Photochemical Pinacol Rearrangements of Unsymmetrical Diols

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The photochemical pinacol reaction of a series of nonsymmetrical 9-fluorenyl-substituted *vic*-diols was investigated and compared with their acid-catalyzed thermal reaction. Unlike the thermal reaction, the radiation-induced processes involve only fluorenyl cations, as is reflected in differences of product distribution between the two reactions. From the product studies, substituent migratory aptitudes are reversed in the photochemical process, suggesting that kinetic control takes place under neutral conditions unlike the acid-catalyzed thermal reactions. The presence of fluorenyl cation intermediates and their lifetimes were established by laser flash spectroscopy studies.

Introduction

The pinacol rearrangement of *vic*-diols has been known since 1860.[1] This transformation involving a dehydration and skeletal rearrangement is one of the earliest documented Wagner−Meerwein rearrangements in carbocation chemistry and has been used as a key step in organic synthesis.[2] The intermediate cations are usually generated under Lewis or Bronsted acid conditions, which often result in regioisomeric mixtures of ketones and aldehydes when unsymmetrical diols are used (eq 1).
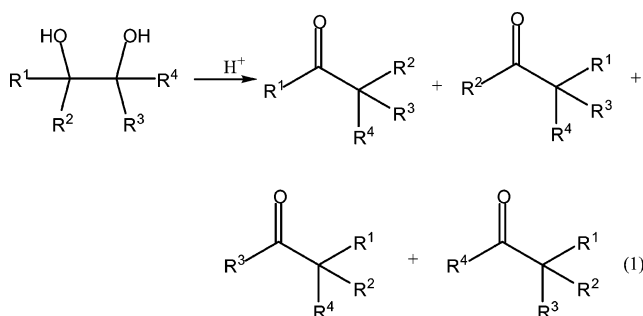
Regioselectivity is determined by stability of the primary formed carbocation as well as migratory aptitudes of the diol substituents, which in turn are predicated by stereoelectronic factors.[3] Furthermore, the aldehydes and ketones produced, under the acid conditions used, are subject to interconversions such that the product distri-

bution is often thermodynamically controlled and dependent on the conditions used.[4] Our interests in destabilized carbocations such as 9-fluorenyl cations generated under photochemical conditions have extended to investigations of their kinetic stabilities as well as their tendency to undergo rearrangements.[5,6] Since the intermediate carbocations are produced in neutral solutions, such rearrangements are not subject to thermodynamic equilibration normally encountered in acid conditions, and thus product distributions are kinetically controlled and more reflective of substituent migratory aptitudes. Several years ago we reported the first photochemical pinacol rearrangement of symmetrical 9-bifluoren-9-ol to the corresponding ketone.[6] Competitive ketyl formation by homolytic cleavage was also observed in acetonitrile solutions. However, the pinacol rearrangement was the principal pathway in 2,2,2-trifluoroethanol (TFE), a solvent known to promote carbocation formation.[7] To assess migratory aptitudes of different substituents in pinacol rearrangements unaffected by acid equilibration, we investigated the photochemistry of a series of *vic*-diols derived from 9-fluorenol. We chose this particular structure motif because fluorenols are susceptible to heterolytic dissociation to fluorenyl cations on photoexcitation[8] and these transients exhibit characteristic visible absorption features in time-resolved spectra.[9] A series of unsymmetrical fluorenyl diols **1** were prepared, and their photochemistry was investigated and compared with their acid-catalyzed dark reaction products.

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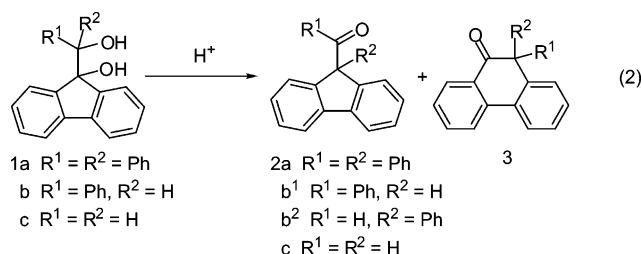
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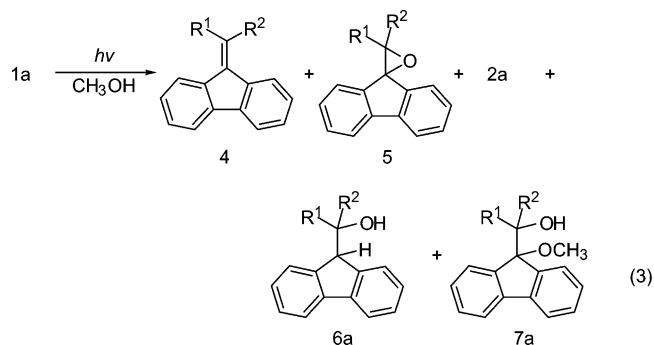
Results and Discussion

