Formation and characterization of the radical cation of pentamethylbenzyl trifluoroacetate from the oxidation of hexamethyl (Dewar benzene) by thallium(III) trifluoroacetate in trifluoroacetic acid—a slow and complex reaction

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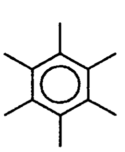
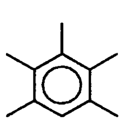
The reaction between hexamethyl (Dewar benzene) (HMD) and Tl^{III} trifluoroacetate (Tl^{III}) in trifluoroacetic acid has been investigated in detail. The first step involves a slow acid-catalysed conversion of HMD into hexamethylbenzene (HMB) which is then oxidized by Tl^{III} to pentamethylbenzyl trifluoroacetate in a process which overall is about 15 times faster than the HMD $\longrightarrow$ HMB reaction. In the formal one-electron transfer reaction between HMB and Tl^{III}, the corresponding radical cation, $HMB^{\bullet +}$, appears in significant concentration and with a lifetime which makes it easy to monitor by EPR spectroscopy. It is shown that the true lifetime of $HMB^{\bullet +}$ in trifluoroacetic acid is shorter by a factor of ≈ 0.03 (22 °C) or ≈ 0.005 (−11 °C) than the 'decay' lifetime recorded during an experiment in which it is generated by the reaction between HMB and Tl^{III} under otherwise identical conditions. Thus the 'decay' rate constant of $HMB^{\bullet +}$ is actually a reflection of its slow rate of formation from HMB–Tl^{III}. The fact that the formal one-electron transfer reaction between HMB and Tl^{III} exhibits a significant kinetic isotope effect of both substrate and solvent type, indicates that this apparently simple step must be complex.

Pentamethylbenzyl trifluoroacetate, as well as the corresponding acetate, alcohol, methyl ether or chloride, exhibits a characteristic 13 × 8 line EPR spectrum when irradiated in trifluoroacetic acid with Tl^{III} trifluoroacetate at −11 °C. The similarity of this spectrum to the previously described, less well-resolved 13-line EPR spectrum from the oxidation of HMD in matrices at low temperatures or on a solid substrate, is profound. The fact that HMD on oxidation by Tl^{III} in trifluoroacetic acid gives the 13 × 8 line spectrum of pentamethylbenzyl trifluoroacetate, indicates that the transformation of HMD into a suitable pentamethylbenzyl derivative might be the origin of the 13-line EPR spectrum recorded by the matrix technique.

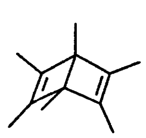
Hexamethylbenzene (**1**-CH_3) is obtained as the final product from the treatment of hexamethyl (Dewar benzene) (hexamethylbicyclo[2.2.0]hexa-2,5-diene, **2**) with an acid[1] or a strong electron acceptor. The acid-catalysed reaction proceeds by a carbocation mechanism *via* initial protonation,[2] whereas the latter is initiated by the formation of $\mathbf{2}^{\bullet +}$, followed by a radical chain mechanism involving **1**-$CH_3^{\bullet +}$ as the propagating species.[3]



1-CH_3



1-H



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Several attempts have been made to characterize the hexamethyl (Dewar benzene) radical cation, $\mathbf{2}^{\bullet +}$, by low-temperature EPR spectroscopy. A 13-line spectrum with a hyperfine splitting constant of ≈ 0.98 mT was assigned[4] to the $^2B_2$ state of $\mathbf{2}^{\bullet +}$, but as pointed out later,[5] other interpretations are possible. The spectrum is, for example, very similar to that of $[\text{pentamethylbenzene}]^{\bullet +}$ (**1**-$H^{\bullet +}$), the parent of which would, in principle, be available through demethylation of hexamethylbenzene under the prevailing reaction conditions. Recently,[6] the 13-line spectrum was also obtained by vapour deposition of **2** onto solid dioxygenyl hexafluoroantimonate and shown to be observable even at room temperature; a virtually identical spectrum was obtained by similar treatment of pentamethylbenzene.

Hexamethylbenzene is a good electron donor which can be oxidized to its radical cation, **1**-$CH_3^{\bullet +}$, by a variety of methods. The eventual fate of **1**-$CH_3^{\bullet +}$ is to form a side-chain substitution product by a mechanism involving proton abstraction by a base B:, further one-electron oxidation of **1**-$CH_2^{\bullet}$ to the carbocation and reaction of the latter with a nucleophile Nu^- [eqns. (1)–(3)] to give **1**-CH_2Nu.

$$\mathbf{1}\text{-}CH_3^{\bullet +} + B{:} \longrightarrow \mathbf{1}\text{-}CH_2^{\bullet} + BH^+ \quad (1)$$

$$\mathbf{1}\text{-}CH_2^{\bullet} \xrightarrow{-e^-} \mathbf{1}\text{-}CH_2^{+} \quad (2)$$

$$\mathbf{1}\text{-}CH_2^{+} + Nu^- \longrightarrow \mathbf{1}\text{-}CH_2Nu \quad (3)$$

There is conflicting evidence regarding the reactivity of **1**-$CH_3^{\bullet +}$, *e.g.*, as documented by the following conclusions and/or observations regarding **1**-$CH_3^{\bullet +}$: (*i*) it is 'very short lived' at room temperature in trifluoroacetic acid,[7] when generated by anodic oxidation of **1**-CH_3, (*ii*) it is persistent enough to be detected by EPR spectroscopy in *acetic* acid at room temperature,[8] when generated by chlorine oxidation of **1**-CH_3, (*iii*) it has a half-life of ≈ 10 min in trifluoroacetic acid–lithium trifluoroacetate (0.125 mol dm^{-3}) at −10 °C,[9a] when generated by thallium(III) trifluoroacetate oxidation of **1**-CH_3, and (*iv*) it has a half-life of ≈ 1.5 s in trifluoroacetic acid at 25 °C,[10] when generated by photolysis of the **1**-CH_3-mercury(II) trifluoroacetate charge-transfer complex.

Clearly, these facts are contradictory. We became acutely aware of the problem when we noted that **1**-$CH_3^{\bullet +}$, generated

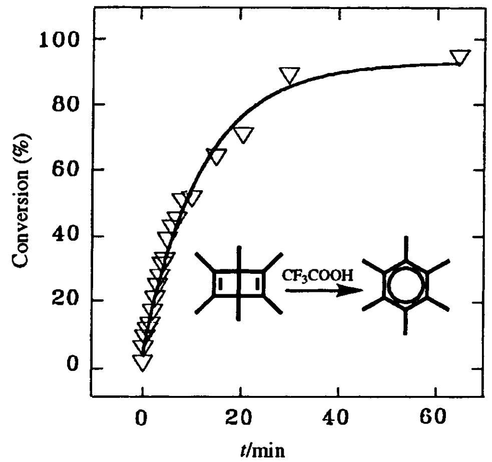


Fig. 1 Conversion of **2** into **1**-CH_3 in trifluoroacetic acid at +22 °C ($[\mathbf{2}]_0$ = 24 mmol dm^{-3}). The curve corresponds to a first-order rate constant for formation of **1**-CH_3 of 0.083(6) min^{-1}.

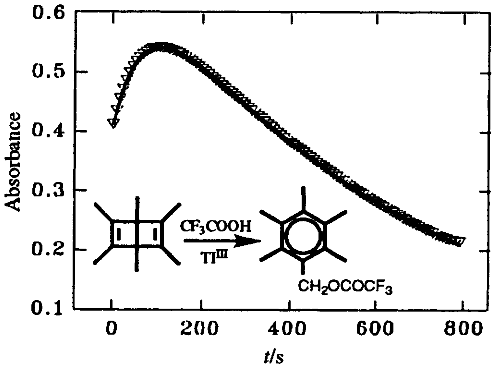


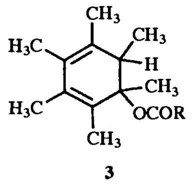
Fig. 2 Formation and decay of **1**-CH_3 from **2** ($[\mathbf{2}]_0$ = 20 mmol dm^{-3}) in trifluoroacetic acid in the presence of Tl^{III} trifluoroacetate ($[Tl^{III}]_0$ = 5.0 mmol dm^{-3}), as monitored by UV spectroscopy at the 360 nm maximum of the **1**-CH_3–Tl^{III} CT complex in a 2 mm cell. The curve corresponds to a double exponential with k_{up} = 0.88(1) min^{-1} and k_{down} = 0.089(1) min^{-1}.

by phenyliodine(III) bis(trifluoroacetate) oxidation of **1**-CH_3 in trifluoroacetic acid at −11 °C, could not be detected by EPR spectroscopy unless the mixing of the reagents was in the pre-cooled sample tube inserted into the cavity; the half-life of **1**-$CH_3^{\cdot +}$ was ≈7 s under these conditions.[11] At the other extreme, Tl^{III} oxidation of hexamethyl (Dewar benzene) in trifluoroacetic acid at −11 °C produced an EPR signal of **1**-$CH_3^{\cdot +}$ with a half-life of several hours. In the course of this study, it was found that side-chain substitution products of **1**-CH_3, such as pentamethylbenzyl acetate or alcohol (**1**-CH_2–OAc or **1**-CH_2–OH), upon photolysis in trifluoroacetic acid at −11 °C in the presence of Tl^{III} gave resolved 13 × 8-line spectra which in their less well resolved versions were virtually identical with the 13-line spectrum obtained from hexamethyl (Dewar benzene) **2**. In view of the ready availability of **1**-CH_3 from **2** under oxidizing and/or acidic conditions, and consequently of *O*-side-chain substituted derivatives of **1**-CH_3, we suggested[12] that radical cation structures of the type (**1**-CH_2–O–X)$^{\cdot +}$ should be considered as the origin of the 13-line spectrum. In what follows, we give a full account of this work.

