC_6H_6^+$	−43
(b) $Me_2Cl^+ + C_6H_6 \rightarrow MeCl + p\text{-}MeC_6H_6^+$	−36
(c) $CF_3^+ + C_6H_6 \rightarrow m CF_3C_6H_6^+$	−59
(d) $Me_2F^+ + p\text{-}Me_3CC_6H_4Me \rightarrow p$-xylene $+ MeF + Me_3C^+$	−23
(e) $Me_2F^+ + p\text{-}Me_3CC_6H_4Me \rightarrow p$-xyleneH$^+$ $+ MeF + i\text{-}C_4H_8$	−23
(f) $Me_2F^+ + p\text{-}Me_3CC_6H_4Me \rightarrow p\text{-}Me_3CC_6H_4CH_2^+ + MeF + i\text{-}C_4H_{10}$	−29
(g) $Me_2Cl^+ + p\text{-}Me_3CC_6H_4Me \rightarrow p$-xylene $+ MeCl + Me_3C^+$	−16
(h) $Me_2Cl^+ + p\text{-}Me_3CC_6H_4Me \rightarrow p$-xyleneH$^+$ $+ MeCl + i\text{-}C_4H_8$	−16
(i) $Me_2Cl^+ + p\text{-}Me_3CC_6H_4Me \rightarrow p\text{-}Me_3CC_6H_4CH_2^+ + MeCl + i\text{-}C_4H_{10}$	−22
(j) $CF_3^+ + p\text{-}Me_3CC_6H_4Me \rightarrow p\text{-}CF_3C_6H_4Me + Me_3C^+$	−63

[a] Thermochemical data at 298 K for neutrals and ions are from Ref. [13], except for the following: $\Delta H_f^{\circ}(m\text{-}CF_3{-}C_6H_6^+) = 56$ kcal mol^{-1} was estimated from the MNDO-calculated PA of $PhCF_3$ [14]; $\Delta H_f^{\circ}(Me_3C^+) = 170$ kcal mol^{-1} was taken from Ref. [15]; $\Delta H_f^{\circ}(Me_2F^+) = 152$ kcal mol^{-1} and $\Delta H_f^{\circ}(Me_2Cl^+) = 184$ kcal mol^{-1} were derived from methyl cation affinities (MCA) of MeF and MeCl [16(a)], corrected by the approximately 4 kcal mol^{-1} difference of the recently revised value of MCA of N_2, the reference compound of the MCA scale [16(b)]. $\Delta H_f^{\circ}(p\text{-}Me_3CC_6H_4Me) = -13$ kcal mol^{-1} was estimated by group additivity rules.

were analysed by GC–MS using the following columns, mounted on a Hewlett–Packard 5890 gas chromatograph in series with a Model 5970B mass-selective detector: (i) a 50 m long, 0.20 mm i.d. fused silica capillary column, coated with a 0.50 μm cross-linked methylsilicone film (PONA column from Hewlett–Packard) operated at 100°C and then heated at the rate of 4 deg min^{-1} to 150°C and subsequently at 15 deg min^{-1} to 230°C; (ii) a 30 m long, 0.25 mm i.d. poly(ethylene glycol) (Supelcowax 10) bonded-phase column (0.25 μm film thickness) from Supelco Co, operated isothermally (2 min) at 120°C and then heated at the rate of 3 deg min^{-1} to 230°C. The identity of the products was checked by comparison of their retention times with those of authentic specimens and from their mass spectra.

3. Results and discussion

The cationic reagents Me_2F^+, Me_2Cl^+ and CF_3^+ have been formed by the γ radiolysis of gaseous mixtures at nearly atmospheric pressure, from ionization of MeF, MeCl and CF_4, respectively, further accompanied by fragmentation (to give CF_3^+) [10] or followed by a sequence of well-defined ion/molecule reactions (to give Me_2F^+ and Me_2Cl^+) [11]. Their reaction with BDPE and BDPP gives rise to a product pattern quantitatively summarized in Table 1, which includes product distribution data from TBT used as model substrate. Upon attack by gaseous cations, *tert*-butyltoluenes are known to undergo easy loss of *tert*-butyl, both under radiolytic and mass spectrometric conditions [8(c),12]. For example, the CH_4/CI mass spectra of *tert*-butyltoluenes are dominated by the loss of Me_3C^+, and the radiolytic reaction of CH_5^+/Et^+ and i-Pr^+ results in extensive formation of proto-de-*tert*-butylated and alkyl-de-*tert*-butylated products [12]. Such a reactivity pattern is confirmed by the present data, regarding ionic reagents which can, however, exclusively act as Lewis acids, being unable to behave as proton donors. The reaction of Me_2F^+, Me_2Cl^+, and CF_3^+ with TBT leads in fact to (trifluoro)methylated products accompanied by significant amounts of de-*tert*-butylated products. The relative fraction of the latter $MeC_6H_4R^2$ products (30–38%,