Product Studies. Diol **1a** was prepared by treating methyl 9-hydroxy-9*H*-fluorenecarboxylate with phenyl-magnesium bromide according to a literature procedure.[10] Diol **1b** was obtained by condensation of 9,9-dichloro-fluorene with benzaldehyde via the 9-chlorofluorenyl anion obtained by metal halogen exchange. The inter-mediate epoxide underwent rapid ring opening in the acidic aqueous workup, giving diol **1b** in 75% yield. Diol **1c** was synthesized by LAH reduction of 9-hydroxy-9-fluorenecarboxylic acid. The acid-catalyzed thermal reac-tions were carried out in CDCl$_3$ solutions with catalytic quantities of toluenesulfonic acid. Diol **1a** under these conditions gave two principal ketones, **2a** and **3** ($R^1 = R^2$ = Ph) in a ratio of 3:1 (eq 2) similar to observations

$$1a \quad R^1 = R^2 = Ph$$
$$b \quad R^1 = Ph, R^2 = H$$
$$c \quad R^1 = R^2 = H$$

$$2a \quad R^1 = R^2 = Ph$$
$$b^1 \quad R^1 = Ph, R^2 = H$$
$$b^2 \quad R^1 = H, R^2 = Ph$$
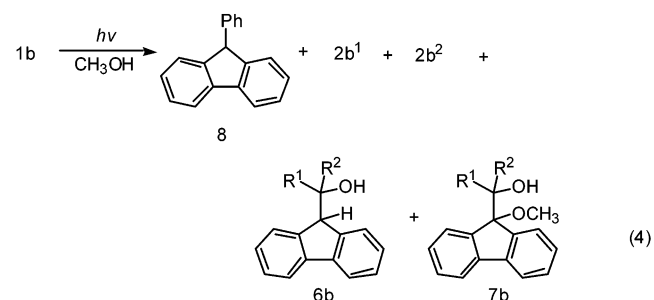$$c \quad R^1 = R^2 = H$$

$$3$$

previously reported for the reaction of the same diol.[11] This distribution is dependent on the acid concentration, with the thermodynamic product **3** predominating in more acidic solutions. Equilibration between the two ketones takes place in strong acid. Irradiation of **1a** in methanol/acetonitrile (4:1 v/v) solution produced 9-ben-zoyl-9-phenyl fluorene (**2a**) as the major product (31%) along with epoxide **5** ($R^1 = R^2 = Ph$) (18%) representing dehydration of diol **1a**. Formation of epoxide intermedi-ates in acid-catalyzed pinacol rearrangements has been previously observed.[12] The product from methanol quench-ing (4%) represents a minor component of the reaction mixture, indicating the relatively high efficiency of the unimolecular process as compared to solvent quenching. Some 9-phenylfluorene (**8**) was observed on prolonged radiation and was established to be a secondary photo-product derived from **2a** by independent experiments. It is interesting to note the absence of ketone **3** in the photochemical process, suggesting that fluorenyl cation is the principal ionic species involved in the photochemi-cal reaction. The remaining products **4** and **6a** appear to be derived from radical pathways involving homolytic C−O or C−C dissociations. Alkene **4** is likely derived from deoxygenation of epoxide **5** by a carbene such as tetraphenylmethylene or fluorenylidene, a process which has been previously documented.[13] The same alkene **4** is obtained from the photolysis of epoxide 5 (*vide infra*).

The acid-catalyzed thermal reaction of **1b** gave two regioisomeric carbonyl derivatives, **2b¹** and **2b²** in a 2:1

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ratio, respectively. Under these conditions no product from biphenyl migration (i.e., **3**) was produced, suggesting that the primary intermediate involved is the more stable fluorenyl rather than benzyl cation. By contrast, irradia-tion of **1b** resulted in the formation of 9-phenyl fluorene (**8**) as the major product (33%) with minor amounts of ketone **2b¹** (8%) and aldehyde **2b²** (trace amount) (eq 4).

Hydrocarbon **8** is likely a secondary photoproduct arising from photodecarbonylation of aldehyde **2b²**. Irradiation of a solution of aldehyde **2b²** gave clean conversion to 9-phenylfluorene (**8**) under the same conditions. On the other hand, photodecarbonylation of ketone **2b¹** is not a favorable process, as was verified independently showing **2b¹** to be photostable under these conditions. Thus, the major pathway involves a phenyl migration in the photochemical process, in contrast to the acid-catalyzed dark reaction. A small amount of the methanol quenched product **7b** (2%) from the corresponding 9-fluorenyl cation accompanied the photoproducts. A small amount of the radical derived product **6b** was also observed in this mixture.

The photolysis of diols **1a** and **1b** in TFE, a solvent used to detect the intermediate carbocations (*vide infra*), did not show significant differences in product distribu-tion from methanol/acetonitrile solutions except for slightly larger yields of cation-derived products and the absence of TFE-quenched products.
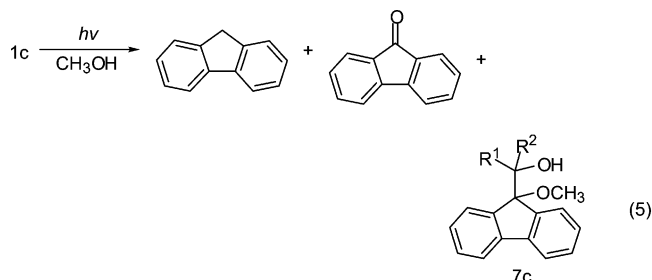
Diol **1c** was stable to the acid-catalyzed thermal reaction conditions used for the pinacol rearrangement of diols **1a** and **1b**. On the other hand, photolysis of diol **1c** resulted in the formation of fluorenone (22%) and parent fluorene (10%) as the major products, with a small yield of the methanol quenched product **7c** (eq 5). The remaining material consists of oligomeric products that could not be identified. The formation of fluorene can be rationalized in terms of an ionic process involving hydride shift of the corresponding fluorenyl cation to give 9-formylfluorene followed by photodecarbonylation. Al-ternatively, a radical process involving C−C homolysis