Results

Conversion of hexamethyl (Dewar benzene) into hexamethylbenzene in trifluoroacetic acid

It is known[1] that carboxylic acids react with **2** with formation of 5-acyloxy-1,2,3,4,5,6-hexamethylcyclohexa-1,3-dienes **3**, which



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on treatment with strong acid eventually produce **1**-CH_3. Dissolution of **2** in trifluoroacetic acid led to its complete disappearance within < 20 s, but the rate of appearance of **1**-CH_3 was slow by comparison, with a rate constant of 0.083(6) min^{-1} at 22 °C (Fig. 1, yields of **1**-CH_3 evaluated by GLC). Evidently, a reservoir of 5-trifluoroacetoxy-1,2,3,4,5,6-hexamethylcyclo-1,3-diene (**3**, R = CF_3) is formed immediately upon dissolution of **2** in trifluoroacetic acid,[1] and the ester then slowly eliminates CF_3COOH to give **1**-CH_3.

In the presence of Tl^{III} trifluoroacetate, a strong electron acceptor, the possibility of electron transfer catalysis of eqn. (1) *via* a radical chain mechanism can be envisaged,[3] thus further increasing the overall rate of the conversion of **2** into **1**-CH_3. Since the rate of addition of trifluoroacetic acid is high enough for the initial step of this reaction (*i.e.*, $\mathbf{2} \longrightarrow \mathbf{3}$, R = CF_3) to occur during mixing of the reagents we did not expect to detect any effect of electron transfer catalysis. Nevertheless, in order to verify the generation and disappearance of **1**-CH_3 from a trifluoroacetic acid solution containing both **2** and Tl^{III} trifluoroacetate we monitored such a solution by UV spectroscopy. It is known[9a] that **1**-CH_3 gives a relatively strong charge transfer (CT) complex with $Tl^{III}(OCOCF_3)_2^{\ +}$, the kinetically active species formed in trifluoroacetic acid by dissociation of Tl^{III} trifluoroacetate, and that the first-order kinetics of the appearance/disappearance of the CT complex can be monitored UV spectroscopically at wavelengths around 360 nm, the absorption maximum of the charge transfer complex. Fig. 2 shows an absorbance–time trace at 360 nm of the reaction between **2** ($[\mathbf{2}]_0$ = 20 mmol dm^{-3}) and Tl^{III} trifluoroacetate (5 mmol dm^{-3}) in trifluoroacetic acid at +22 °C. With the assumption that the two consecutive reactions can be treated as being pseudo-monomolecular or monomolecular, the well reproducible rate constants for formation of **1**-CH_3, k_{up}, was evaluated to be 0.85(5) min^{-1} and for its disappearance, k_{down}, 0.089(5) min^{-1}. The value of $[\mathbf{1}\text{-}CH_3 \cdots Tl^{III}]_{max}$ was reached after 120 s and was *ca.* 0.25 mmol dm^{-3}, as estimated from ε_{330} of the CT complex = 4794 [ref. 9(*a*)] and the measured $\varepsilon_{360}/\varepsilon_{330}$ ratio = 2.25, giving ε_{360} = 10 800 $dm^3\ mol^{-1}\ cm^{-1}$.

Conversion of hexamethylbenzene into pentamethylbenzyl trifluoroacetate

It is well established that the oxidation of **1**-CH_3 by Tl^{III} trifluoroacetate[9a] or Hg^{II} trifluoroacetate–photolysis[10] in trifluoroacetic acid gives a good yield of pentamethylbenzyl trifluoroacetate; the same is true for the anodic oxidation of **1**-CH_3 in this solvent.[7,13] The reaction follows the mechanism indicated in eqns. (1)–(3), although mechanisms which are second order in the radical cation concentration must be additionally postulated in the anodic case.[14]

The rate constant of the **1**-CH_3–Tl^{III} reaction in trifluoroacetic acid was obtained by monitoring $[\mathbf{1}\text{-}CH_3 \cdots Tl^{III}]$ at 360 nm (see above). With $[Tl^{III}]_0$ in the range 0.26–1.04 mmol dm^{-3} and $[\mathbf{1}\text{-}CH_3]_0$ = 1.40 mmol dm^{-3}, the first-order rate constant was 0.65(2) min^{-1}. With fully deuteriated hexamethylbenzene but under otherwise identical conditions, the rate constant was 0.27(1) min^{-1}. In the $[\mathbf{1}\text{-}CH_3]_0$ range 1.4–5.6 mmol dm^{-3} an apparent second-order rate constant of 8(2) $dm^3\ mol^{-1}$

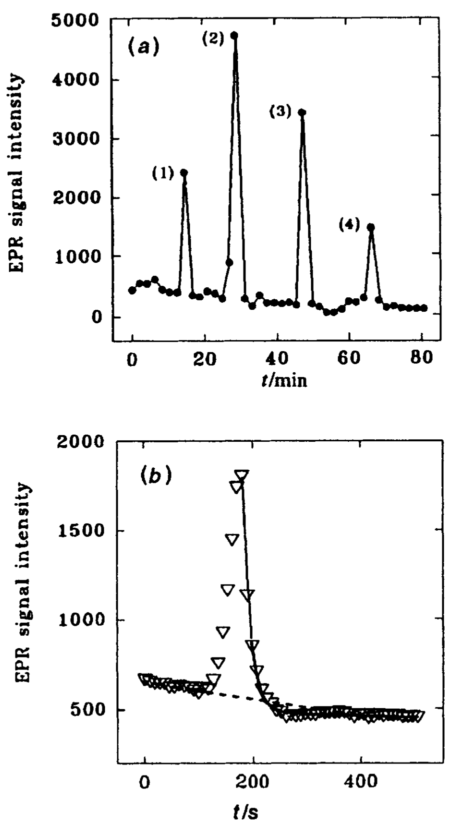


Fig. 3 (*a*) EPR signal intensity from a solution containing **2** (5.0 mmol dm^{-3}) and Tl^{III} trifluoroacetate (2.0 mmol dm^{-3}) in trifluoroacetic acid at − 11 °C (mixing performed at − 10 °C). Irradiation was performed with UV light at: (1), 30 s; (2), 60 s; (3) 150 s and with light of λ > 430 nm at: (4), 60 s. (*b*) EPR signal intensity from a solution containing ($^2H_{18}$)**1**-CH$_3$ (5.0 mmol dm^{-3}) and Tl^{III} trifluoroacetate (2.0 mmol dm^{-3}) in trifluoroacetic acid at − 11 °C (mixing performed at − 10 °C). Irradiation was performed with UV light. The dashed curve corresponds to an exponential with k = 0.024 min^{-1} and the solid line to an exponential of k = 4.2 min^{-1}.

s^{-1} was determined. At a higher [**1**-CH$_3$]$_0$/[Tl^{III}]$_0$ ratios, mixed zero- and first-order behaviour[15] made the kinetic analysis less reliable. At higher initial concentrations, [**1**-CH$_3$]$_0$ = 5.0 mmol dm^{-3} and [Tl^{III}]$_0$ = 10.0 mmol dm^{-3}, the rate constant was 1.2(1) min^{-1}; completely deuteriated hexamethylbenzene gave k = 0.30(1) min^{-1} under these conditions. In (^{2}H)trifluoroacetic acid, the corresponding rate constants were 0.43(1) and 0.175(4) min^{-1}, respectively.

Formation and disappearance of the hexamethylbenzene radical cation

In the reaction between Tl^{III} trifluoroacetate and **1**-CH$_3$, a significant concentration of **1**-CH$_3^{\cdot +}$ developed. As shown previously,[9a] the rate of disappearance of its EPR signal could be monitored, using initial concentrations of **1**-CH$_3$ at a fairly high level (25 mmol dm^{-3}). However, it should be noted from the beginning that the rate of decay of the EPR signal is not necessarily related to the true life-time of **1**-CH$_3^{\cdot +}$, as will be elaborated below. We found that the rate constant for the decay of the EPR signal of **1**-CH$_3^{\cdot +}$ could be conveniently determined with [**1**-CH$_3$] = 5 mmol dm^{-3} and [Tl^{III}] = 10 mmol dm^{-3} at 22 °C, and then was 1.1(1) min^{-1}. When instead **2** was used as a source of **1**-CH$_3$ in a similar experiment, both the appearance and decay of the signal of **1**-CH$_3^{\cdot +}$ could be monitored, the first-order rate constants k_{up} and k_{down} being 0.4(1) and 0.17(3) min^{-1}, respectively, and [**1**-CH$_3^{\cdot +}$]$_{max}$ being reached within 5–6 min. The latter rate constant thus is almost five times smaller than for the decay of the **1**-CH$_3^{\cdot +}$ EPR signal as generated by Tl^{III} oxidation of **1**-CH$_3$.

