Photochemical Generation of the 9-(Trimethylsilylmethyl)fluoren-9-yl Cation. Flash Photolysis Observation of a β-Silyl-substituted Carbenium Ion

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The 9-(trimethylsilylmethyl)fluoren-9-yl cation, an example of a β-silyl-substituted carbenium ion, is observed following photolysis of the corresponding fluoren-9-ol.

Despite the stabilizing effect of a silyl group β to a carbenium ion centre,[1,2] examples where such cations have been directly observed in solution are limited. Only within the last two years has the superacid approach yielded examples, in the form of some β-silyl-substituted vinyl cations[3] and the 2-[1-(trimethylsilyl)-vinyl]-2-adamantyl cation.[4] In the latter case, the silyl group is forced to lie perpendicular to the π system of the allyl cation, the wrong geometry for the hyperconjugative or 'vertical' interaction principally responsible for the silyl stabilization. In general, attempts to generate cations which can achieve the correct geometry, for example the diphenyl(trimethylsilylmethyl)-methyl cation 1 [eqn. (1)],[5] result in the observation of products of desilylation, even under superacid conditions.

(1)
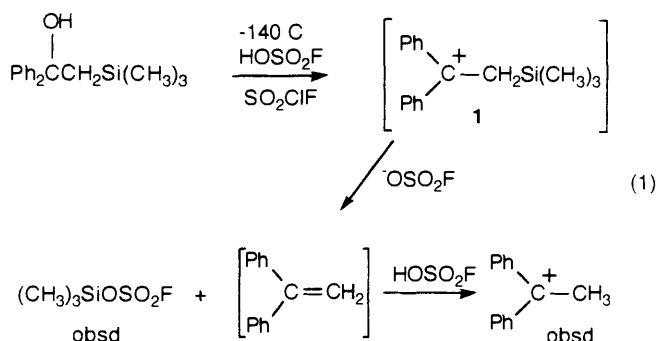
In this paper, we report the flash photolysis observation of a fluorenyl analogue of 1, the 9-(trimethylsilylmethyl)fluoren-9-yl cation 3, the ion being produced photochemically from the corresponding alcohol precursor 2. Flash photolysis has seen considerable recent use for the study of carbocationic intermediates. This technique provides direct kinetic and mechanistic information relating to further reactions of cations, and has also permitted the observation of ions that have defied detection in superacids because of low barriers for rearrangements or fragmentations. The fluoren-9-ol system was chosen for the present investigation because of the known ease of formation of cationic fluoren-9-yl intermediates through photodehydroxylation, as has been demonstrated previously through both product and flash photolysis studies with the parent compound and the 9-methyl and 9-phenyl derivatives.[6–10]

Initial studies were carried out following 254 nm lamp photolysis of 2 in 2,2,2-trifluoroethanol (TFE), followed by analysis of the products employing HPLC and GC. For short irradiation times (up to 20% conversion), the only species observed is the elimination product 9-methylenefluorene 4, although at longer times the ether 7 appears. The latter is also obtained on irradiation of isolated 9-methylenefluorene under the same conditions, and is explained by protonation of the exocyclic C=C in excited 4 to give the 9-methylfluoren-9-yl cation 6, followed by combination with solvent. Photoaddition of TFE to styrene derivatives by such a mechanism has been observed previously.[11,12] Irradiation of 9-methylfluorene-9-ol 5 gives both 4 and 7, in a 1:4 ratio at 10% conversion. From the retention time of 7 relative to 5, an estimate can be made of the approximate GC retention time of the ether 8 that would be derived from 2. The absence of any peak in the expected region places a limit of <2% on the yield of this ether relative to the
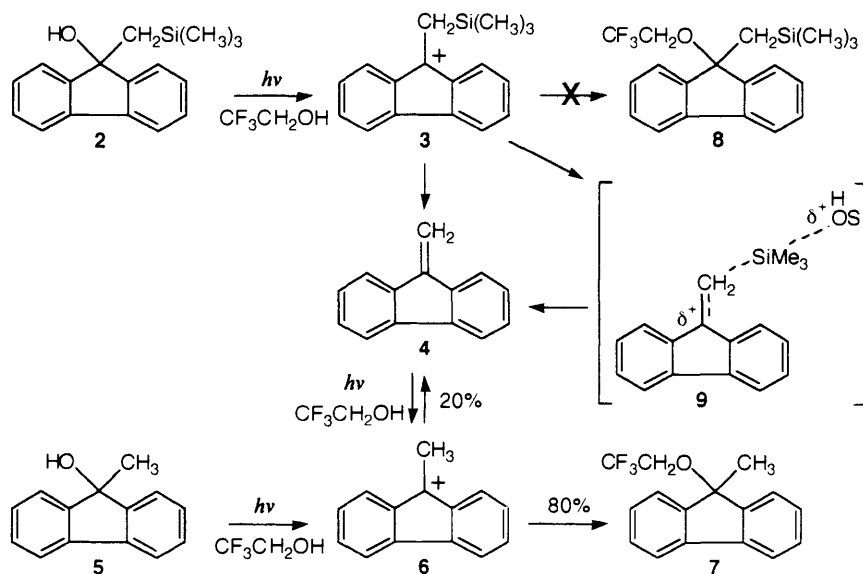
Scheme 1

