7168 *J. Org. Chem.* **1998,** *63,* 7168−7171

Photochemical Pinacol Rearrangement

Mary Hoang,[†] Timothy Gadosy,[‡] Hedieh Ghazi,[†] Dong-Feng Hou,[†] Alan C. Hopkinson,[†]
Linda J. Johnston,*,[‡] and Edward Lee-Ruff*,[†]

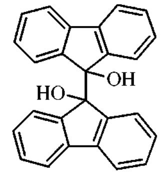
Department of Chemistry, York University, Toronto, Ontario M3J 1P3, Canada, and Steacie Institute for Molecular Science, National Research Council Canada, Ottawa, Ontario K1A 0R6, Canada

Received January 27, 1998

Irradiation of 9,9′-bifluorene-9,9′-diol (**1**) gave 9-fluorenone and spiro[9*H*-fluorene-9,9′(10′-*H*)-phenanthren]-10′-one (**4**), the latter arising from a pinacol rearrangement. The distribution of fluorenone and ketone **4** was solvent dependent with the latter being the major product in trifluoroethanol, a solvent known to stabilize carbocation intermediates. Laser flash photolysis of diol **1** in 2,2,2-trifluoroethanol or hexafluoro-2-propanol showed two transients absorbing at 350 and 505 nm with a weak band at 700 nm. The latter two peaks are assigned to the corresponding substituted 9-fluorenyl cation (**5**) formed from photoheterolysis of diol **1**. Comparison of the decay kinetics between cation **5** and other 9-fluorenyl cations, the parent 9-fluorenyl and 9-phenyl-9-fluorenyl cations, showed that the decay of **5** was relatively insensitive to the nature of the solvent as compared to the latter two carbocations suggesting that unimolecular rearrangement in **5** competes with nucleophilic quenching.

Introduction

Destabilized carbocations in which one or more of the α-substituents are electron-withdrawing and cations incorporated in a 4n cyclic π-framework have been of interest as intermediates in solvolysis,[1−4] as species directly observable under stable ion conditions,[5,6] or as transients obervable under laser flash photolysis in neutral solutions.[6−9] The 9-fluorenyl cation can be readily produced by irradiation of 9-fluorenols unlike other diarylmethyl cations which require more photolabile leaving groups. This is associated with the ease of photosolvolysis processes of cyclic π-chromophores possessing 4n electrons in the internal cyclic array (ICA).[10] The photosolvolysis rates of fluorenols exceed those of dimethoxybenzyl alcohol which supports theoretical studies suggesting that antiaromatic systems (in this case, the 9-fluorenyl cation) in the ground state may possess aromatic stabilization in the excited state.[11]



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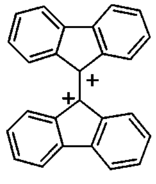

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With the ease with which 9-fluorenyl cations can be generated by irradiation of the corresponding alcohols, we were interested in the possibility of using 9,9′-bifluorene-9,9′-diol (**1**) as a precursor to the corresponding dication **2**, a "doubly destabilized" cation.[3] Dications of the 1,1,2,2-tetraarylethane-1,2-diyl type have been observed under stable ion conditions from oxidations of the corresponding 1,1,2,2-tetraarylethylenes.[12] In this study we report on the photochemistry of **1** and the first example of a photochemical pinacol rearrangement performed in neutral solutions.[13]

Results and Discussion

Diol **1** was prepared by reductive coupling of 9-fluorenone (**3**) according to a procedure described by Tanaka.[14] Irradiation of **1** in acetonitrile gave two major products, 9-fluorenone and the rearranged pinacolone **4**, in a ratio of 85:15, respectively.[22] The characterization of **4** was based on comparison of its spectral data with those reported in the literature[15] as well as comparison with an authentic sample prepared from the acid-catalyzed pinacol rearrangement of diol **1**. Irradiation of deaerated solutions of **1** in acetonitrile gave a slightly

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[†] York University.

[‡] National Research Council of Canada.