This finding led to a study of the kinetics of **1**-CH$_3^{\cdot +}$ disappearance when **1**-CH$_3^{\cdot +}$ had been generated by other methods. Such a study had to be performed at a lower temperature, − 11 °C, since the true rate of decay of **1**-CH$_3^{\cdot +}$ in trifluoroacetic acid was too high to be monitored at ambient temperature. The thermal Tl^{III}–**2** reaction was very slow at − 11 °C, yielding a very low background concentration of **1**-CH$_3^{\cdot +}$. This permitted a study of the effect of light upon the reaction. The result of this experiment is shown in Fig. 3(*a*), where the solution was irradiated by UV light at (1) for 30 s, at (2) for 60 s, and (3) for 150 s. The peak at (4) was obtained by irradiation with filtered light of λ > 430 nm. After discontinuation of each illumination period, [**1**-CH$_3^{\cdot +}$] went down to background level in *ca.* 30 s. Thus the Tl^{III}–**1**-CH$_3$ reaction can be photochemically activated to give a significant photostationary concentration of **1**-CH$_3^{\cdot +}$. When the light source was shut off, the decay of the radical cation could be monitored EPR-spectroscopically and the rate constant determined. At − 11 °C, it was 7(1) min^{-1} and at − 16 °C 5(1) min^{-1}.

When fully deuteriated hexamethylbenzene was oxidized by Tl^{III} in TFA at − 11 °C, its radical cation was formed in significant concentration and decayed slowly, the rate constant being 0.024(1) min^{-1} when measured separately. Photoactivation gave a much higher radical cation concentration [Fig. 3(*b*)], the decay of which was monitored in the same way as described above. Evaluation of this rate constant by fitting the data to a double-exponential expression gave k = 4.2(8) min^{-1} for the fast process [see Fig. 3(*b*)].

Thus the intrinsic reactivity of **1**-CH$_3^{\cdot +}$ in trifluoroacetic acid is much higher than is indicated by reactions in which Tl^{III} trifluoroacetate is used to oxidize **1**-CH$_3$. The explanation for this discrepancy is simple: the measured rate of disappearance of **1**-CH$_3^{\cdot +}$ actually reflects its *slow rate of formation* from **1**-CH$_3$ and Tl^{III}, *i.e.*, shows the effect of a sequence involving a slow initial step, followed by the fast decay of an intermediate (see the Discussion). Thus the 'decay' rate constant of **1**-CH$_3^{\cdot +}$ found above, 1.2 min^{-1}, actually reflects the rate constant for reaction between **1**-CH$_3$ and Tl^{III}, 1.1 min^{-1}.

At − 11 °C, the reaction between **1**-CH$_3$ and Tl^{III} in trifluoroacetic acid at initial concentrations of 5.0 and 10.0 mmol dm^{-3}, respectively, gave a monitorable concentration of **1**-CH$_3^{\cdot +}$ with a 'decay' rate constant of 0.031(1) min^{-1}. An identical experiment with ($^2H_{18}$)hexamethylbenzene gave k_{decay} = 0.014(1) min^{-1}. Starting instead with **2** as the substrate ($\approx$ 15 mmol dm^{-3}) and [Tl^{III}] $\approx$ 5 mmol dm^{-1}, the 'decay' rate constant of **1**-CH$_3^{\cdot +}$ was 0.012(3) min^{-1}.

EPR spectrum on irradiation of an aged solution of 2-Tl^{III} trifluoroacetate in trifluoroacetic acid

A solution of **2** (10 mmol dm^{-3}) and Tl^{III} trifluoroacetate (50 mmol dm^{-3}) in trifluoroacetic acid was kept at room temperature for *ca.* 1.5 h in order to allow the initial strong EPR signal of **1**-CH$_3^{\cdot +}$ to disappear. The solution then contained pentamethylbenzyl trifluoroacetate (**1**-CH$_2$-OCOCF$_3$) + the excess Tl^{III} trifluoroacetate left after the redox reaction. Irradiation of the solution at − 11 °C by UV light gave the spectrum of Fig. 4, a 13 × 8 line pattern with a^H = 1.04 mT (12 H), a^H = 0.080 mT (2 H) and a^H = 0.040 mT (3 H), assigned to the radical cation of pentamethylbenzyl trifluoroacetate. Upon discontinuation of the irradiation, the spectrum disappeared within < 10 s. The weak singlet lines with a spacing of 0.65 mT belong to the EPR spectrum of residual **1**-CH$_3^{\cdot +}$.

When a solution of authentic pentamethylbenzyl trifluoroacetate and Tl^{III} trifluoroacetate in trifluoroacetic acid was

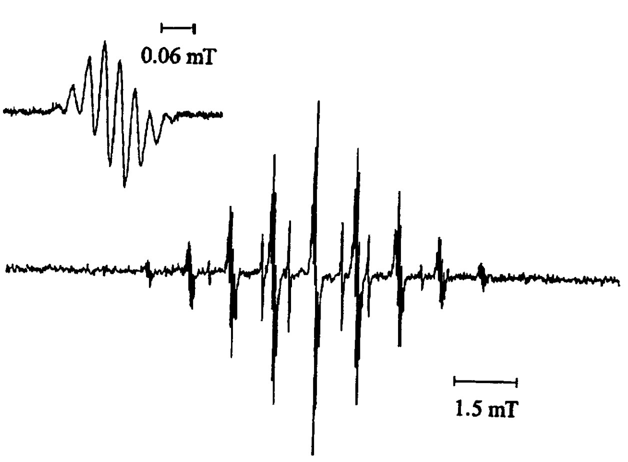


Fig. 4 EPR spectrum of an irradiated solution of **2** (10 mmol dm^{-3}) and Tl^{III} trifluoroacetate (50 mmol dm^{-3}) in trifluoroacetic acid at −11 °C, recorded after the initial strong signal of **1**-CH$_3$$^{•+}$ had been allowed to decay at room temperature. The insert shows the 8-line splitting of each major line.

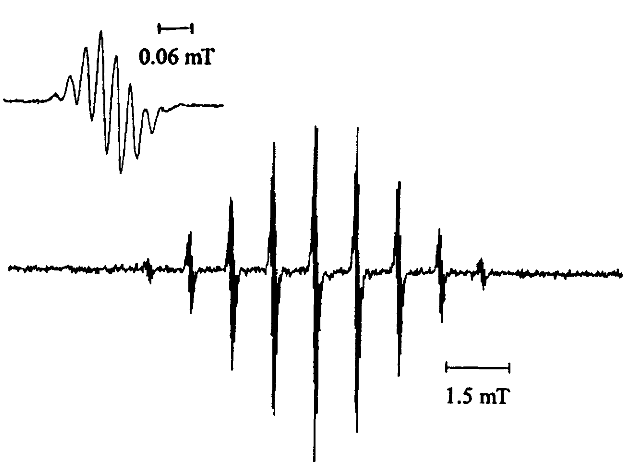


Fig. 5 EPR spectrum of an irradiated (UV) solution of pentamethylbenzyl acetate (20 mmol dm^{-3}) and Tl^{III} trifluoroacetate (25 mmol dm^{-3}) in trifluoroacetic acid at −11 °C. The insert shows the 8-line splitting of each major line.

subjected to the same treatment, the same 13 × 8 line spectrum appeared (a^H 1.02, 0.080 and 0.040 mT, respectively).

EPR spectra of irradiated solutions of pentamethylbenzyl acetate–, pentamethylbenzyl alcohol– or methyl pentamethylbenzyl ether–Tl^{III} trifluoroacetate in trifluoroacetic acid

UV irradiation (3 min) of a solution of pentamethylbenzyl acetate (**1**-CH$_2$OAc, 20 mmol dm^{-3}) and Tl^{III} trifluoroacetate (25 mmol dm^{-3}) in trifluoroacetic acid at −11 °C gave the 13 × 8 line spectrum shown in Fig. 5 (a^H = 1.03, 0.078 and 0.039 mT), virtually identical with that of Fig. 4. Upon discontinuation of the irradiation, the signal disappeared within 10 s. In (^{2}H)trifluoroacetic acid, a spectrum of identical appearance and behaviour was obtained. The same spectrum, although of much lower intensity, could be generated by UV irradiation of **1**-CH$_2$OAc with Hg^{II} trifluoroacetate or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in trifluoroacetic acid, both at −11 °C.

We also attempted to generate the 13-line spectrum from **1**-CH$_2$OAc at lower temperatures, but then the resolution of Figs. 4 and 5 was lost. Fig. 6 shows the spectrum obtained by UV irradiation of **1**-CH$_2$OAc–Tl^{III} trifluoroacetate in dichloromethane–trifluoroacetic acid (0.8 mol dm^{-3}) at −60 °C; this spectrum could not be further resolved when run with a low modulation amplitude.

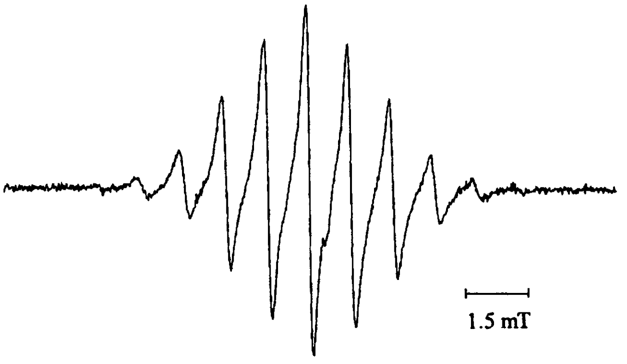


Fig. 6 EPR spectrum of an irradiated (UV) solution of pentamethylbenzyl acetate (20 mmol dm^{-3}) and Tl^{III} trifluoroacetate (25 mmol dm^{-3}) in dichloromethane–trifluoroacetic acid (0.8 mol dm^{-3}) at −60 °C

A solution of **1**-CH$_2$OAc in trifluoroacetic acid was examined by ^{1}H NMR spectroscopy at room temperature. The acetyl group was rapidly split off, as shown by the methyl signal appearing at the same shift as a solution of acetic acid in trifluoroacetic acid.

