

Studies of 9-Fluorenyl Carbocations. Intramolecular Hydride Migration in a Substituted 9-Fluorenyl Carbocation

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The substituted fluorenyl cation, 9-(diphenylmethyl)fluorene-9-yl cation (**4**), is formed under stable ion conditions (low temperature/strong acid) from its corresponding alcohol **3**. This ion is transformed to a substituted diphenyl methyl cation **8** at ambient temperature via an apparent 1,2-hydride shift. Irradiation of 9-(diphenylmethyl)fluorene-9-ol in methanol gives products derived from the corresponding cation along with radical-derived products from C–C and C–O homolysis processes. The laser flash photolysis of this alcohol gave a transient corresponding to cation **4**. All of the photoproducts are derived from cation **4** or radical pathways. High level MO calculations point to a high barrier (23.8 kcal mol⁻¹) for the 1,2-hydride shift. This barrier is the consequence of the minimum energy conformation of this fluorenyl cation which is less than ideal for the periplanar geometry necessary for this process.

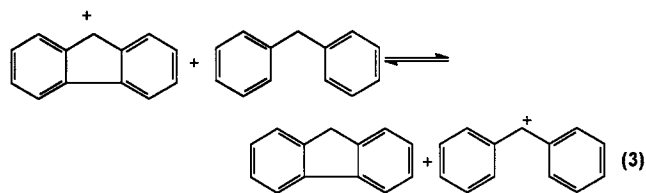
Introduction

Destabilized carbocations in which the positive charge center is incorporated in a 4n cyclic π -framework have been of interest as intermediates in solvolysis,^{1–3} as observable species under stable ion conditions,^{4–6} and as transients observable by laser flash photolysis in neutral solutions.^{7–10} Fluorenyl cations, an example of this class of cations, can be readily generated from their alcohol precursors under acidic conditions or on photoexcitation. Carbocations undergo rearrangements by 1,2-alkyl or hydride migration, and we recently reported a photochemical pinacol rearrangement originating from a fluorenyl cation in neutral solutions.¹⁰ Carbocations are also known to undergo inter-¹¹ as well as intramolecular¹² hydride transfer reactions from carbon–hydrogen donors. These are thermodynamically driven, giving the more stable species.¹⁷ Solution stabilities of carbocations have

been classically measured using the pK_R^+ scale based on eq 1. This scale is restricted only to the more stable carbocations since the reference state is that of a dilute aqueous solution. Another scale which has been referred to in comparing stabilities is the hydride affinity as shown in eq 2. Whereas gas-phase hydride affinities



of carbocations have been provided,¹³ direct thermodynamic measurements in solution are not feasible due to the immeasurably small extent of ionization associated with eq 2. Indirect measurements of solution hydride affinities of carbocations have been obtained using thermochemical cycles.^{14,15} Comparison of stabilities between 9-fluorenyl and diphenylmethyl cations (eq 3) indicates



an exoergic reaction of 4 kcal mol⁻¹ in DMSO¹⁴ and 8–9 kcal mol⁻¹ in acetonitrile.¹⁵ These compare with MO