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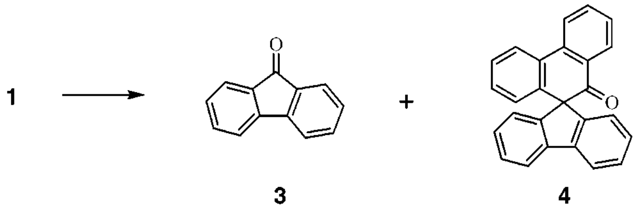
S0022-3263(98)00148-0 CCC: $15.00 © 1998 American Chemical Society
Published on Web 09/30/1998

higher yield of **4** affording a 74:26 ratio of ketones **3** and **4**, respectively.[22]



Attempted trapping of carbocations generated by irradiation of diol **1** in methanol gave only ketones **3** and **4** in a 67:33 ratio.[22] The use of 2,2,2-trifluoroethanol (TFE), a solvent known to promote carbocation formation,[16] gave the pinacolone **4** as the principal product along with minor amounts of fluorenone **3**[23] (*vide infra*). No dark reactions of diol **1** in any of these solvents were observed. The solvent dependence of the product distribution suggests that pinacolone **4** and fluorenone **3** arise via different mechanisms and that **4** is likely the product from a carbocationic intermediate. To probe the nature of these intermediates, we carried out laser flash photolysis (LFP) studies of diol **1**.

Transient spectra obtained following 308 nm excitation of diol **1** in 1:1 TFE/hexafluoro-2-propanol (HFIP) showed a strong absorption at 505 nm, a weak band centered at approximately 700 nm, and a third band at 350 nm (Figure 1). Neither the intensity nor the decay kinetics of the 505 and 700 nm bands was affected by oxygen; the two bands decay with similar kinetics with measured rate constants of 1.4 and 2.0 × 10^6 s^{-1} in nitrogen-purged solution. These numbers are in good agreement, given the small amplitude of the longer wavelength signal and indicate that the two bands belong to the same species. This is substantiated by the fact that similar rate constants for reaction with nucleophiles are measured at both 505 and 700 nm. Second-order rate constants for reaction with water and methanol of $k_w = 1.8 \times 10^6$ M^{-1} s^{-1} and $k_{MeOH} = 1.2 \times 10^7$ M^{-1} s^{-1}, respectively, were determined from the slopes of the plots of the observed decay rate constant at 505 nm as a function of the quencher concentration. The 350 nm signal shown in Figure 1 decays much more slowly than the two longer wavelength bands in nitrogen-purged solution and is partially removed by oxygen, as shown in Figure 1A,B. This clearly demonstrates that two transient species are produced upon excitation of diol **1**.

LFP of diol **1** was also examined in several other solvents. Spectra that were virtually identical to those shown in Figure 1 were obtained in HFIP. The 505/700 nm species decayed with a rate constant of 4.4 × 10^5 s^{-1} (measured at 510 nm for an oxygen-purged sample) and reacted with water and methanol with second-order rate constants of $k_w = 2.7 \times 10^5$ M^{-1} s^{-1} and $k_{MeOH} = 2.1 \times 10^6$ M^{-1} s^{-1} (Figure 2). The lifetime of the 505 nm transient was substantially shorter in neat TFE, with an observed decay rate constant of 1.2 × 10^7 s^{-1}. In acetonitrile, only the 350 nm signal was observed and there was no evidence for the 505/700 nm transient, even on short time scales. The 350 nm signal decayed slowly by second-order kinetics in nitrogen-purged acetonitrile. In oxygen-saturated solution, approximately two-thirds of the signal decayed within 100 ns, leaving a long-lived residual absorption that did not decay over hundreds of microseconds. Neither the intensity nor the decay kinetics of the 350 nm transient is affected by the addition of 0.028 M 2,3-dimethyl-1,3-butadiene, a triplet state quencher.