The UV irradiation of pentamethylbenzyl alcohol (**1**-CH$_2$OH) with Tl^{III} trifluoroacetate in trifluoroacetic acid [also in (^{2}H)trifluoroacetic acid] at −11 °C gave a 13 × 8 line spectrum almost identical with that of Fig. 4 or 5 (a^H = 1.02, 0.086 and 0.043 mT, respectively). When methyl pentamethylbenzyl ether was treated in the same way, a 13-line EPR spectrum (a^H = 1.01 mT) was recorded, each line somewhat broadened compared with the spectrum of **1**-CH$_2$OCOCF$_3$$^{•+}$ (0.41 and 0.35 mT, respectively) and not as well resolved. At least seven splittings of about 0.04 mT were discernible.

EPR spectrum of pentamethylbenzyl chloride–Tl^{III} trifluoroacetate in dichloromethane–trifluoroacetic acid (0.8 mol dm^{-3})

In neat trifluoroacetic acid at −11 °C, UV irradiation of pentamethylbenzyl chloride (**1**-CH$_2$Cl) and Tl^{III} trifluoroacetate gave a weak 13-line EPR spectrum with a^H = 1.02 mT, each line split into eight, $a^H \approx 0.04$ mT. This spectrum is probably derived from **1**-CH$_2$OCOCF$_3$$^{•+}$, formed by photosolvolysis[16] of **1**-CH$_2$Cl. The latter was thermally stable in trifluoroacetic acid under the prevailing conditions (NMR). An attempt was also made to record the EPR spectrum of **1**-CH$_2$Cl$^{•+}$ at −60 °C, where it was necessary to use dichloromethane as the solvent and add trifluoroacetic acid (0.8 mol dm^{-3}) in order to solubilize the Tl^{III} salt. The spectrum had very similar characteristics to that observed in neat trifluoroacetic acid, except for lower resolution of the major lines. The same was true for a run in which Hg^{II} trifluoroacetate was used as the electron acceptor.

EPR spectrum on irradiation of an aged solution of (^{2}H$_{18}$)hexamethylbenzene–Tl^{III} trifluoroacetate in trifluoroacetic acid

A solution of fully deuteriated pentamethylbenzyl trifluoroacetate was obtained by reaction of (^{2}H$_{18}$)hexamethylbenzene (15 mmol dm^{-3}) and Tl^{III} trifluoroacetate (40 mmol dm^{-3}) in trifluoroacetic acid [or in (^{2}H)trifluoroacetic acid] at room temperature for 1.5 h. As expected, irradiation of this solution by UV light at −11 °C gave an EPR spectrum with 19 visible lines of the spacing 1.02/6.5 = 0.157 mT (Fig. 7); no further resolution of the lines was possible.

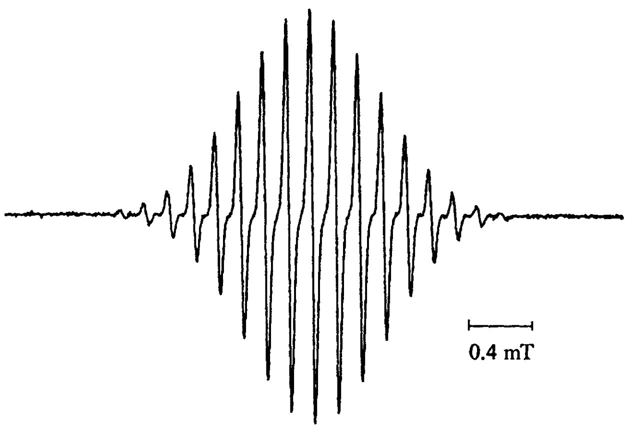


Fig. 7 EPR spectrum of an irradiated solution of ($^2H_{18}$)hexamethylbenzene (15 mmol dm^{-3}) and Tl^{III} trifluoroacetate (40 mmol dm^{-3}) in trifluoroacetic acid at −11 °C, recorded after the initial strong signal of ($^2H_{18}$)hexamethylbenzene$^{\cdot+}$ had been allowed to decay at room temperature. The spacing between the lines is 0.157 mT.

EPR spectra of pentamethylbenzene (1-H) and its ring-deuteriated isotopomer

It was recently proposed[5] that the 13-line spectrum obtained from **2** might be assigned to the pentamethylbenzene radical cation **1**-H$^{\cdot+}$. The latter has a 13-line EPR spectrum with a splitting of 1.02 mT, with no further resolution seen.[9,17] This suggestion is reasonable in view of the widespread occurrence of methyl migrations in solutions of polymethylbenzenes in trifluoroacetic acid under oxidative conditions,[18,19] and therefore the spectrum of **1**-H$^{\cdot+}$ had to be generated and recorded under conditions of full resolution. However, the oxidative generation of the EPR spectrum of pentamethylbenzene in trifluoroacetic acid is complicated by its concurrent conversion into 1,2,3,4,5,6,7,8-octamethylanthracene radical cation,[18] which is a persistent species and strongly disturbs the middle part of the **1**-H$^{\cdot+}$ spectrum.

This difficulty could be avoided by the following procedure. The mixing of a trifluoroacetic acid solution of **1**-H (50 mmol dm^{-3}) and Tl^{III} trifluoroacetate (60 mmol dm^{-3}) was performed at −15 °C, and the sample tube inserted into the precooled cavity (−15 °C). The first spectrum recorded was a superposition of those of **1**-H$^{\cdot+}$ (relatively weak) and 1,2,3,4,5,6,7,8-octamethylanthracene radical cation. UV irradiation of the sample strongly enhanced the spectrum of **1**-H$^{\cdot+}$ and after a period of 1–2 min almost obscured the signal of the 1,2,3,4,5,6,7,8-octamethylanthracene radical cation. The resulting spectrum is shown in Fig. 8(*a*), whereas Fig. 8(*b*) shows the five-line splitting of each of the major lines. The hfs coupling constants were a^H = 1.02 mT [1,2,4,5-(CH_3)$_4$, 12 H], 0.047 (3-CH_3, 3 H) and 0.040 (1-H, 1 H) mT. When the light was shut off, the characteristic EPR spectrum of 1,2,3,4,5,6,7,8-octamethylanthracene radical cation appeared immediately, and was strongly amplified by leaving the solution overnight.

A sample of ring-deuteriated pentamethylbenzene (1-^{2}H)**1**-H was treated in the same way in (^{2}H)trifluoroacetic acid and then gave a spectrum with the same major splitting as that in Fig. 8(*a*) (1.02 mT) but with each major line split into a quartet [3-CH_3 0.047 mT, see Fig. 8(*c*)] with no further fine structure detectable. When the light was shut off, the characteristic EPR spectrum of 1,2,3,4,5,6,7,8-octamethylanthracene radical cation, deuteriated in the 9,10-positions, appeared immediately, and was strongly amplified by leaving the solution overnight.

The fully resolved EPR spectrum of **1**-H$^{\cdot+}$ was also obtained upon photolysis of **1**-H with Hg^{II} trifluoroacetate in trifluoroacetic acid at −15 °C [a^H 1.02 (12 H), 0.041 (3 H), 0.047 (1 H) mT].

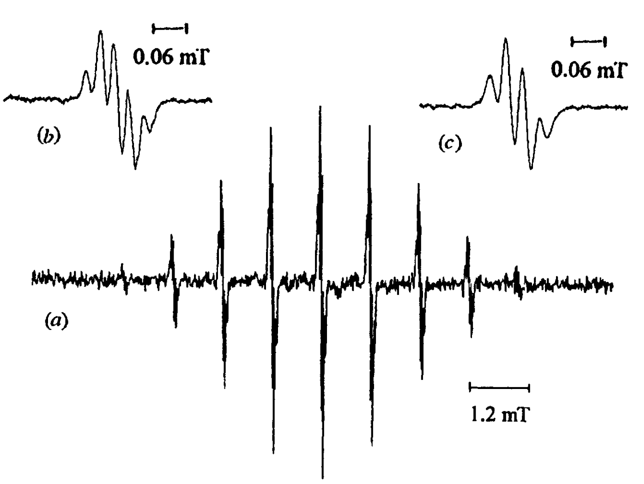


Fig. 8 (*a*) EPR spectrum of an irradiated (UV) solution of **1**-H (50 mmol dm^{-3}) and Tl^{III} trifluoroacetate (60 mmol dm^{-3}) in trifluoroacetic acid at −15 °C. (*b*) The middle line of the spectrum in (*a*). (*c*) The middle line of the EPR spectrum of a solution made up and treated as in (*a*), but with (1-^{2}H)**1**-H as the substrate and (^{2}H)trifluoroacetic acid as the solvent.

EPR spectra of some isotopomers of 1-CH$_3$

The isotope effects found above for the reaction between **1**-CH_3 and Tl^{III} might in principle be accompanied by exchange of one proton for a deuterium in **1**-$CH_3$$^{\cdot+}$ or *vice versa*, for example *via* the equilibrium of eqn. (1). Simulations showed that this should have a profound effect upon the EPR spectrum of **1**-$CH_3$$^{\cdot+}$ or ($^2H_{18}$)**1**-$CH_3$$^{\cdot+}$ [Fig. 9(*a*)]. Experimentally, spectra of ($^2H_1$)**1**-$CH_3$$^{\cdot+}$ and ($^2H_{17}$)**1**-$CH_3$$^{\cdot+}$ were recorded [Fig. 9(*b*)] by taking advantage of the known fact[20] that pentamethylbenzyl acetate is reduced to **1**-CH_3 by treatment with acid in the presence of a hydride donor, such as methylcyclohexane. When methylcyclohexane [($^2H_{14}$)methylcyclohexane] was added to solutions similar to those employed for Fig. 7 (Fig. 6), except for lower substrate concentrations being used, the EPR spectra of the corresponding singly exchanged ($^2H_{17}$)**1**-$CH_3$$^{\cdot+}$ [(^{2}H)**1**-$CH_3$$^{\cdot+}$] could be recorded immediately; after 1–2 h at −11 °C, further irradiation of the samples showed the presence of doubly exchanged species.