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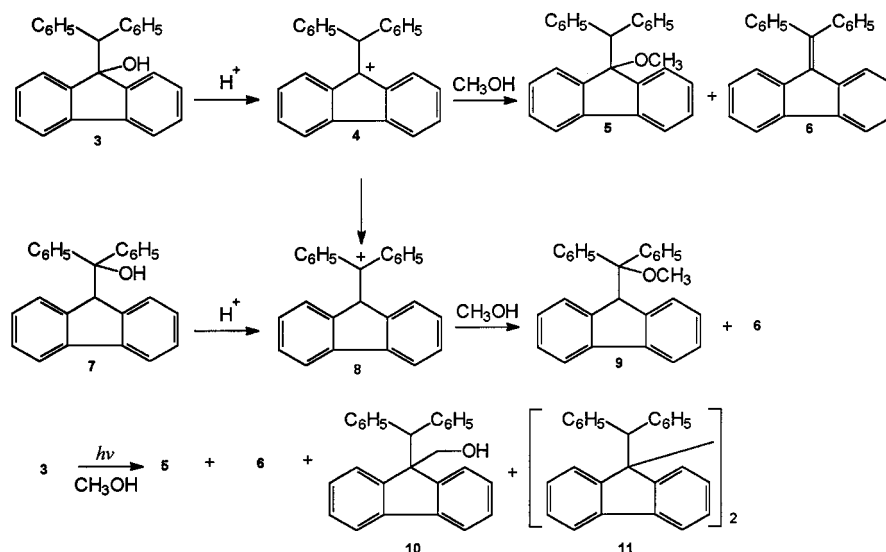
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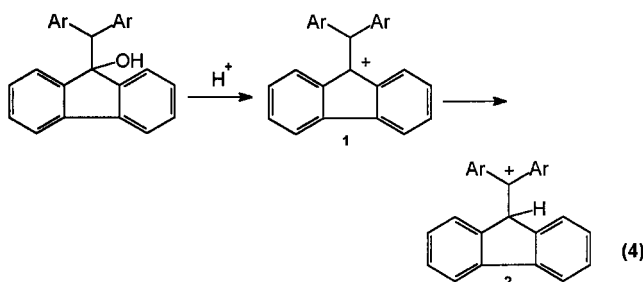
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Scheme 1



calculated values of ΔE_{el} of -9.8 and -11.0 kcal mol⁻¹ (at HF/6-31G (dp) and MP2/6-31 G(d), respectively), and with a correction to 298 K a value of ΔH° of -10.4 kcal mol⁻¹ (at MP2)¹⁶ in the unsolvated system. In an attempt to compare relative kinetic and thermodynamic stabilities of 9-fluorenyl cation with various diarylmethyl cations we chose to investigate the possible intramolecular hydride transfer associated with the transformation of cation **1** to cation **2** (eq 4). Such intramolecular hydride



transfer reactions in uncongested cations usually occur with low activation barriers.¹⁷ We report in this study the reactions of cation **1** (Ar = C₆H₅) generated under stable ion conditions as well as by photoheterolysis.

Results and Discussion

Observations under Stable Ion Conditions. The precursor to the fluorenyl cation **4** was 9-fluorenyl (**3**) which was prepared by a modified method (Scheme 1) as described in the literature¹⁸ with improved yields. When a methylene chloride solution of **3** was added to a cooled (-78 °C) solution of chlorosulfonic acid, a deep red-colored species was observed which exhibited an intense band at $\lambda_{max} = 494$ nm in the UV/visible spectrum (Figure 1a). Upon quenching of the cold red-colored solution with methanol, two major products were observed whose structures were assigned to the methanol-quenched product **5** (15%) derived from cation **4** and the dehydration product **6** (60%). When the cold red-colored solution was warmed to room temperature, a color change to yellow was observed. The UV/visible spectrum of this

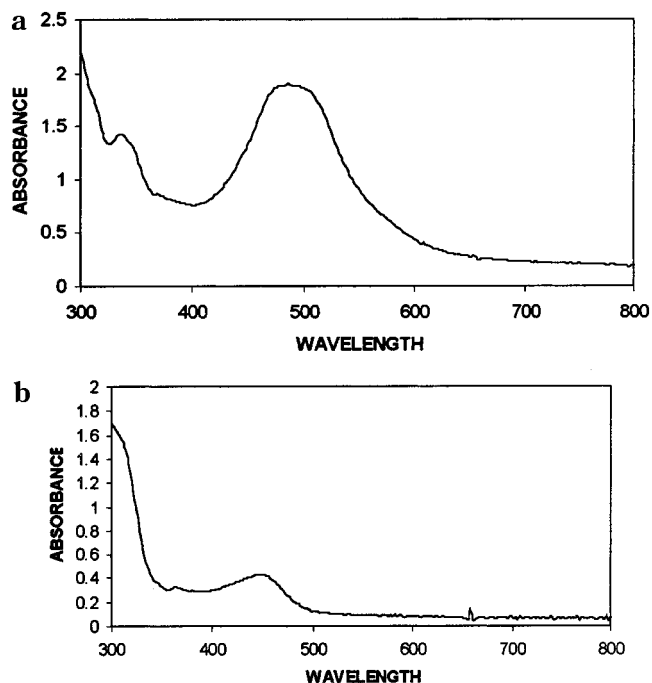


Figure 1. (a) UV/visible spectrum of alcohol **3** in CISO₃H/CH₂Cl₂ at -78 °C. (b) UV/visible spectrum of alcohol **3** in CISO₃H/CH₂Cl₂ after warming to room temperature.