R^2 = Me; 90%, $R^2 = CF_3$) appears related to the reaction exothermicity. The highly exothermic CF_3^+ attack (e.g. see $\Delta H°$ of the exemplary reaction of CF_3^+ with benzene (c), compared to $\Delta H°$ of the methylation of benzene by Me_2F^+ and Me_2Cl^+, (a) and (b) in Table 2) proceeds most efficiently to de-*tert*-butylation products (overall processes described by routes (d)–(e), (g)–(h), (j)). The isomeric composition of de-*tert*-butylated products show an approximately 10% fraction of *p*-$MeC_6H_4R^2$, which is indicative of a minor but significant contribution of direct attack at the *tert*-butyl-substituted carbon. In fact, the known reluctance of Me and CF_3 groups to undergo migration between the sites of an arenium ion [4] makes unlikely the possibility of tracing the origin of *p*-$MeC_6H_4R^2$ from a complex multi-step pathway involving such an unfavourable migration.

The reaction of BDPE and BDPP differs from that of TBT in two respects: (i) the reactant ion may attack either the *tert*-butyl-substituted or the unsubstituted ring; (ii) the second ("spectator") aryl ring, which is not the primary site of electrophilic attack, can however more or less actively participate in the overall reaction sequence due to its π-electron density, which may display nucleophilic reactivity or provide internal solvation to the positively charged moiety. In general, one finds both de-*tert*-butylation products and products of (trifluoro)methyl for H/D substitution bearing the Me/CF_3 and Me_3C groups either on the same ring or on two different rings (Table 1). However, the product pattern from the (trifluoro)methylation of BPDE and BDPP is not only more complex than that of TBT, but the individual classes of products listed in Table 1 may include different contributions, some of them implying multiple reactive steps. To identify them, the presence of a labelled C_6D_5 ring in BDPE proved to be essential. In fact, $R^3C_6H_4(CH_2)_2C_6D_4R^4$ type products undergo a net cleavage of the C–C bond between benzylic carbons upon EI ionization [17]. Such a clean fragmentation process has previously allowed the detection of interannular hydrogen migration processes [2] and now yields valuable information on otherwise undetectable processes. Unfortunately, the same does not hold for $R^3C_6H_4(CH_2)_3C_6D_4R^4$ type products where the EI-induced fragmentation occurs with scrambling of ring and side-chain hydrogens, thereby obscuring the information on whether an alkyl group R^3 was bound to the deuterated or unlabelled ring in the original neutral molecule.

3.1. CX_3 ($X = H, F$) for Me_3C substitution

(Trifluoro)methyl-substituted DPEs arise from primary (trifluoro)methylation of both the *tert*-butyl-substituted ring of BDPE and from the unsubstituted, labelled one, with the relative contributions shown in Fig. 1 for three exemplary cases. Such relative contributions differ widely between the Me_2F^+/Me_2Cl^+ and the CF_3^+ reaction. The former two reactant ions give de-*tert*-butylation products originating mainly from attack at the *tert*-butyl-substituted ring at variance with CF_3^+, which displays an opposite behaviour. This difference may arise from a weighted balance between the individual steps of the overall complex reaction Scheme 2. The alkylation step is expected to favour the *tert*-butyl-substituted ring on account of its electronic activation. This expectation is fulfilled by the markedly greater fraction of CH_3 for H/D substitution at the *tert*-butyl-substituted ring shown by the reaction of both Me_2F^+ and Me_2Cl^+ ions with BDPE and BDPP. Such distributions are fairly representative of the regiochemistry of the methylation reaction, since the extent of *tert*-butyl loss and Me_3C transfer (see below) following Me_2F^+/ Me_2Cl^+ attack is relatively small. The