(5)

SCHEME 1

of the corresponding fluorenyl radical would result in 9-fluorenyl radical, which on hydrogen abstraction gives fluorene (Scheme 1). In a labeling experiment, the photolysis of 9-(α,α-dideutero-hydroxymethyl)-9-fluorenol resulted in exclusive formation of 9,9-dideutero-fluorene with no monodeuterated fluorene detected as evident from ^{1}H NMR spectroscopy and mass spectrometry. The latter observation is consistent with the ionic pathway leading to 9-deuteroformyl-9-deuteriofluorene as an intermediate followed by a photodecarbonylation via a radical cage complex. Photodecarbonylation of β,γ-unsaturated aldehydes occurs with high quantum efficiencies, with incorporation of the aldehydic hydrogen as was reported from deuterium labeling.[14]

The formation of epoxides as intermediates in pinacol rearrangements has been attributed to internal capture of the carbocation by the β-hydroxyl group.[12] The possibility of the epoxide-derived zwitterion (from fluorene-C(9)−O bond cleavage) formed on irradiation of **1a** in neutral solution was explored in view of the significant amounts of epoxide **5** ($R^1 = R^2 = Ph$) produced. Such a species might be expected from heterolytic dissociation of hydroxide followed by proton transfer from the resulting fluorenyl cation. A similar zwitterion was observed in the photolysis of 9-hydroxyfluorene-9-carboxylic acid in neutral solution.[9] Although the zwitterion is expected to be the thermodynamic product from the more acidic carboxylic acid group, similar proton transfer in the case of the diols is not as apparent. Epoxide **5** ($R^1 = R^2 = Ph$) was prepared independently by a literature procedure[15] and subjected to photolysis under the same conditions as **1a**. A similar distribution of photoproducts was observed as in the case of diol **1a** with the exception that the methanol-quenched product **7a** was not detected in the epoxide photolysis. Although the presence of the zwitterion intermediate in the diol photolysis could not be unequivocally established from the epoxide photoproduct distribution, the absence of **7a** in the epoxide reaction suggests that such zwitterions if formed are shorter-lived relative to their conjugate acid (the corresponding fluorenyl cation) so as to preclude solvent capture. Such behavior for the zwitterion would be expected as a result of the "push-pull" effect on the mechanism for rearrangement.

Laser Flash Photolysis. Time-resolved absorption spectroscopy was used in order to probe for the presence of fluorenyl cations in these photoreactions. Transient spectra obtained following 308 nm excitation of diol **1b**
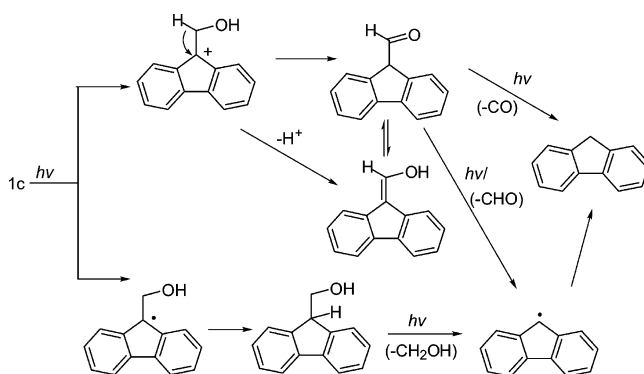
in nitrogen-saturated and aerated hexafluoro-2-propanol (HFIP) are shown in Figure 1. The spectra show a strong band with λ_{max} at 510 nm and a shoulder at 470 nm that decays with a rate constant of 2.0×10^5 s^{-1} in both air- and nitrogen-purged solutions. There is a second absorption with λ_{max} at 370 nm that decays with a rate constant of 3×10^5 s^{-1} in nitrogen-saturated solution. Part of the 370 nm absorption decays rapidly in the presence of air or oxygen; the transient spectra shown in Figure 1B are measured after this rapid oxygen-induced decay. There is still a weak absorption below 370 nm that decays with kinetics similar to those of the 510 nm species. This indicates that there are two species at 370 nm: a weak band that has kinetics similar to those at 510 nm and a second species that reacts rapidly with oxygen and thus is not visible in the spectrum for the aerated sample. The
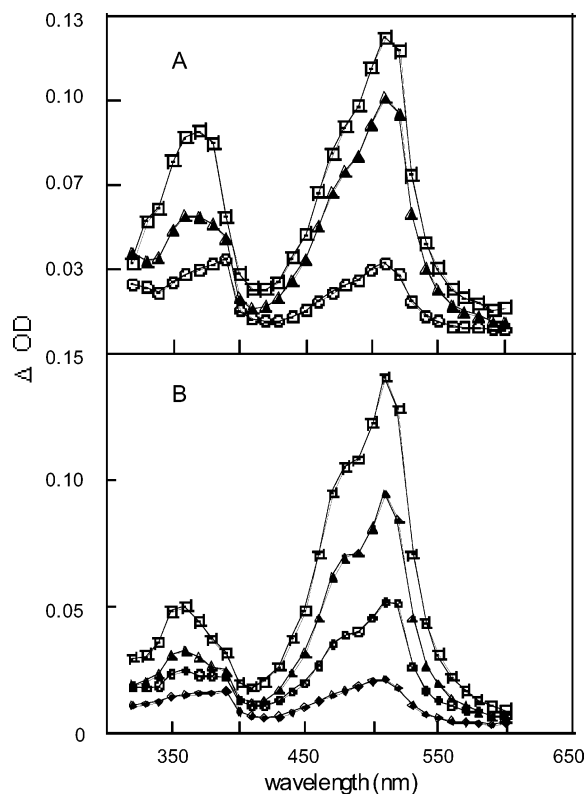