solution showed a peak at $\lambda_{max} = 410$ nm (Figure 1b). Quenching of this solution with methanol gave two major products which were identified as ether **9** (65%) and alkene **6** (16%). We assign the red-colored species to the fluorenyl cation **4** and the yellow-colored one to the isomeric cation **8** based on the observed methanol-quenched products as well as the similarity of their UV-visible spectra to those for typical 9-fluorenyl and diphenylmethyl cations.^{7,20} Furthermore, cation **8** (a yellow-colored solution) was generated independently from alcohol **7** under similar conditions and upon quenching with methanol gave a similar product distribution as

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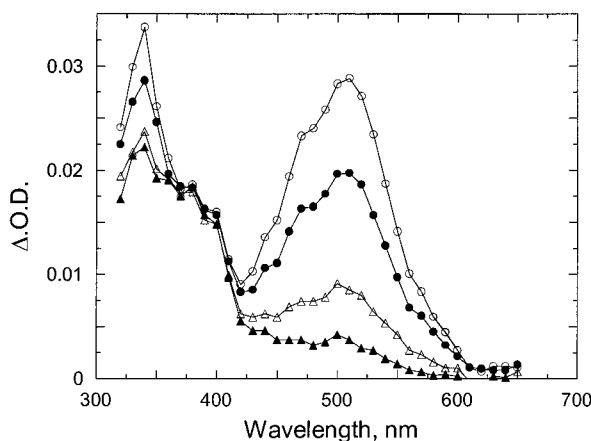


Figure 2. Transient absorption spectrum measured after 308-nm excitation of diphenylmethyl-9-fluorenyl in 2,2,2-trifluoroethanol. Spectra were recorded 0.4 (○), 5.2 (●), 15.2 (△) and 27.2 (▲) μs after laser excitation.

observed for the methanol quenching of the room-temperature solution obtained from alcohol **3** in chlorosulfonic acid.

Photoproduct Studies. Irradiation (1 h, medium-pressure Hg lamp, Pyrex filter) of a methanolic solution of alcohol **3** gave a complex mixture of products from which ether **5** and alkene **6** were obtained in 20% and 5% yields, respectively, and compared with the same products obtained from the strong acid experiments. The remaining portion consisted of unreacted alcohol (29%), fluorenone (14%), 9-(diphenylmethyl)fluorene (3%),¹⁸ alcohol **10** (12%), and hydrocarbon **11** (10%). All photoproducts except **10** and **11** were characterized by comparison with authentic samples or literature data for the same compounds. Alcohol **10** and hydrocarbon **11** were characterized by NMR and mass spectrometry. The presence of ether **5** and alkene **6** suggests the intermediacy of cation **4** with the remaining products accountable from C–C and C–O homolysis reactions. The absence of ether **9** in the photolysis mixture as indicated by the ¹H NMR spectrum of the crude mixture would indicate that cation **8** was not involved and that 1,2-hydride migration in the transformation of cation **4** to **8** did not take place in the photolytic process. Control experiments showed that ether **9** was photostable under the irradiation conditions. To gain further insight as to the intermediates involved in the photoexcitation of alcohol **3**, we carried out laser flash photolysis experiments.