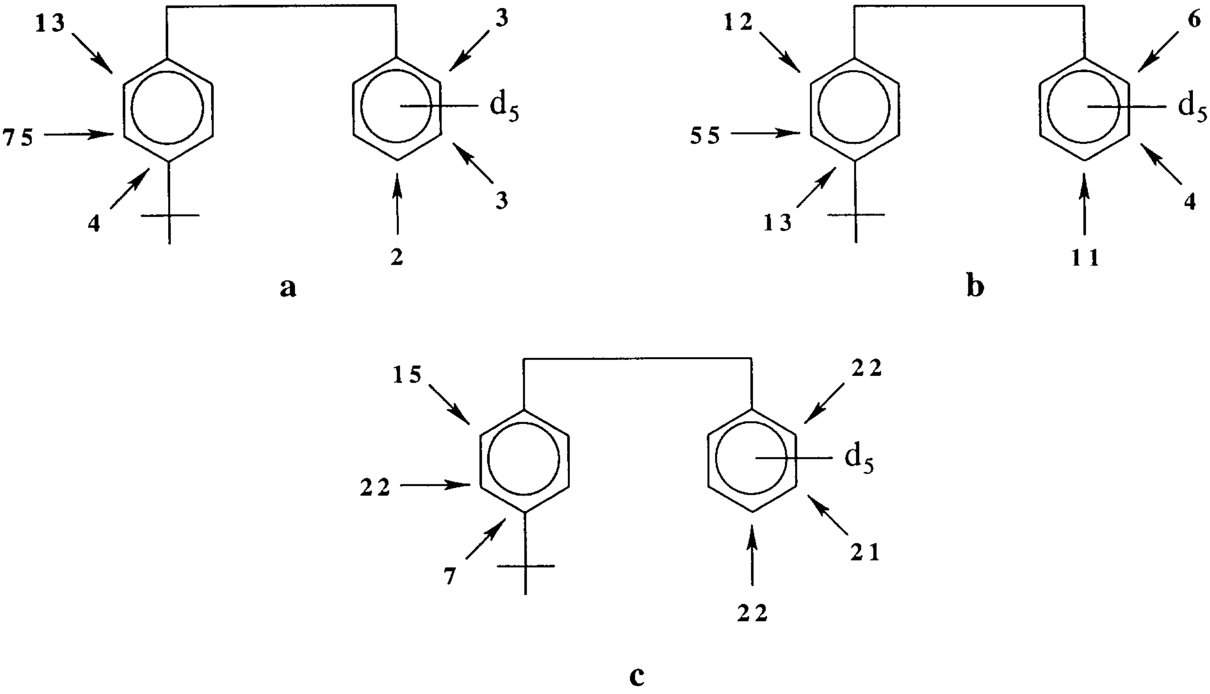
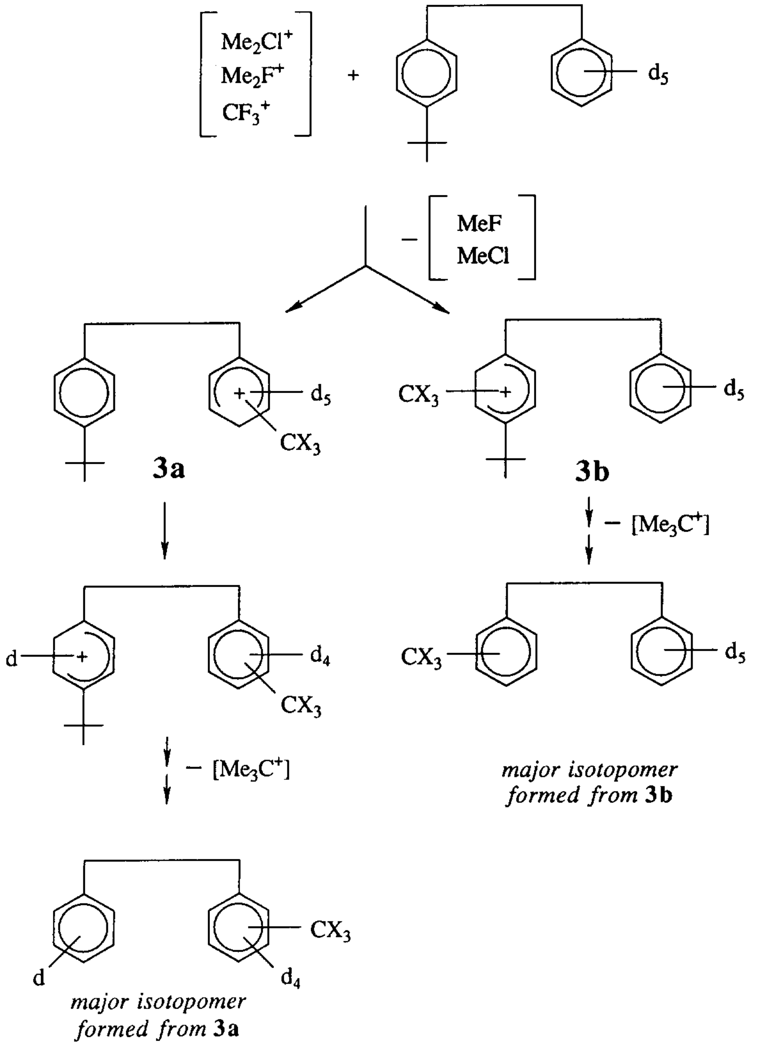