FIGURE 1. Transient absorption spectra obtained after 308 nm excitation of diol **1b** in (A) nitrogen- and (B) air-saturated HFIP. The delays for the spectra are (□) 240 ns, (▲) 1.16 μs, and (○) 6.0 μs after the laser pulse for A and (□) 480 ns, (▲) 2.5 μs, (○) 5.7 μs, and (◆) 11.3 μs after the laser pulse for B.

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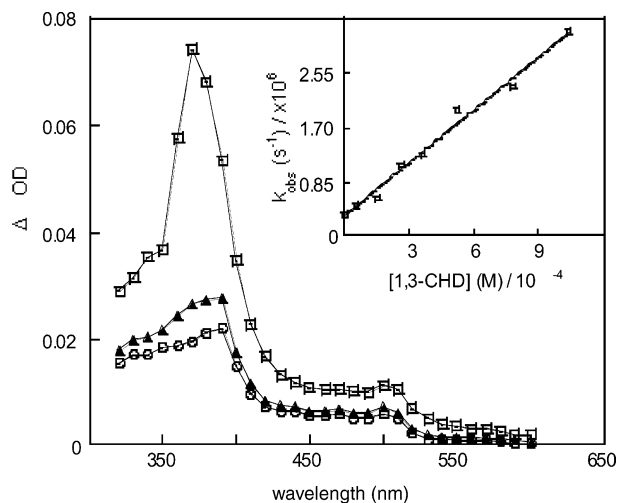
FIGURE 2. Transient absorption spectra measured at delays of (□) 120 ns, (▲) 640 ns, and (○) 2.2 μs after 308 nm excitation of diol **1b** in aerated TFE. The inset shows the quenching of the signal centered at 370 nm with the triplet quencher, 1,3-CHD.

510 nm species reacts with methanol; a plot of the observed rate constant for decay at 510 nm vs methanol concentration gives a second-order rate constant of 5.9×10^6 M^{-1} s^{-1}. The 510 nm transient is assigned to the fluorenyl cation **9b** on the basis of its absorption properties, which are similar to those of many other fluorenyl cations, its insensitivity to oxygen, and its methanol reactivity.

9a R^1 = R^2 = Ph
b R^1 = Ph, R^2 = H
c R^1 = R^2 = H

10
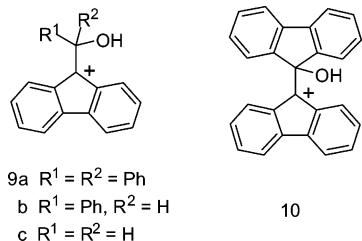
Excitation of diol **1b** in aerated TFE gave a spectrum with λ_{max} at 370 nm and only very weak absorption at 510 nm (Figure 2). The 370 nm transient decays with rate constants of 1×10^6 s^{-1} and 3.9×10^6 s^{-1} in nitrogen- and air-saturated solutions, respectively. Because the oxygen sensitivity is consistent with either radical or triplet species, an additional experiment with 1,3-cyclohexadiene was carried out. The diene quenched the 370 nm transient with a rate constant of 2.8×10^9 M^{-1} s^{-1}, indicating that it can reasonably be assigned to a triplet. This assignment is also consistent with the reported triplet−triplet absorption of fluorene at 376 nm in ethanol.[16] After decay of the 370 nm transient in oxygen- or air-purged samples there is a weak and longer lived signal with λ_{max} at 390 and 500 nm. There is no evidence for a cation with a lifetime in excess of 20−30 ns in HFIP. However, a cation is readily detectable at 510 nm in 1:1 TFE/HFIP and decays with a rate constant of $\sim 7 \times 10^6$ s^{-1}, over an order of magnitude larger than that measured in HFIP.

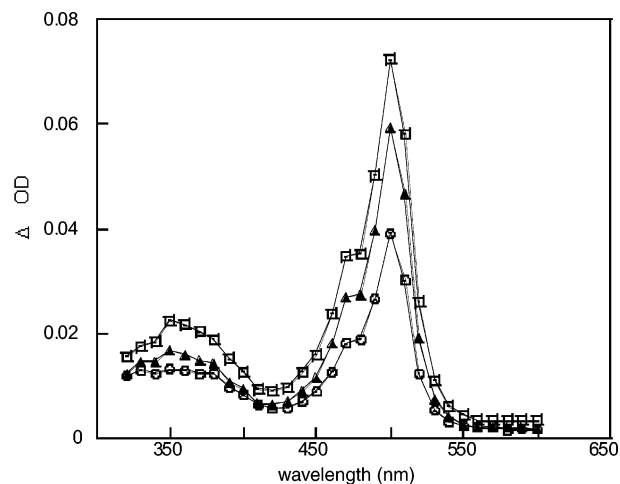(16) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1−250.