Laser Flash Photolysis Studies of Alcohol 3. Transient spectra obtained by 308 nm laser excitation of alcohol **3** in aerated 2,2,2-trifluoroethanol (TFE) are shown in Figure 2. The spectra show a transient with λ_{max} at 505 nm that decays cleanly to baseline with a lifetime of $\sim 14 \mu\text{s}$ as well as a second absorption below 400 nm. Part of the short wavelength signal decays with kinetics (measured at 340 nm) that are comparable to those obtained at 505 nm. The residual absorption (see 27 μs spectrum in Figure 2) is long-lived and does not decay appreciably over a 100 μs time window. The 505 nm transient is insensitive to oxygen but reacts rapidly with nucleophiles such as bromide ion and alcohols. On the basis of these results and the spectral similarity to a number of other substituted 9-fluorenyl cations, we assign this transient to cation **4**. Note that the cation

Table 1. Bimolecular Quenching Rate Constants for Cation 4 in TFE and 9-Fluorenyl Cation (9-FI⁺) in HFIP

quenchers	k_q ($\text{M}^{-1} \text{s}^{-1}$) cation 4	k_q ($\text{M}^{-1} \text{s}^{-1}$) 9-FI ⁺ ^a
Br ⁻	9.5×10^8	9.6×10^9
MeOH	2.3×10^6	1.8×10^7
EtOH	1.1×10^6	1.3×10^7
i-PrOH	5.9×10^3	7.9×10^6
H ₂ O	1.9×10^5	1.5×10^6

^a Reference 6.

clearly has an additional absorption at 340 nm that is responsible for some of the short wavelength signals observed at early times after laser excitation. Similar results were obtained in 1:1 TFE/hexafluoro-2-propanol (HFIP), except that in this case the cation was much longer-lived, with a lifetime of 300 μs .

Cation **4** is much longer-lived than the parent 9-fluorenyl cation which decays too rapidly to be observed on a nanosecond time scale in TFE and has a lifetime of $\sim 30 \mu\text{s}$ in HFIP.⁸ By contrast, cation **4** is approximately five times shorter-lived than the 9-phenyl-9-fluorenyl cation.²⁴ Steric crowding is likely to be responsible for the enhanced lifetime of both **4** and the 9-phenyl-9-fluorenyl cation. π -Stabilization of the phenyl substituent in the latter would not be expected to be of any significance due to the nonplanar conformation expected for this ion. The 9-methyl-9-fluorenyl cation is shorter-lived than either **4** or the 9-phenyl cation, although significantly stabilized with respect to the parent 9-fluorenyl cation.²³

As noted above, cation **4** reacts efficiently with nucleophiles; bimolecular quenching rate constants are listed in Table 1 along with data for the parent 9-fluorenyl cation in HFIP. The variation in quenching rate constants shows a similar trend with other 9-fluorenyl cations. Cation **4** is approximately one order of magnitude less reactive toward bromide ion than the parent 9-fluorenyl cation in HFIP; the difference between the two would be more pronounced if the reactivity of **4** was also measured in HFIP. The rate constants for bromide ion quenching are similar for **4** and the 9-phenyl-9-fluorenyl¹⁸ cations (6.8 and $9.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively, in TFE), consistent with the relatively modest differences in lifetime between the two.

The broad residual absorption between 330 and 380 nm that remains after decay of cation **4** is not affected by either oxygen or nucleophiles. The lack of oxygen sensitivity suggests that this is not a triplet excited state. Other possibilities are 9-fluorenyl radicals or radical cations; however, these would both be expected to have additional longer wavelength absorptions at 500 and 640 nm (for radicals and radical cations, respectively).^{6,8,9} The radical cation of **3** was generated independently using triplet chloranil in acetonitrile and shows two maxima at 620 and 400 nm in good agreement with literature data. Thus, the long-lived species does not correspond to the radical cation based on the spectral data. Similar long-lived short wavelength species have been observed upon laser excitation of other 9-fluorenyl cation precursors.

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sors and are probably related to product formation. Another possibility for this long-lived species is the 9-benzhydryl-9-fluorenyl radical. Such an intermediate would be expected to be relatively inert toward oxygen due to steric crowding. LFP of alcohol **3** in a nonpolar solvent such as cyclohexane purged with oxygen gave a long-lived transient similar to that observed in the TFE experiments. The continuous photolysis of alcohol **3** in oxygen-saturated methanol solution resulted in fluorenone and benzophenone as the principal photoproducts, an indication of radical processes involving oxidative cleavage of the carbon-carbon bond.