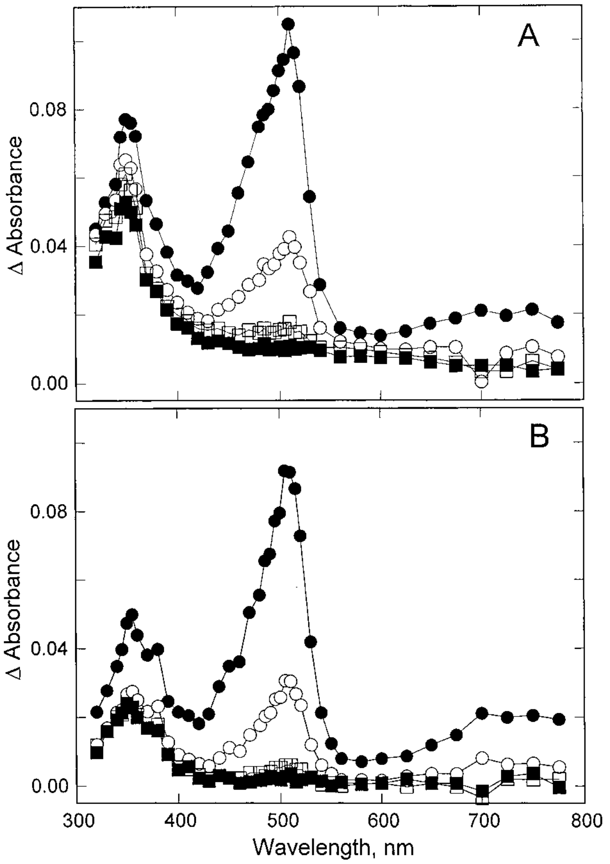


Figure 1. Transient spectra measured after 308 nm excitation of diol **1** in 1:1 TFE/HFIP (A, nitrogen, and B, oxygen). Spectra were measured at the following time delays after the laser: ●, immediately after laser pulse; ○, 0.48 μs; □, 1.3 μs; ■, 3.2 μs.

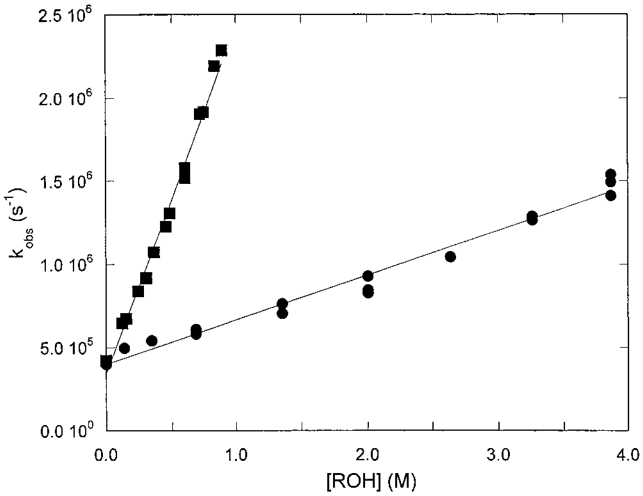


Figure 2. Plots of the observed rate constant for the decay of transient **5** (510 nm) generated from diol **1** as a function of water (●) and methanol (■) concentration.

The above results are consistent with the assignment of the 505 nm transient to the 9-fluorenyl cation **5** formed by photoheterolysis of diol **1**. The assignment is based on the observed reactivity of the transient to nucleophiles,

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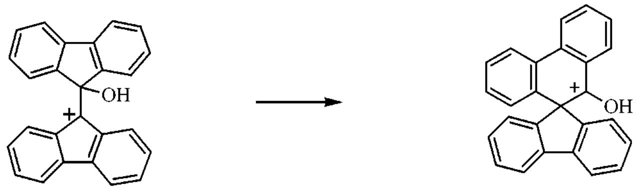
its insensitivity to oxygen, and comparison of its spectral features with known 9-fluorenyl cations. For example, the parent 9-fluorenyl cation shows a λ_{max} at 515 nm in HFIP[8] and both the 9-phenyl and 9-methyl derivatives are slightly blue-shifted with λ_{max} values of 490 and 485 nm, respectively, in alcohol solutions.[7,17] The kinetic data obtained for trapping by methanol and water are also in good agreement with the data obtained for other substituted 9-fluorenyl cations. The modest decreases in rate constants for HFIP vs TFE/HFIP are in line with kinetic data for other cations and reflect the stronger solvating ability of HFIP as compared to TFE.[16]