elimination product **4** for the irradiation of **2**. This assumes that the ether **8** survives the GC conditions.

As expected from the products, the transient absorption spectra observed upon irradiation of both **4** and **5** in TFE correspond to that of the 9-methylfluoren-9-yl cation **6**. There is no ambiguity in this assignment, since this cation can be obtained as a stable ion in 96% H_2SO_4 [Fig. 1(a)],[13] and the absorption spectrum in this solution is identical with the transients. Mecklenburg and Hilinski have previously observed **6** upon irradiation of **5** in methanol–water, in this case employing a picosecond flash photolysis apparatus because of the short lifetime of the cation in this solvent.[8] In TFE the 9-methylfluoren-9-yl cation decays with a rate constant of 8.6×10^6 s^{-1} at 25 °C. The absorption spectrum of **6** is typical of fluoren-9-yl cations, other 9-alkyl derivatives (9-ethyl, 9-isopropyl, 9-tert-butyl)[14] having identical spectra, 9-phenyl a λ_{max} at 490 nm,[10] and the parent a λ_{max} at 515 nm.[8,9] In all of these cases there is also a shoulder at 30–40 nm lower wavelength.

The transient spectrum obtained following irradiation of **2** is given in Fig. 1(b). This shows three bands, with λ_{max} at 340, 370 and 425 nm, all decaying with the same rate constant, 2.4×10^7 s^{-1} in 100% TFE at 25 °C. As shown by the comparison with the 9-methyl derivative, this spectrum is quite different from those of simple 9-alkylfluoren-9-yl cations. The transient, however, does show the characteristics of a cationic intermediate, being unaffected by oxygen but sensitive to the nucleophilicity of the medium. Coupled with the observed products and the well established photochemistry of fluoren-9-ols, this leads to the conclusion that this is the transient cation **3**. The possibility does exist that this spectrum, obtained with ca. 20 ns laser pulses, represents a rearranged species. To investigate this possibility, picosecond experiments were carried out, with monitoring above 400 nm. These indeed show that the 425 nm band is completely formed within a ca. 25 ps laser pulse. This is not surprising since previous picosecond studies have demonstrated that dehydroxylations of excited fluoren-9-ols occur in less than 25 ps.[8] With **2**, the key observation is that there is no 'initial' absorbance at 485 nm typical of a 9-alkylfluoren-9-yl cation. Thus the spectrum in Fig. 1(b) represents an intermediate formed on the 25 ps timescale.