The transient spectrum obtained for alcohol **3** did not show any evidence for formation of a peak at 410 nm associated with cation **8**. This plus the kinetic data obtained for cation **4** are consistent with the continuous irradiation product studies in which ether **9** was not detected. Thus, none of the photolysis experiments in solution at room temperature provide any evidence for a 1,2-hydride shift in cation **4**.

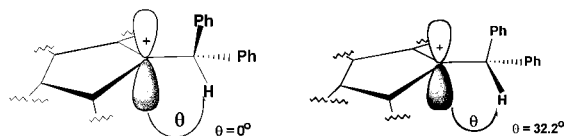
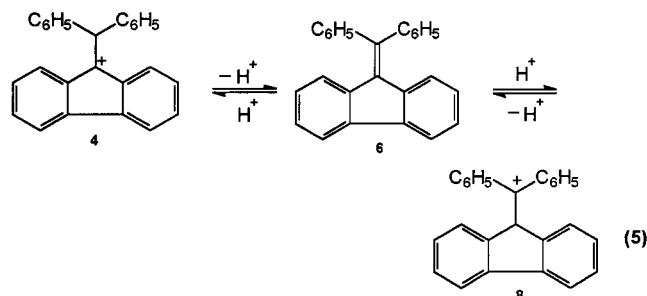


Figure 3. Conformations of cation **4**. (left) Periplanar geometry for C-H migration. (right) Minimum energy conformation.

Theoretical Calculations for the 1,2-Hydride Shift in Cation 4. To probe the energetics and conformations for the hydride shift in the transformation of cation **4** to **8**, theoretical calculations for both ions and the transition state were performed using semiempirical (AM1) and ab initio (HF/6-31++G(d,p)) calculations. The difference in the AM1 heats of formation favors cations **8** over **4** by 5.6 kcal mol⁻¹ with an activation enthalpy of 23.8 kcal mol⁻¹. At the higher level calculations (HF/6-31++G(d,p)), the transformation of **4** to **8** is exothermic by only 1.1 kcal mol⁻¹ ($\Delta G_{298} = 0.44$ kcal mol⁻¹) with an activation enthalpy of 24.7 kcal mol⁻¹ ($\Delta G_{298} = 24.2$ kcal mol⁻¹). The large activation barrier is associated with the less than ideal periplanar geometry between C-H and the vacant p-orbital required for the hydride shift (Figure 3). The dihedral angle for the minimum energy conformer was calculated to be 32.18° (at the HF/6-31++ G(d,p)) level (Figure 2). The small calculated difference in the free energy of formation between cations **4** and **8** suggests that "antiaromaticity" does not contribute to any significant extent in the destabilization of cation **4**. Recent high level calculations on the magnetic susceptibility and chemical shifts of the 9-fluorenyl cation suggest that it is a nonaromatic system as compared to the antiaromatic character of cyclopentadienyl and indenyl cations. Amyes, Richard, and Novak³ measured the pK_R^+ value for fluorenyl and diphenylmethyl cations (-15.9 and -11.7, respectively) and calculated a destabilization energy of 5.7 kcal mol⁻¹ for 9-fluorenyl cation. Alkyl substitution

in 9-fluorenyl cations such as **4** would be expected to further decrease this destabilization energy.

The strong acid studies of alcohol **3** appear to be in contradiction to the photochemical investigations in that direct evidence for the hydride shift **4** → **9** is obtained from the UV/visible spectral data and product studies in the former. This difference can be rationalized in terms of a deprotonation-protonation equilibrium through intermediate **6** (eq 5). Such processes are well-known in