The decay kinetics for the 9-fluorenyl and 9-phenyl-9-fluorenyl cations were also measured in several solvents for comparison with the data obtained for **5**. Both cations were obtained by photolysis of the corresponding alcohol. The decay kinetics for the 9-fluorenyl cation decrease by over 2 orders of magnitude when the solvent is changed from 1:1 TFE/HFIP to HFIP, as shown in Figure 3. By contrast the rate constant for decay of **5** decreases by only a factor of 5. The 9-phenyl-9-fluorenyl cation decays with a rate constant of $1.6 \times 10^4\ s^{-1}$ in TFE, in good agreement with literature data,[17] as compared to $1.2 \times 10^7\ s^{-1}$ for cation **5**. If nucleophilic addition of solvent was responsible for the decay of both cations then one would expect cation **5** to decay with similar kinetics or even more slowly than the 9-phenyl analogue, as a result of steric effects. The rapid decay for cation **5** and the relative insensitivity of its decay to variation in the solvent composition as compared to other 9-fluorenyl cations suggest that nucleophilic addition is not the primary pathway. It is not surprising that attempted nucleophilic trapping of cation **5** by irradiation of diol **1** in methanol only gave rearrangement product **4** and fluorenone. Both these results and the product studies are consistent with unimolecular decay of **5** via pinacol rearrangement to give the stabilized cation **6**.



5 **6**

The measured rate constant of $5 \times 10^5\ s^{-1}$ for decay of cation **5** in HFIP in the absence of quencher (Figure 3) represents an upper limit for the pinacol rearrangement. This suggests an activation barrier of $\Delta G^{\dagger} = 9$ to 10 kcal/mol in HFIP which is in line with activation barriers of 3−12 kcal/mol reported for 1,2-alkyl migrations in less solvating media with the lower values associated with alkyl migrations between tertiary carbocation centers.[18]

The transient observed at 350 nm may be associated with the ketyl radical **7** formed from C−C homolysis of diol **1**. The fluorenyl ketyl radical **7** has been reported to show an absorption at λ_{max} at 360 nm which is solvent dependent.[19] The observed fluorenone byproduct could readily arise from oxidation of **7** under ambient conditions. Similar observations were obtained from other 1,1,2,2-tetraaryl-1,2-ethanediols in which the only products obtained were the corresponding benzophenones and other oxidation products derived from ketyl radicals.[20]

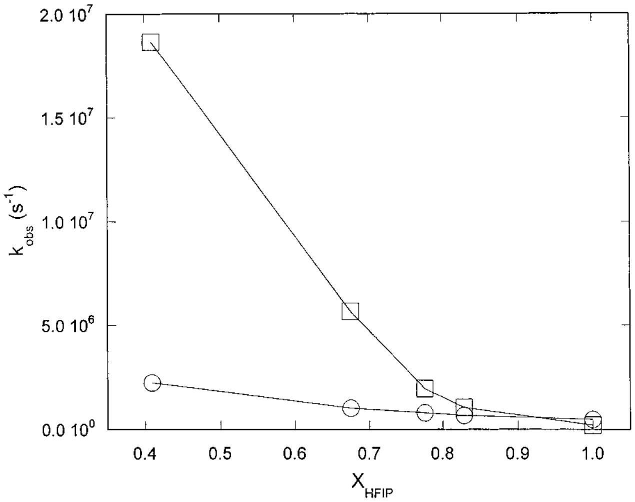
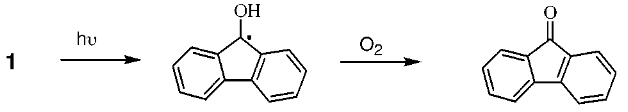


Figure 3. Effect of solvent composition (X_{HFIP}) in TFE/HFIP mixtures on the rate constant for decay of 9-fluorenyl cation (□) and the substituted 9-fluorenyl cation **5** (○).