The ability to study the kinetics of the decay of **3** provides the opportunity directly to probe the mechanism of its desilylation, with a few exceptions,[15] the common fate of β-silylcarbenium ions. As shown in Fig. 2, the decay is sensitive to the nucleophilicity of the medium, rate constants decreasing in a regular manner on proceeding from TFE to the more weakly nucleophilic 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP). Such behaviour, with a 10^3–10^4 TFE : HFP rate ratio, is typical of cationic intermediates that decay by reaction with the solvent. The acceleration in HFP by small amounts of methanol (see the insert to Fig. 2) is obviously also characteristic of a bimolecular pathway, as is a negative entropy of activation (-71 J mol^{-1} K^{-1} in 3:7 TFE–HFP). The conclusion is that the desilylation of **3** occurs in a one-step process via a transition state such as **9**, with participation by the solvent or other added nucleophiles. A similar conclusion has been reached for the desilylation of some silyl-substituted cyclohexadienyl cations.[16]

Silicon interacts with an adjacent positive charge principally via a hyperconjugative or vertical interaction,[1,2,17] as shown for the present case in the structure below.
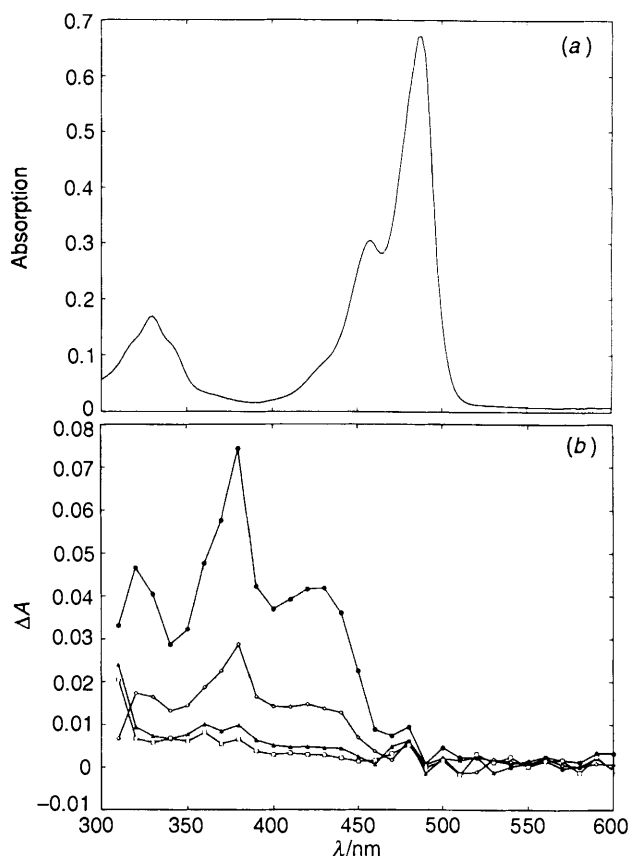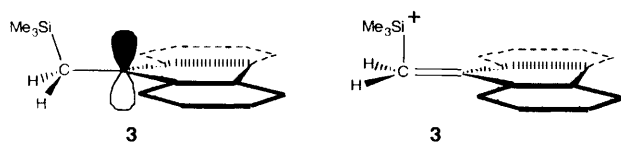
3   **3**

Fig. 1 (a) Absorption spectrum of the 9-methylfluoren-9-yl cation **6** in 96% H_2SO_4, and (b) transient absorption spectra obtained upon laser flash photolysis of 9-(trimethylsilylmethyl)fluoren-9-ol **2** in TFE
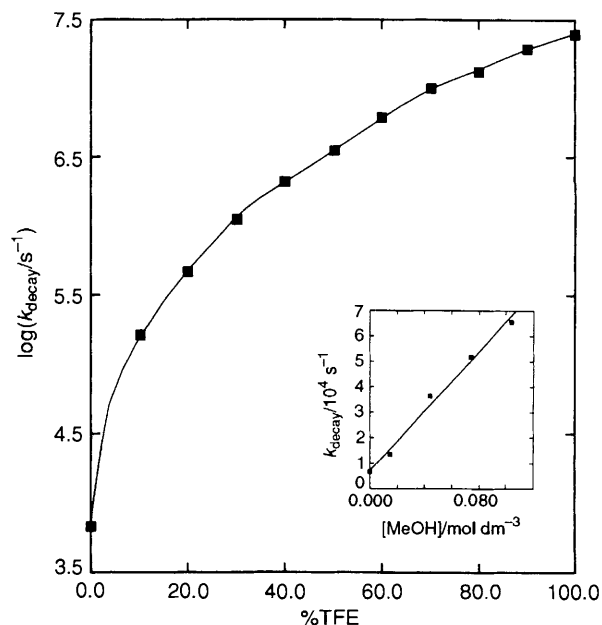
Fig. 2 log rate constants for the decay at 25 °C of the 9-(trimethylsilylmethyl)fluoren-9-yl cation **3** as a function of the volume% of TFE in TFE–HFP mixtures. The insert plots k_{decay} as a function of methanol concentration in 100% HFP; the slope of the line is 5.9×10^5 dm^3 mol^{-1} s^{-1}.