Fig. 1. Site of electrophilic (trifluoro)methylation initiating the de-*tert*-butylation process. Positional distribution of the CX_3 group in the de-*tert*-butylated products derived from experiments run at 120°C: (a) reactant Me_2Cl^+ ion formed in 610 Torr MeCl, to which 10 Torr O_2 and 0.33 Torr EtOH were added; (b) reactant Me_2F^+ ion formed in 660 Torr MeF, to which 10 Torr O_2 were added; (c) reactant CF_3^+ formed in 680 Torr CF_4 to which 10 Torr NO were added.

so-formed arenium ions should not be prone to undergo fast interannular hydrogen migration in view of the distinct basicity difference between the doubly alkylated and unsubstituted phenyl groups. For example, the gas phase basicity at 300 K of PmTE is about 5.3 kcal mol^{-1} higher than that of DPE, as the result of a single additional *m*-Me substituent on one phenyl group [5(a)]. Rather, they may evolve to de-*tert*-butylated products by faster [2] intraannular hydrogen shifts to the *tert*-butyl-substituted carbon, a process that may also be favoured on steric grounds if it relieves an unfavourable coplanar relationship of ortho Me and Me_3C groups. Attack at the unsubstituted ring is clearly more pronounced in the more exothermic reaction of CF_3^+ and implies necessarily an interannular hydrogen migration to evolve into de-*tert*-butylation products. Interannular hydrogen migration from the trifluoromethylated arenium ion is favoured by the decreased basicity of the trifluoromethyl-substituted ring and is obviously more productive in activating the loss of *tert*-butyl when the Me_3C group is placed on the aryl ring to which the migrating hydrogen is directed.

Thus, two factors contribute to the greater fraction (65%) of de-*tert*-butylation following CF_3^+ attack at the unsubstituted ring of BDPE: (i) greater ease of attack at the least activated ring; (ii) greater ease of interannular hydrogen migration to the *tert*-butyl-substituted ring. It is of interest to compare the extent of interannular H/D scrambling in the trifluoromethyl-substituted 1,2-diphenylethane formed from reaction of CF_3^+ with BDPE and DPE-d_5. The latter reaction is accompanied by extensive interannular H/D migration, giving rise to a pattern of



Scheme 2. The individual steps of the overall complex reaction. The formulae of the σ complexes are representative of other isomers as well.

$C_6Y_5CH_2^+$ (Y = H, D) fragment ions shown in the EI mass spectrum reported in Fig. 2(b). The same product shows instead almost negligible interannular H/D scrambling when it derives from CF_3^+-induced de-*tert*-butylation of BDPE (Fig. 2(a)).[1] This result can be explained by the fact that the presence of the Me_3C group, besides altering the relative basicities of the two rings, provides an easy exit channel for the primary arenium ions **3a** and **3b**, which prefer to evolve by loss of Me_3C rather than to engage in a multiple interannular hydrogen migration sequence. The same trend is observed in the methylation products of DPE-d_5 and BDPE by Me_2F^+ and Me_2Cl^+, though the dissimilarity of H/D scrambling is

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[1] Inspection of Fig. 2(a) shows how the data given in Fig. 1 were obtained. The MS peaks clustering around *m/z* 92 ($C_6H_4DCH_2^+$) and *m/z* 96 ($C_6D_5CH_2^+$) reflect the relative abundances of *m*-CF_3-$C_6D_4(CH_2)_2C_6H_4D$ and *m*-CF_3-$C_6H_4(CH_2)_2C_6D_5$ arising from CF_3^+ attack at the unsubstituted and Me_3C-substituted rings of BDPE, respectively.

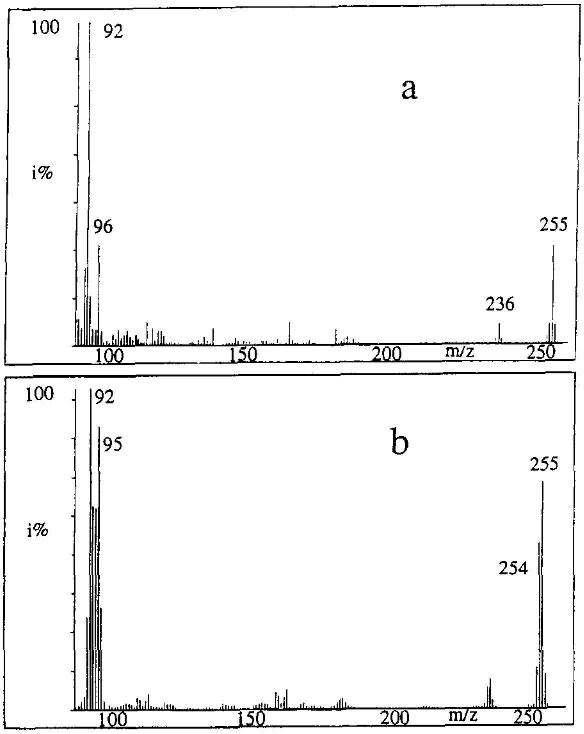

Fig. 2. 70 eV mass spectra of *m*-(trifluoromethyl)diphenylethane formed (a) from BDPE (0.3 Torr) and (b) from DP-d_5 (0.8 Torr) [18] in CF_4 at 690 Torr, 120°C.