Discussion

Kinetics of the conversion of 2 into 1-CH$_2$OCOCF$_3$

The reaction between Tl^{III} trifluoroacetate and aromatics containing at least one C–H position in the ring (ArH) leads to the formation of thalliated products,[21] ArTl^{III}($OCOCF_3$)$_2$, which have found widespread use as synthetic intermediates.[22] As a side-reaction, the radical cation of ArH is often formed, and this phenomenon has been utilized as a method to generate ArH$^{\cdot+}$ for EPR observation.[9b,23] The mechanism of thalliation has been thoroughly studied, and is similar to that of mercuriation, displaying a kinetic isotope effect, k_H/k_D, of about 5. Both absolute and relative rates for the thalliation of a number of ArH have been determined.[24]

The system under study here, hexamethylbenzene, is obviously a special case since it cannot undergo nuclear thalliation. Instead, its radical cation, **1**-$CH_3$$^{\cdot+}$, is formed in an easily detectable concentration *via* a formal electron transfer mechanism and is eventually transformed into pentamethylbenzyl trifluoroacetate according to a mechanism well established from electrochemical studies[7,14] [eqns. (1)–(3)]. The kinetic study performed above was originally limited to finding rate parameters for the various processes leading from **2** and Tl^{III} trifluoroacetate, using trifluoroacetic acid as the medium, to pentamethylbenzyl trifluoroacetate in order to be able to

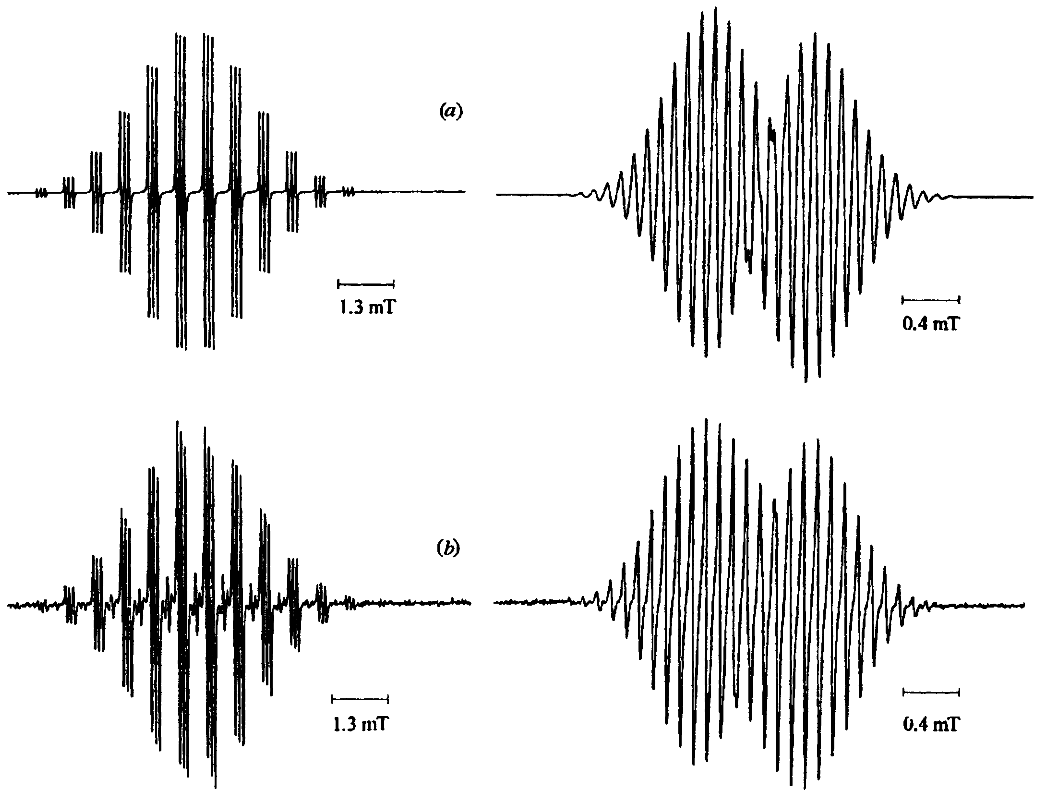


Fig. 9 (*a*) Simulated EPR spectra of ($^2H_1$)**1**-CH$_3$$^{•+}$ and ($^2H_{17}$)**1**-CH$_3$$^{•+}$, using a^{H} = 0.62 mT and $a^{^2H}$ = 0.097 mT with a line width of 0.04 mT. (*b*) EPR spectrum of an irradiated solution of **1**-CH$_3$ (10 mmol dm^{-3}) and Tl^{III} trifluoroacetate (40 mmol dm^{-3}) in trifluoroacetic acid at −11 °C, recorded after the initial signal of **1**-CH$_3$$^{•+}$ had been allowed to decay at room temperature and ($^2H_{14}$)methylcyclohexane added, and of an irradiated solution of ($^2H_{18}$)**1**-CH$_3$ (10 mmol dm^{-3}) and Tl^{III} trifluoroacetate (40 mmol dm^{-3}) in trifluoroacetic acid at −11 °C, recorded after the initial signal of ($^2H_{18}$)**1**-CH$_3$$^{•+}$ had been allowed to decay at room temperature and methylcyclohexane added.

establish a credible kinetic model. The detailed kinetics of Tl^{III}–arene reactions were worked out by Lau and Kochi[9a] and provided the general framework for the choice of reaction conditions. However, the problem of assessing the true reactivity of **1**-CH$_3$$^{•+}$ necessitated an extended study, during the course of which some novel features of the Tl^{III}–**1**-CH$_3$ reaction became apparent.

Lau and Kochi[9a] postulated that Tl^{III} trifluoroacetate oxidation of **1**-CH$_3$ occurs by the mechanism shown in eqns. (4)–(7), comprising (*i*) initial dissociation of Tl^{III} trifluoroacetate

$$\mathrm{Tl^{III}(OCOCF_3)_3} \overset{K_4}{\rightleftharpoons} \mathrm{Tl^{III}(OCOCF_3)_2{}^+ + CF_3COO^-} \quad (4)$$

$$\mathbf{1}\text{-CH}_3 + \mathrm{Tl^{III}(OCOCF_3)_2{}^+} \overset{K_5}{\rightleftharpoons} \underset{\text{CT complex}}{[\mathbf{1}\text{-CH}_3 \cdots \mathrm{Tl^{III}(OCOCF_3)_2{}^+}]} \quad (5)$$

$$[\mathbf{1}\text{-CH}_3 \cdots \mathrm{Tl^{III}(OCOCF_3)_2{}^+}] \xrightarrow{k_6} \mathbf{1}\text{-CH}_3{}^{\bullet+} + \mathrm{Tl^{II}(OCOCF_3)_2} \quad (6)$$

$$1/k_{\mathrm{obs}} = 1/k_{\mathrm{max}} + 1/(K_4K_5\,k_{\mathrm{max}}[\mathbf{1}\text{-CH}_3]) \quad (7)$$

into a cationic Tl^{III} species and trifluoroacetate ion, (*ii*) formation of a CT complex between the cationic Tl^{III} species and **1**-CH$_3$, (*iii*) electron transfer within the complex to give **1**-CH$_3$$^{•+}$ and Tl^{II}(OCOCF$_3$)$_2$, and (*iv*) further follow-up reactions of **1**-CH$_3$$^{•+}$ according to eqns. (1)–(3).

The scheme of eqns. (4)–(6) obeys Michaelis–Menten type kinetics {eqn. (7), assuming that [**1**-CH$_3$] > [Tl^{III}]}, and the parameters K_4K_5 = 2.3 and k_{max} = 0.25 s^{-1} were evaluated for **1**-CH$_3$ in trifluoroacetic acid at 25 °C. Thus at [**1**-CH$_3$] between 1 and 20 mmol dm^{-3} k_{obs} should vary approximately linearly from 0.035 to 0.66 min^{-1}. However, our value of k_{obs} = 0.65 min^{-1} at [**1**-CH$_3$]$_0$ = 1.4 mmol dm^{-3} is considerably larger than the calculated one from eqn. (7), 0.024 min^{-1}. Runs at [**1**-CH$_3$]$_0$ = 5.6 mmol dm^{-3} with [Tl^{III}] around 0.25 mmol dm^{-3} gave k_{obs} = 3.9(8) min^{-1}, again much larger than the value calculated from eqn. (7) and the parameters above, 0.17 min^{-1}. At the latter ratio of reactant concentrations, the kinetics were complicated by a zero-order component, and thus the calculations of the rate constants had to be made on the non-linear part of the kinetic curve.[15] The difference between our values and those derived from published kinetic parameters[9a] can be traced presumably to the fact that previous evaluations of K_4K_5 and k_{max} were made by methods which included the presence of lithium trifluoroacetate and variation of its concentration in order to be able to use a modified version of eqn. (7). Trifluoroacetate ion will affect the equilibrium of eqn. (4) so as to suppress [Tl^{III}(OCOCF$_3$)$_2$$^+$] and thus decrease the observed rate constant.