The markedly different absorption spectrum for **3** compared with simple 9-alkylfluoren-9-yl cations clearly indicates that this interaction has a significant perturbing effect. This is interesting in the light of the recent discussion of the nature of the interactions in an $[Et_3Si–toluene]^+$ complex whose crystal

structure with a tetraarylborate counterion[18] has been interpreted as representing a silyl cation with weak coordination to toluene,[18] a π-bonded complex,[19] or a silyl-substituted arenium ion.[20] Whatever the exact description, the geometry in the toluene, as revealed in both the crystal structure[18] and in *ab initio* calculations,[20] remains much like that of a typical aromatic ring, being significantly perturbed from that of an alkyl-substituted cyclohexadienyl cation.[20] A similar situation with **3** would correspond to a structure such as **3'**, with flattening of the CH_2 group towards the geometry of 9-methylenefluorene. The placement of significant positive charge on silicon would obviously explain why this is the sole site of nucleophilic attack in the cation. The transient spectrum, however, is quite different from that of 9-methylenefluorene, which has λ_{max} at 255 nm, with a shoulder at 300 nm. Thus a geometry intermediate between a classic 9-alkylfluoren-9-yl cation and a 9-methylenefluorene–Me_3Si^+ complex is most likely.

Experimental

Flash photolysis experiments were carried out in the standard fashion with *ca.* 20 ns pulses at 248 nm (*ca.* 60 mJ pulse^{-1}) of a Lumonics excimer laser (KrF emission), with *ca.* 10 ns pulses at 266 nm (*ca.* 80 mJ pulse^{-1}) from a Lumonics HY750 Nd/YAG laser,[21] and with *ca.* 25 ps pulses at 266 nm (*ca.* 4 mJ pulse^{-1}) from a Continuum YG-601-C Nd/YAG laser.[22] Product analyses were carried out by gas chromatography and HPLC, with authentic samples of the products as standards. Solutions of *ca.* 10^{-4} mol dm^{-3} substrate were irradiated at 254 nm in a Rayonet reactor, followed by direct injection into the GC or HPLC.

9-Methylfluoren-9-ol **5** is a known compound.[7]

9-(Trimethylsilylmethyl)fluoren-9-ol **2** was prepared through the reaction of trimethylsilylmethyllithium with fluorenone, followed by standard work-up and chromatography. Samples of this compound proved to be unstable, and were employed immediately after purification. M.p. 144–146 °C. $\delta_H(CDCl_3)$ −0.65 (9 H, s), 1.79 (2 H, s), 2.06 (1 H, br s, OH) and 7.25–7.64 (8 H, m) (Found: M^+, 268.1296. Calc. for $C_{17}H_{20}OSi$: M, 268.1283).

9-Methylenefluorene **4** was prepared by adding a small amount of HCl to a solution of **2** in methanol, followed by neutralization of the solution with $NaHCO_3$, removal of the methanol and chromatography. This compound also proved unstable on standing. $\delta_H(CDCl_3)$ 6.07 (2 H, s), 7.23–7.41 (4 H, m) and 7.70–7.75 (4 H, m) (Found: M^+, 178.0781. Calc. for $C_{14}H_{10}$: M, 178.0783).

9-Methyl-9-(2,2,2-trifluoroethoxy)fluorene **7** was prepared by adding a small amount of HCl to a dilute solution of **5** in TFE, followed by neutralization, removal of the solvent and chromatography. $\delta_H(CDCl_3)$ 2.48 (3 H, s), 4.35 (2 H, q,

CH_2CF_3) and 7.20–7.75 (8 H, m) (Found: M^+, 278.0913. Calc. for $C_{16}H_{13}F_3O$: M, 278.0918).

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