less pronounced. In fact, interannular hydrogen migration is much less extensive in the methylation of DPE-d_5 than in its trifluoromethylation [18].

It can finally be noted that, in addition to products of CX_3 for Me_3C substitution (first column products in Table 1), the Me_2Cl^+ reaction yields also $[R^2C_6H_4R^1 - Y_2]$ type products (Y = H, D; last column in Table 1). Such products imply overall loss of a hydrogen molecule (Y_2) and are normally formed only in minute amounts. Interestingly, they represent the final neutrals formed by the major ionic reaction sequence following protonation of BDPE and BDPP under mass spectrometric conditions [9]. In fact, they conceivably arise from side-chain hydride abstraction by the Me_3C^+ ion departing from **3b**. The ensuing $[R^2C_6H_4R^1 - Y]^+$ ion may undergo rearrangement processes before final deprotonation[2].

3.2. CX_3 (X = H, F) for H/D substitution

The CX_3 substitution products of BDPE mainly differ in the ring of CX_3 attachment, which may (class A) or may not (class B) bear also the Me_3C group. Each class comprises several isomers, some of which are explicitly indicated in Table 1. The methylation products of BDPE show a varying degree of interannular H/D migration, a feature that characterized also the same radiolytic methylation of DPE-d_5 [18]. The extent of such interannular H/D migration is different in the two classes of products. In the products of class (A) it is a minor process, involving at most one H/D transfer in the direction of the doubly substituted phenyl group. The interannular migration is more pronounced in class (B) products, which is consistent with the closer basicity of the two alkyl-substituted rings. On the contrary, the Me and Me_3C substituents on the same ring in class (A) products enhance its basicity to the point that a proton displays no tendency to migrate to the unsubstituted phenyl ring. This result marks a difference with the extremely fast interannular proton transfer relative to the arene elimination process revealed by MIKES even with an estimated PA difference of 14 kcal mol^{-1} between the aromatic rings [19].

Such a finding confirms the superior information afforded by the radiolytic technique in the kinetic study of fast processes undergone by ionic species in *thermal* equilibrium with

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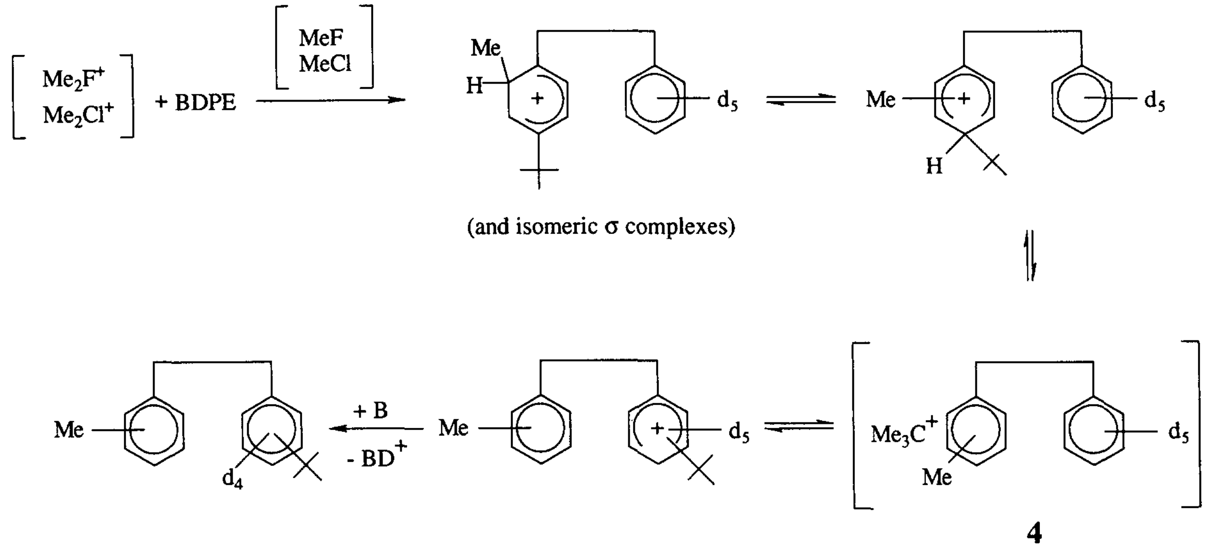
[2] The conditions favouring formation of $[DPA - H]^+$ ions and their subsequent evolution to products are the topics of research in progress. From the evidence available in the present study, we note that H^- abstraction by Me_3C^+ is inhibited by the presence of CF_3 as ring substituent (no $[R^2C_6H_4R^1 - Y_2]$ products are observed in CF_4) and by the addition of bases (they were purposely not added to MeF but the 0.2 mol% content of Me_2O is apparently enough to inhibit the process).