Table 1 shows the rate constants which are pertinent for modelling the overall kinetics of the conversion **2** ⟶ **1**-CH$_2$OCOCF$_3$. To start with the first step, conversion of **2** (at [**2**]$_0$ = 24 mmol dm^{-3}) into **1**-CH$_3$ in trifluoroacetic acid, the rate constant for formation of **1**-CH$_3$ obtained from the determination of [**1**-CH$_3$] by GLC analysis was 0.083 min^{-1}, whereas the rate constants for formation and decay of the **1**-CH$_3$ ··· Tl^{III} complex from a solution containing **2** (20 mmol dm^{-3}) and Tl^{III} (5 mmol dm^{-3}) were 0.85 and 0.089 min^{-1}, respectively.

Table 1 Rate constants for reactions involved in the conversion of **2** into **1**-CH_2OCOCF_3; TFA = trifluoroacetic acid

Experiment No.	Reaction	Method	T/°C	k_{obs}/min^{-1}	Comment
1	$\mathbf{2} \longrightarrow \mathbf{1}\text{-}CH_3$ in TFA	GLC	22	0.083	
2	$\mathbf{2} \longrightarrow \mathbf{1}\text{-}CH_3$ in TFA with concurrent Tl^{III} oxidation	UV	22	0.85 (up) 0.089 (down)	
3	$\mathbf{1}\text{-}CH_3 \longrightarrow \mathbf{1}\text{-}CH_2OCOCF_3$ by Tl^{III} oxidation in TFA	UV	22	0.65	Apparent k_2 = 8(2) dm^3 mol^{-1} s^{-1} in the range [**1**-CH_3]$_0$ = 1.4–5.6 mmol dm^{-3}
4	$(^2H_{18})\mathbf{1}\text{-}CH_3 \longrightarrow (^2H_{18})\mathbf{1}\text{-}CH_2OCOCF_3$ by Tl^{III} oxidation in TFA	UV	22	0.27	Comparable to # 3, k_H/k_D = 2.4
5	$\mathbf{1}\text{-}CH_3 \longrightarrow \mathbf{1}\text{-}CH_2OCOCF_3$ by Tl^{III} oxidation in TFA	UV	22	1.2	[**1**-CH_3]$_0$ = 5.0 mmol dm^{-3} [Tl^{III}] = 10.0 mmol dm^{-3}
6	$\mathbf{1}\text{-}CH_3 \longrightarrow \mathbf{1}\text{-}CH_2OCOCF_3$ by Tl^{III} oxidation in [^{2}H]TFA	UV	22	0.43	Comparable to # 5, k_H/k_D = 2.8
7	$(^2H_{18})\mathbf{1}\text{-}CH_3 \longrightarrow (^2H_{18})\mathbf{1}\text{-}CH_2OCOCF_3$ by Tl^{III} oxidation in TFA	UV	22	0.30	Comparable to # 5, k_H/k_D = 4.0
8	$(^2H_{18})\mathbf{1}\text{-}CH_3 \longrightarrow (^2H_{18})\mathbf{1}\text{-}CH_2OCOCF_3$ by Tl^{III} oxidation in (^{2}H)TFA	UV	22	0.175	Comparable to # 5, k_H/k_D = 6.9

The second step, Tl^{III} oxidation of **1**-CH_3 to give **1**-CH_2OCOCF_3 in trifluoroacetic acid, had an apparent second-order rate constant at 22 °C of 8(2) dm^3 mol^{-1} s^{-1} in the range of [**1**-CH_3]$_0$ from 1.4 to 5.6 mmol dm^{-3}. This value can be checked by starting from the second-order rate constant for thalliation of benzene, 1.47 × 10^{-4} dm^3 mol^{-1} s^{-1} in trifluoroacetic acid at 22.4 °C.[24c] The rate of thalliation of mesitylene was found to be 7750 times larger than for benzene at 0 °C,[24a] and the rate of electron transfer from hexamethylbenzene 10 times larger than the rate of thalliation of mesitylene at 25 °C.[9a] This gives an estimated second-order rate constant for the **1**-CH_3–Tl^{III} reaction of ≈11 dm^3 mol^{-1} s^{-1}, in satisfactory agreement with our value considering the large rate differences involved.

The first-order rate constant at [**1**-CH_3]$_0$ = 1.4 mmol dm^{-3} was 0.65 min^{-1}, showing an isotope effect of k_H/k_D of 2.4 in relation to ($^2H_{18}$)**1**-CH_3 under identical conditions. Kochi and Lau found a k_H/k_D of 3.1 (in the presence of $LiOCOCF_3$) and associated it with the proton abstraction step from the radical cation [eqn. (1)].

In a higher concentration range, selected for making a comparison between the UV monitored runs above and the EPR monitored runs to be described below possible ([**1**-CH_3]$_0$ = 5.0 and [Tl^{III}]$_0$ = 10.0 mmol dm^{-3}), the rate constant (Table 1) for decay of the **1**-$CH_3 \cdots Tl^{III}$ complex in trifluoroacetic acid was 1.2 min^{-1}, displaying a k_H/k_D of 4.0 in relation to ($^2H_{18}$)**1**-CH_3 under identical conditions. Runs in [^{2}H]trifluoroacetic acid revealed the existence of solvent isotope effects, being 2.8 and 1.7, respectively, for **1**-CH_3 and ($^2H_{18}$)**1**-CH_3.

It is now possible to connect the rate data for the two processes involved in the conversion of **2** into **1**-CH_2OCOCF_3. The rate constant for the rearrangement of **2** to **1**-CH_3 is 0.083 min^{-1} (Fig. 1), whereas the reaction between **1**-CH_3 and Tl^{III} proceeds with a rate constant > 10 times larger, 1.2 min^{-1} (Table 1). The rate constant for the initial formation of the **1**-$CH_3 \cdots Tl^{III}$ complex during the reaction between **2** and Tl^{III}, k_{up} = 0.85 min^{-1}, reflects the fast consumption of the small amount of **1**-CH_3 formed during mixing of the reagents; after a short period, the overall rate becomes limited by the slow conversion of **2** into **1**-CH_3, with k_{down} = 0.085 min^{-1}, equal to the GLC monitored rate constant. The kinetics of the overall reaction were simulated[25] by the mechanism of eqns. (8)–(10), using the known rate constants k_8 and k_{10} (0.083 and 1.2 min^{-1})

$$\mathbf{2} \xrightarrow{k_8} \mathbf{1}\text{-}CH_3 \qquad (8)$$

$$\mathbf{1}\text{-}CH_3 + Tl^{III} \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} \mathbf{1}\text{-}CH_3 \cdots Tl^{III} \qquad (9)$$

$$\mathbf{1}\text{-}CH_3 \cdots Tl^{III} \xrightarrow{k_{10}} \mathbf{1}\text{-}CH_2OCOCF_3 \qquad (10)$$

and assuming that the equilibrium constant of eqn. (9) is of the order of 2 × 10^3 dm^3 mol^{-1} (the experimental[9a] value was 2450) with k_9 = 2000 dm^3 mol^{-1} s^{-1} and k_{-9} = 1 s^{-1}. Under the concentration conditions of Fig. 2, [**1**-$CH_3 \cdots Tl^{III}$]$_{max}$ was calculated to be 0.9 mmol dm^{-3} and to be reached 130 s after mixing, to be compared with the experimental values, ≈0.25 mmol dm^{-3} and 110 s. The agreement is satisfactory in view of the many uncertainties involved, in particular with respect to the estimate of [**1**-$CH_3 \cdots Tl^{III}$]$_{max}$. The molar extinction coefficient at 330 nm of this species was determined by a Benesi–Hildebrand type analysis of a series of **1**-CH_3–Tl^{III} solutions of different concentrations in which the redox reaction occurred at a significant speed during measurements, and must be uncertain.

The third important step *en route* from **2** to **1**-CH_2OCOCF_3 is the follow-up reactions of **1**-$CH_3^{\bullet +}$. The finding that **1**-$CH_3^{\bullet +}$ is a highly reactive species in trifluoroacetic acid was originally based on electrochemical studies, yielding high rate constants for the decay of **1**-$CH_3^{\bullet +}$ (see Table 2 for a compilation of previous and present results). A study[14] in dichloromethane–trifluoroacetic acid (up to a concentration of 5.26 mol dm^{-3}) at 20 °C demonstrated that the proton transfer step of eqn. (1) is reversible and subject to a weak isotope effect in relation to ($^2H_{18}$)**1**-CH_3, 2.0(5). At this trifluoroacetic acid concentration, the equilibrium constant of eqn. (1) was estimated to be 2.6 × 10^{-5} and the observed rate constant 0.27 s^{-1}. Extrapolation to neat trifluoroacetic acid gave a rate constant of ≈0.7 s^{-1} or 42 min^{-1}. This value agrees reasonably well with that determined[10] by measuring the decay of **1**-$CH_3^{\bullet +}$, generated by photolysis of the Hg^{II} trifluoroacetate–**1**-CH_3 in trifluoroacetic acid at 25 °C, 29 min^{-1}.

With the approximation that rate constants decrease by a factor of 2 by each 10 K decrease in temperature, the decay rate constant of **1**-$CH_3^{\bullet +}$ at −11 °C should be 4–5 min^{-1}. We measured the rate constant directly at this temperature and obtained 7(1) min^{-1} by generating **1**-$CH_3^{\bullet +}$ by the Tl^{III}–$h\nu$ method and 6(2) min^{-1} by generating it by phenyliodine(III) bis(trifluoroacetate) oxidation.[11] A weak isotope effect was also seen, k_H/k_D being 1.7(5).