FIGURE 3. Transient absorption spectra measured at delays of (□) 320 ns, (▲) 1.5 μs, and (○) 4.7 μs after 308 nm excitation of diol **1c** in aerated HFIP.

Laser flash photolysis of diol **1c** in aerated HFIP gave the spectra shown in Figure 3, which show a strong band at 500 nm with a small shoulder at 470 nm and a much weaker band at 350 nm. The short and long wavelength absorptions decay with similar kinetics ($k = 1.8 \times 10^5$ s^{-1}) and are insensitive to oxygen, suggesting that both belong to cation **9c**. This is confirmed by the fact that both are quenched by methanol with a second-order rate constant of 9.4×10^6 M^{-1} s^{-1}. Nitrogen-purged solutions give a slightly larger amount of signal in the 350−370 nm region, indicating a small amount of triplet formation. By contrast, a strong 370 nm triplet signal is observed in aerated TFE. Similarly to results for diol **1b**, the cation can still be detected in 1:1 TFE/HFIP but decays rapidly ($k \sim 7.4 \times 10^6$ s^{-1}).

Transient spectra obtained following 308 nm excitation of diol **1a** in oxygen-saturated HFIP are shown in Figure 4A. The main feature is a species with λ_{max} at 370 nm that is oxygen-sensitive and that we assign to a triplet as for diols **1b** and **1c**. There is also a weak band at 500 nm that decays with a rate constant of 1.8×10^7 s^{-1}; the kinetics were measured in the presence of sufficient 1,3-cyclohexadiene to reduce the triplet lifetime to <10 ns in order to ensure that the decay kinetics at 500 nm were not complicated by contributions from the triplet. On the basis of these characteristics and its similarity to other fluorenyl cations,[5] the 500 nm species is assigned to cation **9a**. Transient spectra in TFE show only a triplet at 360 nm (which is quenched by 1,3-cyclohexadiene with a rate constant of 2.6×10^9 M^{-1} s^{-1}) with no evidence for a short-lived cation at longer wavelength. Spectra obtained after complete decay of the triplet absorption show a weak residual absorption with λ_{max} at 340 and 500 nm that is consistent with ketyl radical.[17]

Excitation at 308 nm of epoxide **5** in HFIP gave results that were very similar to those for diol **1a** (Figure 4B). A strongly absorbing oxygen-sensitive transient at 370 nm and a weak signal at 500 nm that decayed with a rate constant of 1.3×10^7 s^{-1} were both observed and were assigned to triplet and cation, respectively. The cation

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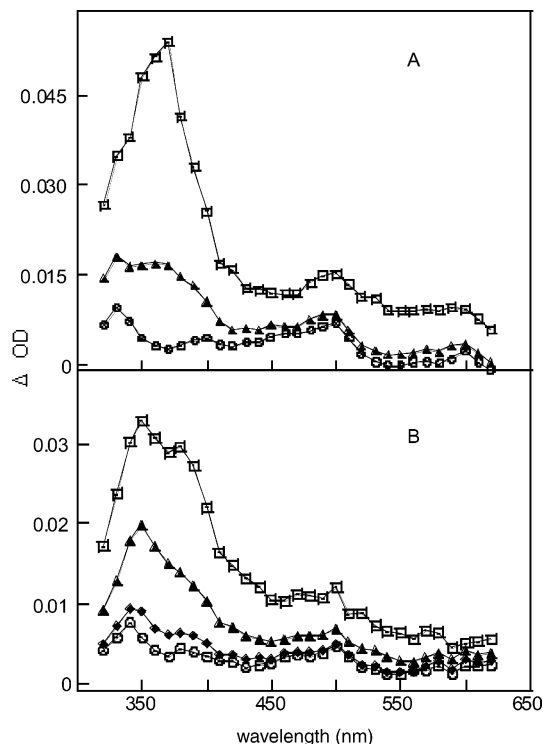
FIGURE 4. Transient absorption spectra measured following 308 nm excitation of (A) diol **1a** in HFIP and (B) epoxide **4** in acetonitrile. The delays for the spectra are (□) 56 ns, (▲) 208 ns, and (○) 928 ns after the laser pulse for A and (□) 28 ns, (▲) 96 ns, (◆) 244 ns, and (○) 424 ns after the laser pulse for B.

TABLE 1. Lifetimes and Methanol Quenching Rate Constants of Fluorenyl Cations

fluorenyl cation	lifetime (s) (solvent)	K_{MeOH} (M^{-1} s^{-1}) (solvent)
9a	5.6×10^{-8} (HFIP)	
9b	1.4×10^{-7} (1;1 TFE/HFIP)	5.9×10^{6} (HFIP)
	5.0×10^{-6} (HFIP)	
9c	1.4×10^{-7} (1:1 TFE/HFIP)	9.4×10^{6} (HFIP)
	5.6×10^{-6} (HFIP)	
10	6.7×10^{-7} (1:1 TFE/HFIP)[a]	1.2×10^{7} (1:1TFE:HFIP)
	2.3×10^{-6} (HFIP)[a]	2.1×10^{6} (HFIP)[a]
	8.3×10^{-8} (TFE)[a]	