Scheme 3.

their environment. The ratio of the yields of class (A) and class (B) products cannot be quantitatively related to the primary partitioning of electrophilic attack at the *tert*-butyl-substituted vs. unsubstituted phenyl ring, as this may be followed by varying degrees of loss and migration of *tert*-butyl. Whereas the former may be directly assessed by the detection of ensuing neutral products, the latter can be unveiled only when CX_3-substituted products bearing the M_3C group on the deuterium-labelled, formerly unsubstituted, ring of BDPE and BDPP are identified. This analysis is made possible by the usually limited extent of interannular H/D migration only in the products of BDPE, which are well behaved in their EI mass spectrometric analysis. The fractions (%) of substitution products showing Me_3C migration to the labelled ring are given in brackets in Table 1. The generally small values found especially in class (A) methylation products look reasonable and are strongly indicative of the occurrence of a **1**$\rightleftarrows$**2** type equilibrium, involving Me_3C-substituted arenium ions in equilibrium with a [neutral $\cdot$ Me_3C^+] complex. Such percentage fractions, though providing an indicator, should, however, underestimate the role of such equilibrium. In fact, only a multiple step pathway can account for the observed Me_3C^+ migration. Scheme 3 illustrates an example of the most direct pathway leading to Me_3C-migration products of class (B). The reaction pattern of Scheme 3, and of a corresponding scheme that may be drawn for class (A) products is complicated by the reversibility of several steps and by competing reactions such as loss of *tert*-butyl or protons from the ionic intermediates, which depress the yield of detected products. In view of the complexity of the overall process, it is not unexpected that both a decrease of temperature (from 120 to 90°C) and the presence of a base (cyclohexanone, EtOH, Et_3N) reduce the extent of interannular Me_3C migration, the former by decreasing the rate of individual steps of the complex patterns and the latter by deprotonating the intermediate ionic species.

*3.3. The de-*tert*-butylation process*

A knowledge of the detailed origin of the de-*tert*-butylated products of BPDE allows a direct comparison to be drawn between the

TBT reference substrate and the *tert*-butyl-substituted ring of BDPE. The Me_2Cl^+ reaction yields a 73 : 8 ratio[3] of Me for H vs. Me for Me_3C substitution at the *tert*-butyl-substituted ring of BDPE. This ratio is paralleled by the results of the Me_2F^+ reaction yielding a 52 : 8 ratio[4] of Me for H vs. Me for Me_3C substitution at the *tert*-butyl-substituted ring of BDPE, to be compared with the 70 : 30 ratio for the TBT reaction. The trifluoromethylation reaction, though less easy to quantify, shows the same general feature: in all cases investigated, the Me_3C loss occurs to a distinctly greater extent from TBT rather than from the *tert*-butyl-substituted ring of BDPE. Such behaviour is to be ascribed to the role played by the spectator phenyl ring of BDPE. As to the detailed mechanism by which such an effect is exerted, some chemically feasible possibilities may be suggested. It may first be argued that the Me_3C loss is activated by the exothermicity of the CX_3^+ addition. Thermodynamic data regarding the CF_3^+ addition to BDPE are not available but relative trends are expected to parallel the prototype reactions with benzene (entries (a), (b), (c) in Table 2). The higher exothermicity of the CF_3^+ reaction results in more extensive Me_3C loss. However, the approximately 7 kcal mol^{-1} difference between the exothermicity of the Me_2F^+ and Me_2Cl^+ reactions [16] does not correspond to a significant difference in the ratios of Me for H vs. Me for Me_3C substitution at the *tert*-butyl-substituted ring of BDPE (52 : 8 and 73 : 8 respectively). This fact suggests that Me_3C loss occurs at a stage where the ionic intermediate is not reminiscent of the energy released in the primary alkylation step, which means that it has probably reached thermal equilibrium with the environment. A further point hinting at energetically equilibrated species comes from the finding that the addition of bases with proton affinities ranging from 188.3 kcal mol^{-1} (EtOH) to 201 kcal mol^{-1} (cyclohexanone) and 232.3 kcal mol^{-1} (Et_3N) [13] lowers the fraction of *tert*-butyl loss products formed in MeCl. This effect can be ascribed to the deprotonation of intermediate arenium ions such as **3a** and **3b** caused by bases, which competes with loss of *tert*-butyl, which is thus bound to occur in the time frame of the reactive collision of **3a** and **3b** with bases at 0.3–0.5 Torr, estimated to be about 10^{-8} s [20], a time lapse allowing several tens of unreactive collisions with the bulk gas to occur, which effectively remove any excess energy contained initially in the intermediate ions. The loss of *tert*-butyl may thus be envisioned as a thermal dissociation process, showing the expected decrease at lower temperatures (e.g. the overall *tert*-butyl loss products from Me_2Cl^+ drop from 21% at 120°C to 9% at 90°C under comparable conditions). In this framework, the higher tendency of Me_3C loss of CF_3^+ adducts is explained by the electron-withdrawing effect of CF_3, which makes both the PA and the binding energy of Me_3C^+ to CF_3-substituted arenes lower, thus facilitating the cleavage process.