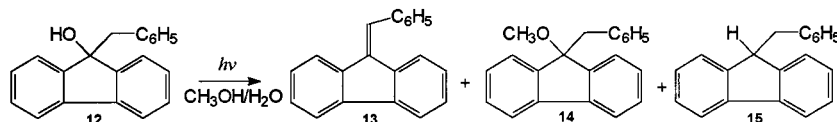


the strong acid chemistry of alkenes¹⁷ where carbocations are significantly longer-lived than in neutral solutions. In nonacidic conditions such as those employed for the photochemical studies protonation of alkene **6** would not be expected to occur. The formation of alkene **6** in the irradiation of alcohol **3** can proceed via deprotonation of cation **4**. In a photosolvolysis study of a related alcohol **12**, Wan and co-workers suggested that dehydration product **13** may have arisen from the corresponding radical intermediate.²² The methanolysis product **14** is the major product which undergoes secondary photochemistry via C-O homolysis to give the reduced product **15** as the exclusive product (Scheme 2). Thus **13**, and in our case **6**, is likely formed from C-O heterolysis in **3** and the intermediacy of cation **4** by an E1 reaction. Evidence for the E1 reaction was obtained when the photosolvolysis was carried out in the more polar solvent, 2,2,2-trifluoroethanol (TFE), which gave a cleaner reaction mixture consisting of a 4:1 mixture of alkene **6** and the TFE quenched product. Alkene formation (E1) would be expected to be more favorable in the case of alcohol **3** than in **12**.

Conclusions

The alcohol, 9-diphenylmethyl-9-fluorenyl **3** produces the corresponding fluorenyl cation **4** at low temperature in chlorosulfonic acid solutions. Under these conditions this cation undergoes a hydrogen migration to give the diphenyl(flourenyl)methyl cation **8** as evident from the UV/visible spectral change and the product analysis. Irradiation of alcohol **3** gave products derived from cation **4** and carbon radicals from both C-O and C-C homolysis. Under these conditions there was no evidence for formation of cation **8**. Laser flash excitation of **3** gave a transient associated with cation **4** which could be quenched with nucleophiles showing a similar trend with other fluorenyl cations. There was no spectral evidence for

Scheme 2



cation **8** in the LFP transient spectrum. Semiempirical and high level calculations for cations **4** and **8**, and the transition state of the 1,2-hydride migration, indicated that the periplanar geometry for this transformation is not attained. The activation barrier is too large for the hydride migration to occur at ambient conditions. The hydrogen shift observed under the strong acid conditions is most likely occurring via a deprotonation–protonation equilibrium process. The enthalpy and free energy difference between cations **4** and **8** are surprisingly small and suggests that **4** is not destabilized.

Experimental Section

Continuous irradiations were performed using a Hanovia 450W medium-pressure mercury arc lamp in a water-cooled quartz immersion well. Pyrex tubes containing samples dissolved in methanol were strapped around the immersion well with the whole assembly immersed in an ice–water bath. The samples were purged with nitrogen prior to irradiation. For the radical-derived photoproduct studies, the solution was purged with oxygen.

Laser flash photolysis were carried out at room temperature with 6-ns pulse, typically <40 mJ of 308 nm monochromatic light from a Lumonics EX-510 excimer laser. The laser system has been described in detail.¹⁹

All chemicals used were purchased from Aldrich. The solvents were dried and distilled freshly prior to use.

9-Hydroxy-9-benzhydrylfluorene (3). To a solution of diphenylmethane (1.0 g, 6.0 mmol) in THF (50 mL) at 0 °C under nitrogen was added *n*-butyllithium (2.4 mL of 2.5 M solution in hexanes). The resulting orange-red solution was left to stir for 30 min. To this solution was added 9-fluorenone (1.08 g, 6.0 mmol) in THF (20 mL) and allowed to warm to room temperature with stirring for 3 h. The reaction was quenched by adding saturated aqueous NaCl, the organic layer was separated, dried with anhydrous MgSO₄, and filtered, and the solvent was evaporated. The residue was purified by column chromatography (silica gel; 8:1 hexane:ethyl acetate) giving 1.5 g (74%) of the title alcohol; mp 185–186 °C (lit.¹⁸ mp 183 °C); ¹H NMR δ 7.55 (d, *J* = 7.6 Hz, 2H), 7.34–7.33 (m, 4H), 7.26 (d, *J* = 7.39 Hz, 2H), 7.19–7.17 (m, 6H), 7.03 (t, *J* = 7.43 Hz, 2H), 6.75 (d, *J* = 7.52 Hz, 2H), 4.39 (s, 1H), 2.32 (s, 1H, OH); ¹³C NMR δ 148.1, 140.7, 139.8, 130.2, 128.9, 127.9, 127.3, 126.7, 125.4, 119.8, 84.4, 60.3; MS *m/z*: 348 (M⁺) (25) 181 (100), 152, 105, 77.