[a] From ref 8.

decay kinetics were measured in the presence of sufficient diene to completely quench the triplet. Both spectra and kinetics were similar for the 500 nm transients derived from diol **1a** and epoxide **5**, although the short lifetime and weak signals make these results less reliable than those for diols **1b** and **1c**. A zwitterion formed by photolysis of epoxide **5** would be expected to have a spectrum and/or decay kinetics different than those of the initial cation derived from diol **1a**, based on earlier observations for 9-hydroxyfluorene-9-carboxylic acid.[9] There is no evidence for this, although the weak and short-lived signals obtained would make it difficult to pick up small differences. These observations do not necessarily preclude the presence of the zwitterion in the photochemistry of **1a** and **5**. The zwitterion once formed may undergo diffusion-controlled protonation with the protic solvents used for the LFP experiments. Laser flash photolysis experiments for epoxide **5** in acetonitrile gave
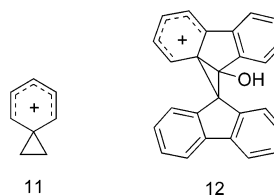
TABLE 2. Activation Energies and Energies for Conversion of Fluorenyl Cations

cation	$\Delta E^{\ddagger}$ (kcal mol^{-1}) (level of calcn)	ΔE (kcal mol^{-1}) (level of calcn)	cation lifetime (s^{-1}) (HFIP)
10	26.1 (AM 1)	−19.0 (AM 1)	2.3×10^{-6}
	20.0 (HF-3-21G*)	−14.6 (HF-3-21G*)	
9a	21.3 (AM 1)	−7.7 (AM 1)	5.6×10^{-8}
	17.0 (HF-3-21G*)	−4.8 (HF-3-21G*)	
9b[a]	27.1 (AM 1)	+10.7 (AM 1)	5.0×10^{-6}
	20.8 (HF-3-21G*)	+8.7 (HF-3-21G*)	
9c	25.4 (AM 1)	+5.9 (AM 1)	5.6×10^{-6}
	30.6 (HF-3-21G*)	+1.0 (HF-3-21G*)	

[a] Energies represent phenyl migration. $\Delta E^{\ddagger}$ for hydride migration is +20.5 (AM1) and +27.2 (HF/3-21G*) kcal mol^{-1}.

only weak signals that were consistent with a small yield of a fluorene-like triplet, with additional weaker residual absorptions that may be due to the fluorenyl ketyl radical.

Cation **9a** is significantly shorter-lived relative to **10**, the cation derived from photoheterolysis of 9,9′-bifluorene-9,9′-diol (Table 1).[8] This is attributed to the relative rates of formation of the phenonium ion intermediates **11** involved in these aryl migrations.[12] The corresponding phenonium ion **12** associated with the biphenylene rearrangement of ion **10** has a strained bicylo[3.1.0]heptane moiety imbedded in its structure leading to an expected larger activation barrier relative to that of **1a**. The longer-

lived cation **9b** as compared to **9a** is likely the result of the absence of a *gem*-phenyl group in the former, which would stabilize the phenonium ion by possible π-interaction. MO calculations for the corresponding phenonium ions show a shallow energy surface near or at the transition state. The calculated activation energies (at AM 1 and HF/3-21G* levels) for the rearrangement of the fluorenyl cations **9a**−**c** and **10** to the corresponding oxonium ions exhibit a qualitative trend with their lifetimes (Table 2).

The kinetic stabilities of these fluorenyl cations as measured by methanol quenching rates (Table 1) show a trend that correlates with steric accessibility of the cationic center.

Summary

The above results demonstrate that there are significant differences between the acid-catalyzed thermal and photochemical reactions of nonsymmetrical pinacols **1a**−**c**. Whereas the thermal reaction products are predicated by the formation of the more stable cation, as well as other factors, the photochemical processes of these diols result in the initial formation of the fluorenyl cations as evident from the LFP observations. These differences are evident in the product distributions obtained from diol **1a**. Whereas biphenylene rearrangement products are observed in the acid-catalyzed dark reactions, the products from the ionic pathway in the photochemical process

originate from the fluorenyl cation. The acid-catalyzed thermal reaction of diol **1b** gives products derived only from the fluorenyl cation. The corresponding benzyl cation from **1b** would be expected to be less stable than the fluorenyl cation. Hydride migration appears to be preferred over phenyl shift by a ratio of 2:1 in the dark reaction. The photolysis of **1b** leads to secondary photoproducts that originate from the pinacol rearrangement. The product distribution indicates a preference for phenyl over hydride migration. This difference may be explained in terms of the presence of acid in the dark reaction, which could result in thermodynamic equilibration between **2b**[1] and **2b**[2] favoring the former, although this speculation could not be independently confirmed under the conditions of the dark reaction. Alternatively, a later transition state in the acid reaction favoring the thermodynamic product may be influencing the course of the dark reaction. Similar observations have been reported by other groups where pinacol rearrangement of 1,2-diphenylethane-1,2-diol under neutral heterogeneous conditions results in products favoring phenyl over hydride migration by a factor of 3:1.[19] These observations are in sharp contrast to classical studies of the same reaction carried out in acidic conditions.[20] Thus, our results show that in neutral solutions phenyl migration is preferred over hydride even though the phenyl group is better than hydrogen in stabilizing the secondary oxonium ion. The pinacol rearrangement of diol **1c** still takes place on photoexcitation unlike the dark acid conditions. The primary product, 9-formylfluorene, undergoes rapid decarbonylation under these conditions as evident from the labeling studies.