Interestingly, the relative yields of de-*tert*-butylated products from BDPE and BDPP are closely similar, both markedly lower than those from TBT. This finding is paralleled by features of the reverse reaction, namely the alkylation of toluene, DPE, DPP, and PmTe by Me_3C^+ ions. Whereas the addition of Me_3C^+ to toluene is a highly reversible process, the association of Me_3C^+ to DPE, DPP, and PmTE is practically irreversible in the

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[3] The 73 : 8 ratio of Me for H vs. Me for Me_3C substitution at the *tert*-butyl-substituted ring of BDPE has been obtained from the gross 74 : 9 ratio of entry no. 7 (Table 1), where the 74 value has been corrected for the 2% contribution of Me attack at the labelled, unsubstituted ring followed by Me_3C migration and the 9 value has been corrected for the 8% contribution (Fig. 1a(a) of de-*tert*-butylation products again arising from methylation at the labelled, unsubstituted ring.

[4] The 52 : 8 ratio was obtained from the gross 55 : 10 ratio of entry no. 2 in Table 1 by the same procedure described in footnote 3 (corrections of 5% and 21%, respectively).

presence of about 0.4 Torr Et_3N, which ensures formation of neutral *tert*-butyl-substituted products by fast deprotonation of ionic intermediates [6].