9-Fluorenyl-diphenylmethanol (7). To a solution of fluorene (1.0 g, 6.02 mmol) in THF (50 mL) at 0 °C under nitrogen was added *n*-butyllithium (2.41 mL of 2.5 M solution in hexanes). The resulting red-colored solution was left to stir for 20 min. To this solution was added benzophenone (1.1 g, 6.0 mmol) dissolved in THF (10 mL), and the solution was allowed to stir for 3 h at room temperature. The reaction was quenched by the addition of an aqueous saturated NaCl solution. The organic layer was separated, dried with anhydrous MgSO₄, and filtered and the solvent evaporated to give a residue which was purified by column chromatography (silica gel; 8:1 hexane:ethyl acetate) to give 1.32 g (63%) of the title alcohol; mp 230–232 °C;²⁵ ¹H NMR δ 7.73–7.67 (m, 6H), 7.39–7.28 (m, 8H), 6.98 (t, *J* = 7.51 Hz, 2H), 6.52 (d, *J* = 7.73 Hz, 2H), 5.29 (s, 1H), 1.95 (s, 1H, OH); ¹³C NMR δ 145.9, 142.8, 142.5, 128.2, 127.8, 127.1, 126.5, 126.4, 126.37, 119.6, 80.2, 56.8; MS *m/z*: 330 (M – H₂O), 183 (100), 165, 105.

9-Benzhydrylidenefluorene (6). To a solution of alcohol **3** (0.5 g, 1.44 mmol) in C₆H₆ (25 mL) was added toluenesulfonic acid (0.025 g, 0.14 mmol). The reaction was left to reflux overnight. The mixture was washed using 2 × 10 mL of sat. NaHCO₃. Separation of the organic layer and evaporation of

solvent gave 0.47 g (99%) of alkene **6**; mp 228–229 °C (lit.²⁶ mp 229.5 °C); ¹H NMR δ 7.69 (d, *J* = 7.50 Hz, 2H), 7.41–7.35 (m, 10H), 7.24 (d × d, 2H), 6.92 (t, *J* = 7.73 Hz, 2H), 6.62 (d, *J* = 7.96 Hz, 2H); MS *m/z*: 330 (M, 100), 253 (30).

9-Methoxy-9-benzhydrylfluorene (5). The alcohol **3** (0.1 g, 0.29 mmol) was dissolved in 25 mL of benzene. To this solution were added 0.02 g of toluenesulfonic acid and 25 mL methanol, and the solution was left to stir for 15 h. This mixture was washed with 2 × 5 mL of saturated NaHCO₃. Separation of the organic layer and evaporation gave a residue which crystallized in methanol, 0.06 g (60%); mp 188–190 °C; ¹H NMR δ 7.58 (d, *J* = 7.56 Hz, 2H), 7.36 (d, *J* = 5.12 Hz, 4H), 7.27 (t, *J* = 7.48 Hz, 2H), 7.18 (m, 6H), 6.99 (t, *J* = 8.92 Hz, 2H), 6.58 (d, *J* = 7.56 Hz, 2H), 4.17 (s, 1H), 2.79 (s, 3H); ¹³C NMR δ 144.7, 141.3, 140.9, 130.4, 128.7, 127.6, 126.7, 126.4, 126.1, 119.6, 90.7, 61.0, 51.4; MS *m/z*: 362 (M), 195 (100), 180, 167, 165, 152.