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In conclusion we have shown that a pinacol rearrangement occurs upon photoexcitation of 9,9′-bifluorene-9,9′-diol (**1**). The reaction proceeds via initial C−O bond heterolysis to give a substituted 9-fluorenyl cation that has been observed by LFP. This cation undergoes rearrangement and deprotonation giving the final product. The fluorenone byproduct may arise from a competing homolysis process involving ketyl radical. There is no evidence from either the photoproduct analysis or from the LFP studies for the intervention of dication **2**. The possibility of double photon excitation of diol **1** to give dication **2** through the monocation **5** will be investigated.

Experimental Section

Materials and General Techniques. All the solvents used were reagent grade and were dried before use. Infrared spectra were obtained on a Perkin-Elmer 1310 spectrometer with KBr pellets. Proton NMR spectra were obtained on a Bruker ARX-400 spectrometer using samples dissolved in $CDCl_3$. Chemical shifts are measured in parts per million (δ) relative to TMS as internal standard. Mass spectra were recorded at 70 eV on a Kratos profile mass spectrometer. The continuous photolysis were performed using a Hanovia 450 W medium-pressure mercury arc lamp in a water-cooled quartz immersion well. Quartz tubes containing the samples were strapped around this well, and the assembly was immersed in an ice−water bath. HPLC analyses were carried out using a Waters 715 Ultra Wisp Sampler with a Lamda Max 481 LC detector set at 254 nm. The column was a μ Porasil analytical column using a 30:70 mixture of ethyl acetate/hexane mixture as eluent. Standard solutions of diol

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1, 9-fluorenone (**3**), and ketone **4** were used for calibration purposes in the HPLC analyses of the photolysis mixtures.

Spiro[9H-fluorene-9,9′(10′-H)-phenanthren]-10′-one (4). Diol **1** (0.0691 g, 0.19 mmol) was dissolved in 10 mL of glacial acetic acid containing 3 mL of sulfuric acid (5% aqueous) and heated to reflux for 45 min. The reaction mixture was poured onto ice (50 g) and the precipitate filtered off and washed with water. The solid was recrystallized in methanol giving 0.0575 g of the title compound: mp 254−256 °C (lit. mp 254−255 °C[15]); IR 1683 cm^{-1}; ^{1}H NMR δ 8.33 (d, 1H), 8.23 (d, 1H), 8.02 (d, 1H), 7.83 (m, 4H), 7.49 (t, 1H), 7.42 (m, 4H), 7.32 (t, 1H), 7.24 (t, 1H), 7.08 (d, 1H), 6.66 (d, 1H); MS *m/z* 344 (M), 316 (M − CO).

Preparative Photolysis. A solution of diol **1** (48 mg, 0.132 mmol) in 25 mL of 2,2,2-trifluoroethanol or acetonitrile was purged with argon for 30 min. The solution was irradiated for 45 min at 0 °C. After evaporation of the solvent, the residue was purified by preparative thin-layer chromatography (silica gel; 2:8 ethyl acetate/hexane) giving 10 mg of unreacted **1**, 4 mg (17%) of fluorenone, and 15 mg (40%) of ketone **4** identical in all respects with a sample prepared above. HPLC analysis of the photolysis mixture in 2,2,2-trifluoroethanol indicated 61% of ketone **4**, 12% of 9-fluorenone (**3**), and 18% of diol **1**. Decomposition of diol **1** to 9-fluorenone and polar products which could not be identified led to a less than satisfactory mass balance in the recovery of products.

Photolysis of diol **1** in aerated solution was conducted in an identical manner as above except for the purging with argon prior to the photolysis.

Laser Flash Photolysis. The laser system has been described in detail elsewhere.[21] A Lumonics EX-510 excimer laser (XeCl, 308 nm, 6-ns pulses, <40 mJ/pulse) was used for sample excitation. Solutions were contained in 7 × 7 mm^2 Suprasil quartz cells and were either aerated or purged with nitrogen or oxygen before laser excitaion.

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[22] By HPLC analysis; the fluorenone content is overestimated due to decomposition of unreacted diol **1** to 9-fluorenone (**3**) on silica gel chromatography.

[23] The mixture contained 61% of ketone **4**, 12% of 9-fluorenone (**3**), and 18% of unreacted diol **1** by HPLC analysis.