The intermediacy of a zwitterion, resulting from photoheterolysis of diol **1a** followed by proton transfer, was examined by comparison of photoproducts obtained from epoxide **5**, as well as by comparison of transients in the LFP experiments. Product distributions were similar except for the absence of the methanol-quenched product **7b** in the photolysis of epoxide **5**. Although this suggests that the zwitterion is shorter-lived than its conjugate acid (**9a**), the LFP results indicate that transients with similar spectra and lifetimes are obtained from both diol and epoxide. On the basis of the combined transient and product studies, it is difficult to conclude whether the transient generated from epoxide **5** is an initial zwitterion or whether rapid protonation leads to the conjugate acid, cation **9a**, which is also generated by photolysis of diol **1a**. An alternate possibility is that the zwitterion and conjugate acid **9a** are in equilibrium in HFIP, although the differences in product distribution suggest that this is not the case in methanol/acetonitrile. Because nucleophilic trapping gives little or no product in all of the solvents examined, rearrangement is likely to be the primary reaction in each case. Further studies associated with related diols and epoxides substituted with electron-withdrawing groups so as to stabilize such zwitterions are in progress.

Experimental Section

Photolyses were performed using a 450 W medium-pressure mercury arc lamp in a water-cooled quartz immersion well. Pyrex tubes containing samples dissolved in the solvent system specified were strapped around the immersion well, and the whole assembly was immersed in a water bath. Deaeration of the solutions was accomplished by purging with nitrogen or argon. Diol **1a** was prepared according to a literature procedure.[10] NMR spectra were obtained from a 400 MHz spectrometer.

Laser flash photolysis experiments were carried out at room temperature using 6 ns 308 nm pulses, from an excimer laser (XeCl; <40 mJ/pulse). The laser system has been described in detail.[21] Solutions were prepared by adding a small amount of a stock solution (2×10^{-4} M) of the samples in TFE or HFIP. Solutions were contained in 7×7 mm^2 Suprasil quartz cells and were either aerated or purged with nitrogen or oxygen before laser excitation.

9-(Hydroxy-phenyl-methyl)-9*H*-fluoren-9-ol (1b). To 9,9-dichlorofluorene[22] (0.5 g, 2.14 mmol) in THF (25 mL) cooled to −78 °C was added butyllithium (0.85 mL, 2.5 M in hexane). After 10 min at −78 °C, the mixture was treated with a solution of benzaldehyde (0.22 g, 2.14 mmol) in THF (5 mL). The mixture was left to warm to ambient and added to an aqueous solution (30 mL) acidified with 2 M HCl. The organic layer was extracted with dichloromethane (2×10 mL), and the extract was evaporated to dryness. The mixture was separated by chromatography (silica gel; hexane/ethyl acetate (8:1)) and yielded 0.46 g (75%) of the diol as a white solid, mp 127 °C (lit.[23] mp 126 °C): ^{1}H NMR δ 2.82 (s, 1H, OH), 3.17 (d, 1H, OH, $J = 1.96$ Hz), 5.27 (d, 1H, $J = 3.76$ Hz), 6.75 (d, 2H, $J = 7.6$ Hz), 6.89 (t, 2H, $J = 7.56$ Hz), 6.97 (d, 1H, $J = 8.36$ Hz), 7.28−7.23 (m, 4H), 7.35 (t, 2H, $J = 3.32$ Hz), 7.56 (d, 1H, $J = 3.36$ Hz), 7.64 (d, 1H, $J = 7.16$ Hz).

9-Hydroxymethyl-9*H*-fluoren-9-ol (1c). To a solution of LiAlH$_4$ (0.03 g, 0.78 mmol) in 10 mL THF was added 9-hydroxy-9-fluorenecarboxylic acid (0.2 g, 0.88 mmol) in THF (15 mL), and the mixture was left to stir for 30 min. The mixture was quenched with methanol (5 mL) and then water (10 mL). The mixture was extracted with dichloromethane (3×5 mL) and run through a silica gel plug, and the extract was evaporated to dryness to yield 0.18 g (97%) of the diol as a white solid, mp 94−96 °C: ^{1}H NMR δ 7.64 (dd, 4H, $J = 7.52$, 7.48 Hz), 7.40 (t, 2H, $J = 7.42$ Hz), 7.31 (t, 2H, $J = 7.44$ Hz), 3.85 (d, 2H, $J = 6$ Hz), 2.51 (s, 1H, OH), 2.33−2.30 (t, 1H, OH), $^1J = 6.46$ Hz) ppm. MS data of this compound were previously reported.[24]

Dideuterated 9-Hydroxymethyl-9*H*-fluoren-9-ol (1c-*d₂*). The same procedure as for the preparation of diol **1c** was followed, but LiAlD$_4$ was used instead of LiAlH$_4$. The yield was the same, and the ^{1}H NMR spectrum was identical to that of diol **1c**, except that the peak at δ 3.8 ppm was absent.

Acid-Catalyzed Dark Reactions. General Procedure. Diols **1a**−**c** (10 mg) were dissolved in 1 mL of CDCl$_3$ containing a crystal of toluenesulfonic acid and monitored by NMR spectroscopy with comparison to authentic samples prepared according to the literature.