9-Fluorenyl-diphenylmethoxymethane (9). Alcohol **7** (0.1 g, 0.29 mmol) was dissolved in 25 mL of benzene and 25 mL of methanol. To this solution was added 0.02 g of toluenesulfonic acid, and the solution was left to stir for 15 h. Workup of the reaction mixture as for the preparation of **5** gave 0.08 g (80%) of the title ether; mp 156–158 °C; ¹H NMR δ 7.39 (d, *J* = 7.48 Hz, 4H), 7.26–7.09 (m, 14H), 5.12 (s, 1H), 3.03 (s, 3H); ¹³C NMR δ 143.6, 142.1, 138.0, 129.4, 127.2, 127.1, 127.08, 126.9, 126.1, 119.0, 87.9, 56.9, 52.0; MS *m/z*: 362 (M), 330, 252, 197 (100), 165, 105, 77.

Formation and Methanol Quenching of Cation 4. A solution of alcohol **3** (5 mg) in CH₂Cl₂ (5 mL) was cooled in a dry ice–acetone bath (–78 °C). This solution was added to a cooled (–78 °C) solution of chlorosulfonic acid (1 mL) in 4 mL of CH₂Cl₂ dropwise with stirring. A deep red color was seen immediately after addition (λ_{\max} = 494 nm). This cold solution was immediately transferred to a flask containing 5 mL of methanol whereupon the red color disappeared. Extraction with chloroform (10 mL), washing with water and saturated NaHCO₃, separation of the organic layer, and evaporation gave a residue. The ¹H NMR spectrum of this residue was taken and shown to consist only of alkene **6** and ether **5** in a 4:1 ratio, respectively, by comparison with the ¹H NMR spectra of authentic samples prepared above.

Quenching of Carbocation 8 with Methanol. Carbocation **4** was prepared in the same way as above. However, the carbocation solution was permitted to warm to room temperature for 15 min, and a color change from red to yellow was visible (λ_{\max} = 410 nm). Quenching with methanol and workup in identical fashion as above gave a residue whose ¹H NMR spectrum showed the presence of two main products alkene **6** and ether **9** in a 1:4 ratio by comparison with authentic samples prepared above.

Photolysis of Alcohol 3. A solution containing alcohol **3** (0.05 g, 1.44 mmol) in 50 mL of methanol in a Pyrex tube was irradiated for 1 h in a nitrogen atmosphere. After evaporation of the solvent, the residue was chromatographed by thin-layer chromatography (8:1 hexane/ethyl acetate).

The bands were separated and identified by comparison with authentic samples: unreacted alcohol **3** (29%), fluorenone (14%), ether **5** (5%), alkene **6**, 9-diphenylmethylfluorene¹⁸ (3%), alcohol **10** (12%), and hydrocarbon **11** (10%).

Alcohol 10. ¹H NMR δ 7.70 (d, *J* = 7.57 Hz, 2H), 7.37–7.26 (m, 4H), 7.15 (t, *J* = 7.70 Hz, 2H), 7.10–7.03 (m, 10H), 5.27 (s, 1H), 3.68 (s, 2H), 1.73, (s, 1H, OH), MS *m/z*: 362 (M), 331, 167 (100).

Hydrocarbon 11. ¹H NMR δ 7.52 (d, *J* = 7.56 Hz, 2H), 7.28 (m, 10H), 7.18 (t, *J* = 7.26 Hz, 2H), 7.01 (m, 18H), 6.96 (t, *J* = 7.38 Hz, 2H), 6.87 (d, *J* = 7.71 Hz, 2H), 4.91 (s, 2H); MS *m/z*: 662 (M), 331 (95), 253, 167 (100).

Theoretical Calculations. All calculations were performed using Gaussian 98.^{27,28} Hartree–Fock calculations in conjunc-

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tion with the 6-31++G(d,p) basis set were employed for structure optimizations and for the characterization of critical points using harmonic vibrational frequencies.^{29–32} A guess structure for the transition state was determined using the QST2 method. The first-order saddle point was then found using the Bery transition-state algorithm and the CalcAll method.

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Supporting Information Available: Elemental analyses, ¹H NMR, and mass spectra for compounds **5** and **9** are given. In addition, the ¹H NMR and mass spectra for **10** and **11** are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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