Thus the true rate constant for disappearance of **1**-$CH_3^{\bullet +}$ is large in comparison with the 'decay' rates of **1**-$CH_3^{\bullet +}$ which are

Table 2 Rate constants for the decay of **1**-CH$_3^{\cdot+}$ under different conditions

Experiment No.	Parent compound	Method of generation	T/°C	k/min^{-1}	Reference
1	**1**-CH$_3$	Tl$^{\text{III}}$ oxidation in TFA	22	1.08	This work
2	**1**-CH$_3$	Tl$^{\text{III}}$ oxidation in (^{2}H)TFA	22	0.48	This work
3	**2**	Tl$^{\text{III}}$ oxidation in TFA	22	0.17	This work
4	(^{2}H$_{18}$)**1**-CH$_3$	Tl$^{\text{III}}$ oxidation in TFA	22	0.38	This work
5	(^{2}H$_{18}$)**1**-CH$_3$	Tl$^{\text{III}}$ oxidation in (^{2}H)TFA	22	0.150	This work
	1-CH$_3$	Hg$^{\text{II}}$–$h\nu$ in TFA	25	29	10
	(^{2}H$_{18}$)**1**-CH$_3$	Hg$^{\text{II}}$–$h\nu$ in TFA	25	6.6	10
	1-CH$_3$	Anodic in TFA	20	42	14
6	**1**-CH$_3$	Tl$^{\text{III}}$ oxidation in TFA	−11	0.025	This work
7	(^{2}H$_{18}$)**1**-CH$_3$	Tl$^{\text{III}}$ oxidation in TFA	−11	0.0092	This work
	1-CH$_3$	Tl$^{\text{III}}$ oxidation in TFA–LiOCOCF$_3$	−10	0.10	9(*a*)
8	**2**	Tl$^{\text{III}}$ oxidation in TFA	−11	0.012	This work
9	**1**-CH$_3$	Tl$^{\text{III}}$–$h\nu$ in TFA	−11	7(1)	This work
10	(^{2}H$_{18}$)**1**-CH$_3$	Tl$^{\text{III}}$–$h\nu$ in TFA	−11	4.2(5)	This work
11	**1**-CH$_3$	PhI(OCOCF$_3$)$_2$ in TFA	−11	6(2)	This work
12	**1**-CH$_3$	Tl$^{\text{III}}$–$h\nu$ in TFA	−16	5(1)	This work
	1-CH$_3$	Fe$^{\text{III}}$(phen)$_3$ in TFA	−31	0.8	16(*a*)
13	**1**-CH$_3$	Hg$^{\text{II}}$–$h\nu$ in DCM–TFA (0.8 mol dm^{-3})	−60	1.5	This work
14	(^{2}H$_{18}$)**1**-CH$_3$	Hg$^{\text{II}}$–$h\nu$ in DCM–TFA-(^{2}H) (0.8 mol dm^{-3})	−60	0.50	This work
	1-CH$_3$	Anodic in DCM	−70	1600	16(*b*)

measured when **1**-CH$_3^{\cdot+}$ is generated by Tl$^{\text{III}}$ oxidation of **1**-CH$_3$. The rate ratio is ≈30 at 22 °C and ≈200 at −11 °C (Table 2). The reason that **1**-CH$_3^{\cdot+}$ can be observed at all during the course of this reaction resides in the *slow* initial step between **1**-CH$_3$ and Tl$^{\text{III}}$ which maintains a significant concentration of **1**-CH$_3^{\cdot+}$, the decay of which exactly mirrors the rate of the reaction between **1**-CH$_3$ and Tl$^{\text{III}}$. Experiments 5–8 of Table 1 and 1, 2, 4 and 5 of Table 2 demonstrate this correspondence by the following nearly identical pairs of rate constants 1.2, 1.1; 0.43, 0.48; 0.30, 0.38; 0.175, 0.150.

The finding that the slow step of the reaction between **1**-CH$_3$ and Tl$^{\text{III}}$, presumably the formal electron transfer step of eqn. (6) or some other chemically equivalent scheme, precedes the fast decay of the radical cation [eqns. (1)–(3)] immediately raises the problem of the origin of the isotope effects observed. The isotope effect for the fast decay of **1**-CH$_3^{\cdot+}$ is relatively weak, around 2, and should not be reflected anyway in the observed rate constant. Besides, even if the deprotonation step is reversible, the exchange of protons for deuterons in the experiments conducted in (^{2}H)trifluoroacetic acid *via* eqn. (1) cannot be significant enough to affect the rate. No discernible effect of such an exchange was seen in the hundreds of EPR spectra recorded during the kinetic studies. The recording and simulation of spectra in which one deuterium atom had been introduced into **1**-CH$_3$[^{2}H] or *vice versa* showed that such an exchange would produce significant changes which could not have escaped notice (Fig. 9).

Thus we are forced to conclude that the slow formal electron transfer step between **1**-CH$_3$ and Tl$^{\text{III}}$ involves several steps, in which breaking of one or several bonds to a hydrogen atom occur. Presently the nature of such steps can only be the subject of speculation, but a reasonable suggestion would have to start from the fact that the first one-electron step of the Tl$^{\text{III}}$/Tl$^{\text{I}}$ redox couple has been shown[26] to have a low standard potential, 0.3 V (NHE) in water, whereas that of the second step, Tl$^{\text{II}}$/Tl$^{\text{I}}$, has a much higher standard potential, 2.2 V. Thus Tl$^{\text{III}}$ belongs to the category of two-electron oxidants,[27] exhibiting its main reactivity in elementary steps of electrophilic (bond-forming) nature. Accordingly, thalliation is expected to occur with aromatic substrates, and processes which formally look like one-electron transfer from ArH to Tl$^{\text{III}}$ should presumably have a more complex mechanism.

In the case of **1**-CH$_3$, such a mechanism might have as a first component the slow formation of the side-chain thalliation product [eqn. (11)]. The latter is formally a Tl$^{\text{III}}$ species, but

$$\mathbf{1}\text{-CH}_3 + \text{Tl}^{\text{III}} \xrightarrow{\text{slow}} \mathbf{1}\text{-CH}_2\text{Tl}^{\text{III}} + \text{H}^+ \qquad (11)$$

since Tl is bonded to a carbanionic species it can have considerable Tl$^{\text{II}}$ character through the resonance hybrid **1**-CH$_2$:$^-$Tl$^{\text{III}}$ ⟷ **1**-CH$_2^{\cdot}$Tl$^{\text{II}}$ and thus possess a higher reactivity as a one-electron oxidant [eqn. (12)] than the original Tl$^{\text{III}}$

$$\mathbf{1}\text{-CH}_2\text{Tl}^{\text{III}} + \mathbf{1}\text{-CH}_3 \longrightarrow \mathbf{1}\text{-CH}_2\text{Tl}^{\text{II}} + \mathbf{1}\text{-CH}_3^{\cdot+} \qquad (12)$$

trifluoroacetate species, for which the corresponding Tl$^{\text{II}}$ resonance form is much higher in energy. The transient **1**-CH$_2$–Tl$^{\text{II}}$ species formed in eqn. (12) then cleaves to give ArCH$_2^{\cdot}$ and Tl$^{\text{I}}$, as shown in eqn. (13).

$$\mathbf{1}\text{-CH}_2\text{Tl}^{\text{II}} \longrightarrow \mathbf{1}\text{-CH}_2^{\cdot} + \text{Tl}^{\text{I}} \qquad (13)$$

The possible relationship between the 13-line EPR spectrum from 2 and the EPR spectra of pentamethylbenzyl derivatives

The 13-line EPR spectra recorded earlier from various treatments of **2** are listed in Table 3, together with the resolved spectra from pentamethylbenzyl derivatives **1**-CH$_2$-O-X recorded in this study. To start with the former, it was concluded by Roth[5] that they all refer to the same species, as judged from the value of the hfs constant in the range of 0.91–1.07 mT. Whatever significant difference there is in this set can be ascribed presumably to effects of temperature and the nature of the matrix employed (however, see the discussion below).

The fact that **2** is converted with great ease into pentamethylbenzyl trifluoroacetate **1**-CH$_2$OCOCF$_3$ on treatment with Tl$^{\text{III}}$ in trifluoroacetic acid, and that the EPR spectrum of **1**-CH$_2$OCOCF$_3^{\cdot+}$ in its less resolved version is virtually identical with the 13-line spectrum from **2**, is an indication that side-chain substituted derivatives of **1**-CH$_3$ might be the origin of the latter spectrum. However, as long as the matrix generated spectra cannot be fully resolved, the problem of the existence of **2**$^{\cdot+}$ cannot be resolved with full certainty. The same conclusion applies to the reasonable suggestion[5] that **1**-H$^{\cdot+}$ might be the origin of the 13-line spectrum, even if the conditions required for converting **1**-CH$_3$ into **1**-H appear to be rather drastic when judged by the criterion of facile formation of 1,2,3,4,5,6,7,8-

Table 3 Conditions for formation of radical cations from **2** or compounds related to **2**, and their EPR spectra