Product Studies. General Procedure. Nitrogen-purged solutions of diols **1a**−**c** (2×10^{-3}M) in 50 mL of methanol/acetonitrile (4:1) were irradiated in a Pyrex tube for 1 h. After evaporation of the solvent the residue was separated by preparative TLC (silica gel, ethyl acetate/hexane (1:8)).

Photoproducts from Diol 1a. 9-Benzoyl-9-phenylfluorene (2a): 31%; mp 168−170 °C (lit.[25] 172 °C); ^{1}H NMR δ 7.80

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(d, 2H, J = 7.52 Hz), 7.45−7.38 (m, 4H), 7.32−7.23 (m, 10H), 7.12 (t, 2H, J = 7.64 Hz) ppm.

Epoxide 5 (R^1 = R^2 = C_6H_5): 18%; ^{1}H NMR δ 7.67 (d, 2H, J = 7.52 Hz), 7.31−7.23 (m, 12H), 6.87 (t, 2H, J = 7.60 Hz), 6.11 (d, 2H, J = 7.68 Hz) compared with a sample prepared independently according to a literature method.[15]

(9*H*-Fluoren-9-yl)-diphenyl-methanol (6a): 10.5%; ^{1}H NMR δ 7.70 (dd, 6H, J = 7.60, 7.60 Hz), 7.39−7.30 (m, 8H), 6.99 (t, 2H, J = 7.60 Hz), 6.52 (d, 2H, J = 7.68 Hz), 5.28 (s, 1H), 1.95 (s, 1H, OH). All spectral features identical with a sample prepared independently and fully characterized in our laboratory.[5]

Methanol Adduct 7a: this material coelutes with alcohol **6a**; 0.8 mg (4% by ^{1}H NMR spectroscopy); ^{1}H NMR δ 7.68 (d, 1H, J = 7.56 Hz), 7.53 (d, 1H, J = 4.56 Hz), 7.37−7.25 (m, 12H), 6.83 (t, 2H, J = 7.60 Hz), 6.65 (d, 2H, J = 7.80 Hz), 2.94 (s, 3H, OCH$_3$).

9-Benzhydrilydenefluorene (4): 10%; this material was previously characterized[5] and compared with a commercial sample.

Photoproducts from Epoxide 5 (R^1 = R^2 = C_6H_5). Products compared with those from diol **1a**: 9-benzoyl-9-phenylfluorene (**2a**) (40%), 9-benzhydrilydenefluorene (**4**) (7%), and 9-phenylfluorene (**8**) (10%) (this compound formed as a secondary photoproduct from photoexcitation of **2a** as shown by an independent experiment).

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Photoproducts from Diol 1b. 9-Phenylfluorene (8): 33%; comparison with a commercial sample.

9-Benzoylfluorene (2b^1): 8%; mp 133−134 °C (lit.[25] 135 °C); (7.6%), ^{1}H NMR δ 7.84 (d, 2H, J = 7.60 Hz), 7.73 (d, 2H, J = 5.92 Hz), 7.50 (t, 2H, J = 7.08 Hz), 7.44−7.33 (m, 5H), 7.26 (t, 2H, J = 7.60 Hz), 5.60 (s, 1H) ppm; MS *m/z* 270 (5), 165 (5), 105 (20).

9-Phenyl-9-fluorenecarboxaldehyde (2b^2): 1%; decomposes on silica gel; ^{1}H NMR δ 9.56 (s, 1H), 7.82 (d, 2H), 7.48−7.24 (m, 11H); MS *m/z* 270 (5), 241 (100).

(9*H*-Fluoren-9-yl)-phenyl-methanol (6b): 3.1%; mp 120−121 °C (lit.[26] 118.5−119 °C); ^{1}H NMR δ 5.09 (d, 1H, ^3J = 3.72 Hz), 4.40 (d, 1H, J = 6.04 Hz).

(9-Methoxy-9*H*-fluoren-9-yl)-phenyl-methanol (7b): 1.5%; mp 185−187 °C (lit.[27] 189−190 °C); ^{1}H NMR δ 7.68 (d, 1H, J = 7.60 Hz), 7.54 (d, 1H, J = 4.64 Hz), 7.37−7.27 (m, 6H), 6.96 (t, 1H, J = 7.28 Hz), 6.83 (t, 2H, J = 7.64 Hz), 6.65 (d, 2H, J = 7.68 Hz), 5.28 (s, 1H), 3.57 (s, 1H, OH), 2.94 (s, 3H, OCH$_3$); MS *m/z* 195 (100), 107 (20), 77 (40).

Photoproducts from Diol 1c: fluorene (10%), fluorenone (22%), **(9-methoxy-9*H*-fluoren-9-yl)-methanol (7c)** (4%); ^{1}H NMR δ 7.69 (d, 2H, J = 5.68 Hz), 7.58 (d, 2H, J = 7.44 Hz), 7.44 (t, 2H, J = 7.44 Hz), 7.34 (t, 2H, J = 7.44 Hz), 3.84 (d, 1H, ^3J = 6.40 Hz) 2.89 (s, 3H, OCH$_3$) 2.41 (t, 1H, OH), ^3J = 6.36 Hz).