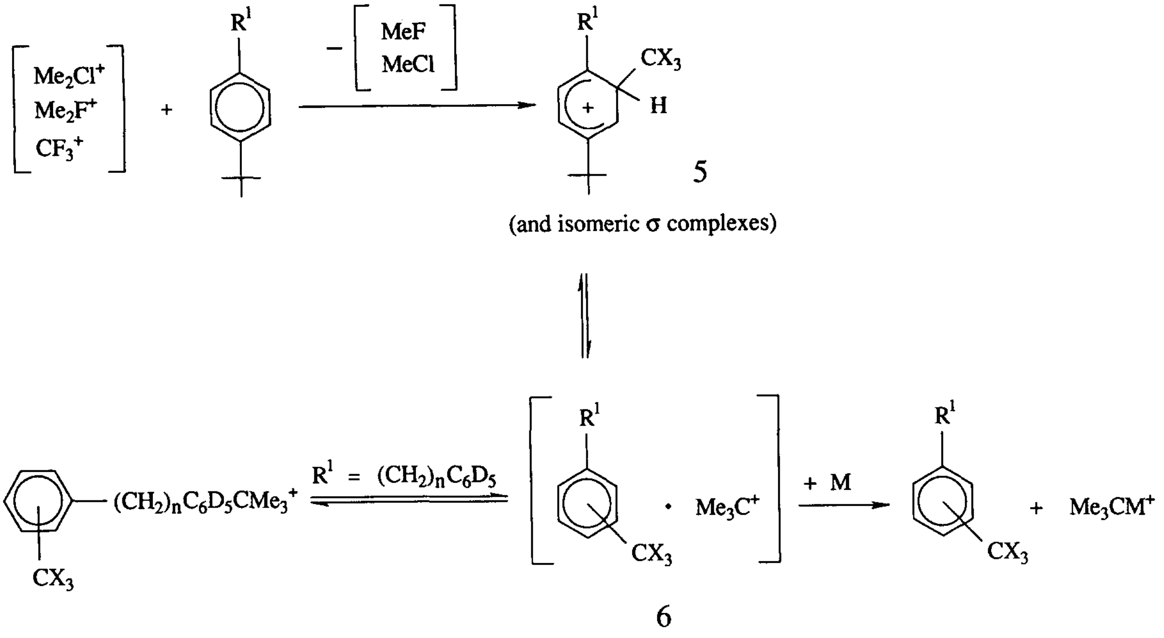
A final question to be addressed concerns the mode of Me_3C departure. The representative reactions in Table 2 show three possible pathways: (i) direct cleavage of Me_3C^+; (ii) cleavage of Me_3C^+ accompanied by proton transfer to the arene; (iii) cleavage of Me_3C^+ accompanied by H^- abstraction from a benzylic C–H bond. The energetically favoured route (iii) is the dominant pathway observed in the metastable decomposition of protonated Me_3C-substituted alkylbenzenes [8(c)] and diphenylalkanes [9]. This pathway is of minor significance in the present radiolytic experiments, leading to the dehydrogenation products observed only in the Me_2Cl^+ reaction. Routes (i) and (ii) are energetically equivalent in the TBT reaction, but their balance shifts in favour of the (ii) pathway in the case of the Me_2Cl^+/Me_2F^+ reaction with BDPE and BDPP in view of the markedly higher basicity of methyl-substituted α,ω-diphenylalkanes with respect to i-C_4H_8 [5(a)]. The Me_3C group should then be lost as neutral i-C_4H_8. This conclusion contrasts with the experimental finding of cationic *tert*-butyl substitution products (i.e. products of aromatic Me_3C-substitution of the same substrates TBT, BDPE and BDPP) in yields comparable to those of de-*tert*-butylated products, which cannot arise from i-C_4H_8. Therefore it is inferred that none of pathways (i), (ii) or (iii) is followed by the Me_2Cl^+/Me_2F^+ reaction with BDPE and BDPP. To account for the limited de-*tert*-butylation process occurring in these reactions, a more likely route involves a bimolecular Me_3C^+ transfer from an intermediate non-covalent complex, such as **4**, to a neutral molecule. The neutral molecule assisting the departure of Me_3C^+ may belong to the bulk gas, for example 75% of the Me_3C^+ ion population is associated to MeCl at 1 atm and 120°C [21], or the substrate itself (BDPE or BDPP). Though the relative concentrations of the bulk gas and the diarylalkanes differ by a factor of 10^3, the latter are endowed with a good capability for solvating positive ions [6].

The same reasoning may be applied to the CF_3^+ reaction. CF_4 shows a smaller tendency to bind Me_3C^+ than MeCl [21], but the Me_3C^+ ion being transferred now departs from a diarylaklane whose electron-donating ability and response to solvation demand is lessened by the presence of a CF_3 substituent.

4. Conclusions

The (trifluoro)methylation of *tert*-butyl-substituted arenes has confirmed the role of [arene • Me_3C^+] complexes, previously anticipated in the Me_3C^+ reaction with α,ω-diphenylalkanes. As expected, the Me_3C group displays a certain tendency to undergo heterolytic cleavage from arenium ions. In the most direct unifying network of the present data, one can view this cleavage as occurring by way of an electrostatically bound complex **6**, as shown by the highly simplified pattern of Scheme 4. When the reaction involves a diarylalkane substrate, such as BDPE and BDPP, the σ complex **5** may equilibrate with the electrostatic complex **6**, both stabilized by the spectator ring. The spectator ring itself may actively participate in the reaction, by undergoing not only interannular hydrogen migration but also interannular Me_3C^+ migration. The ion–neutral complex **6** may undergo a bimolecularly assisted departure of Me_3C^+. However, when the presence of a spectator ring provides additional electrostatic stabilization, the Me_3C^+ departure is largely inhibited, as deduced from the comparative behaviour of TBT vs. BDPE and BDPP.

An alternative pattern avoiding the intermediacy of the ion–molecule complex **6**



Scheme 4.

($R^1 = (CH_2)_nC_6H_5$) and ascribing the intramolecular and intermolecular motion of Me_3C to a direct reaction of the σ intermediate **5** does not appear likely. In fact, molecular models show that an interannular Me_3C^+ transfer within **5** via a concerted process involving a pentacoordinated transition state with simultaneous binding of Me_3C^+ to the two rings is impeded by severe geometry constraints [9(b)]. On the other hand, a reaction pathway via **6** is conceivable and in accordance with the mass spectrometric behaviour of *tert*-butyl-substituted α,ω-diphenylalkanes [9]. The intermediacy of an ion–molecule complex **6** is also supported by the proton-induced isomerization of *o*-$Me_3CC_6H_4Me$, leading to the para isomer as the major kinetic product under radiolytic conditions [12(a)].

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