Parent compound	Method	$T/°C$	EPR spectrum	Reference
Pentamethylbenzyl acetate	$\mathrm{Tl^{III}}$–$h\nu$ in TFA	−11	1.03(12), 0.078(2), 0.039(3)	This work
Pentamethylbenzyl trifluoroacetate	$\mathrm{Tl^{III}}$–$h\nu$ in TFA	−11	1.02(12), 0.080(2), 0.040(3)	This work
Pentamethylbenzyl trifluoroacetate, fully deuteriated	$\mathrm{Tl^{III}}$–$h\nu$ in TFA	−11	0.157(12 ^{2}H)	This work
Pentamethylbenzyl alcohol	$\mathrm{Tl^{III}}$–$h\nu$ in TFA	−11	1.02(12), 0.086(2), 0.043(3)	This work
Methyl pentamethylbenzyl ether	$\mathrm{Tl^{III}}$–$h\nu$ in TFA	−11	1.01(12); at least 7 splittings of 0.041 mT	This work
Pentamethylbenzyl chloride	$\mathrm{Tl^{III}}$–$h\nu$ in DCM–TFA (0.8 mol dm^{-3})	−60	1.02(12); indication of at least 5 splittings of ≈0.04 mT	This work
2	$\mathrm{Tl^{III}}$–$h\nu$ in TFA	−11	1.04(12), 0.080(2), 0.040(3)	This work
2	Ionizing radiation in $CFCl_3$	−196	0.95(12)	4(*a*)
2	Pulsed e^- beam in cyclopentane	−(68–28)	0.92(12)	4(*b*)
2	Ionizing radiation in $CF_2ClCFCl_2$	−196	0.91(12)	4(*c*)
2	$SbCl_5$ or $SbCl_5$–$SOCl_2$	−78	0.98(12)	5
2	On solid $O_2{}^+SbF_6{}^-$	20	1.07(13)	6
1-H	$\mathrm{Tl^{III}}$–$h\nu$ in TFA	−11	1.02(12), 0.047(3), 0.040(1)	This work
1-H	$\mathrm{Tl^{III}}$ in TFA	−16	1.01(12)	9(*b*)
1-H	$\mathrm{Hg^{II}}$–$h\nu$ in TFA	−11	1.02(12), 0.047(3), 0.040(1)	This work
1-H	$\mathrm{Co^{III}}$ in TFA	20	1.01(12) < 0.03(4)	17

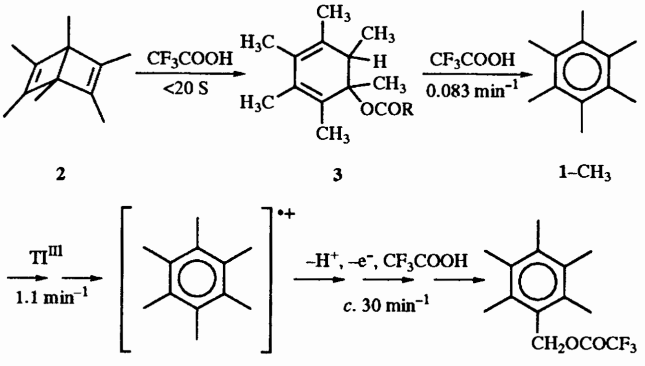
octamethylanthracene from **1-H** (anodic, $\mathrm{Tl^{III}}$, DDQ–$h\nu$ or tetranitromethane/$h\nu$ oxidation in trifluoroacetic acid[28] at temperatures as low as −60 °C) and from **1-CH$_3$** (keeping hexamethylbenzene in 100% sulfuric acid at 20 °C for several h).[29]

The EPR spectrum obtained by the reaction of **2** on solid dioxygenyl hexafluoroantimonate[6] is, in all likelihood, derived from a species of type **1-CH$_2$-O-X$^{\bullet+}$**. The dioxygenyl cation is an exceedingly strong oxidant, E_p for the process $O_2{}^+ + e^- \longrightarrow O_2$ being around 4.5 V *vs.* NHE,[30] and consequently this species should convert **2** into **1-CH$_2$-O-X$^{\bullet+}$** with great ease. The introduction of the oxygen function presumably occurs *via* reaction of **1-CH$_2$$^\bullet$** and dioxygen, one of the best documented reactions of neutral radicals,[31] giving **1-CH$_2$-O-O$^\bullet$** which in turn might undergo further reactions and end up as **1-CH$_2$-O-H$^{\bullet+}$**. In the cases where the 13-line EPR spectrum was obtained by exposing a matrix of **2** in a halogenated solvent to ionizing radiation, the conditions are strongly oxidizing as well. Thus there is no doubt that **2** would be oxidized all the way to **1-CH$_2$$^+$** under such conditions, but there is some uncertainty as to the nature of the group corresponding to O-X of **1-CH$_2$-O-X$^{\bullet+}$**. The matrix solvent contains C–Cl bonds, which upon one-electron reduction[32] should be a source of chloride ion which might combine with **1-CH$_2$$^+$** to give pentamethylbenzyl chloride, **1-CH$_2$-Cl**. This compound is of the same general type as **1-CH$_2$-O-X**, and might give a similar 13-line EPR spectrum. This possibility was checked under the conditions used for the other pentamethylbenzyl derivatives, but only a weak EPR spectrum was detected which was almost identical with that of **1-CH$_2$OCOCF$_3$$^{\bullet+}$**. Presumably, the chloride undergoes photosolvolysis[33] in trifluoroacetic acid. A stronger spectrum was obtained from **1-CH$_2$Cl** in dichloromethane–trifluoroacetic acid (0.8 mol dm^{-3}) at −60 °C, but again the similarity with that of **1-CH$_2$OCOCF$_3$$^{\bullet+}$** made firm conclusions impossible.

The spectra from the pentamethylbenzyl derivatives are almost identical. It is probable that the EPR spectra from **1-CH$_2$OCOCF$_3$** and **1-CH$_2$OCOCH$_3$** are both from **1-CH$_2$-OCOCF$_3$$^{\bullet+}$**, since the NMR spectrum of the acetate in trifluoroacetic acid showed that the acetate group was rapidly split off and replaced by a trifluoroacetoxy group. This is a known reaction for esters where the R-O group corresponds to a stable carbenium ion, for example *tert*-butyl cation.[34] On the other hand, the spectrum of pentamethylbenzyl alcohol most likely is different, even if the difference is manifested only in the values of the smaller hfs constants.

Conclusions

The oxidation of **2** by $\mathrm{Tl^{III}}$ trifluoroacetate in trifluoroacetic acid to give ultimately pentamethylbenzyl trifluoroacetate is a facile, although kinetically complex process. Scheme 1 summarizes the steps involved with rate constants given for room temperature conditions and concentrations given above. In particular, the oxidation of hexamethylbenzene to its radical cation has been shown to exhibit a kinetic deuterium isotope effect and thus must occur in several steps with at least one involving breaking of a C–H bond.



Scheme 1

It is likely that other oxidation processes, applied to **2** can similarly lead to the formation of side-chain substituted derivatives of hexamethylbenzene. Since the radical cations of such compounds have EPR spectra, which under suitable conditions of resolution are almost identical with the ones previously ascribed to **2$^{\bullet+}$** prepared by the matrix technique, the problem of detecting the EPR spectrum of **2$^{\bullet+}$** remains open.

Experimental

Methods and materials

^{1}H NMR spectra were recorded on a Varian 200 MHz spectrometer. UV–VIS monitored kinetics were recorded on a HP 8452A diode-array spectrophotometer, equipped with HP 89532K software. EPR spectra were recorded on an Upgrade Version ESP 3220-200SH of a Bruker ER-200D spectrometer. Photolyses were performed in the photolysis cavity (ER 4104 OR), using a 50 W high-pressure Hg lamp from Bruker (ER 202). For reactions with filtered light, a filter with cut-off at $\lambda < 430$ nm from Schott, Germany, was used. Kinetic experiments were performed using the automation routine of the software, and permitted accurate determinations of spectral intensity (measured as the height of a conveniently accessible line of the first derivative spectrum) with time. All rate constants were determined as the average value from at least three runs, unless otherwise stated.

Tl^{III} trifluoroacetate was either from Strem Chemicals or Merck AG and Hg^{II} trifluoroacetate was from Johnson Matthey. Dichloromethane (SupraSolv), trifluoroacetic acid (Uvasol) and (^{2}H)trifluoroacetic acid (Uvasol) were from Merck AG. Hexamethylbenzene (99%) was purchased from Aldrich, ($^2H_{18}$)hexamethylbenzene (98% ^{2}H) and ($^2H_{14}$)methylcyclohexane from Cambridge Isotope Laboratories, methylcyclohexane (>98%) from Merck AG, pentamethylbenzene (99%) and hexamethyl (Dewar benzene) (97%, checked at intervals by GLC) from Aldrich. The following compounds were synthesized by literature methods or were available from earlier work: pentamethylbenzyl acetate and alcohol,[35] pentamethylbenzyl chloride,[36] methyl pentamethylbenzyl ether[37] and (1-^{2}H)pentamethylbenzene.[9a]

Preparation of pentamethylbenzyl trifluoroacetate

A mixture of 125 mg (0.70 mmol) of pentamethylbenzyl alcohol and 2 cm^3 of trifluoroacetic anhydride was refluxed for 2 h. The excess of anhydride was removed by distillation and the residue was recrystallized from heptane. NMR spectral and MS data were as reported.[9a]

Kinetics of conversion of hexamethyl (Dewar benzene) into hexamethylbenzene

A solution of **2** (15 µl, 146 µmol) in 135 µl of dichloromethane was injected into 3.0 cm^3 of trifluoroacetic acid, to which 15 µl (146 µmol) of nitrobenzene had been added as an internal standard. The conversion was followed by consecutive removal of samples from the stirred reaction mixture. The samples were immediately quenched in aqueous sodium carbonate and then extracted with dichloromethane and analysed by GLC. This experiment was performed only once.

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