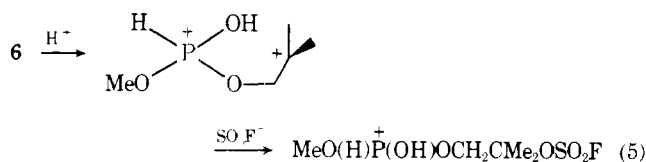
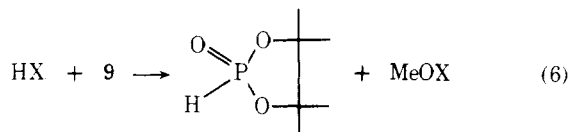


in **6** accords with ring opening at the substituted carbon in order to form an intermediate tertiary carbonium ion (eq 5).



This inference can be drawn from the increasing importance of an $\text{S}_{\text{N}}1$ solvolysis mechanism when bulky alkoxy groups are present in acyclic phosphite esters.^{8,9} Further observations which are consistent with solvolysis with ring opening are the similar ^{31}P chemical shifts and $^1J_{\text{PH}}$ values for the second protonated species in Table II as well as the remarkably similar data for the protonated form of the model compound $\text{MeO(H)P(O)OCH}_2\text{CH}_2\text{OH}$ ¹⁶ in HFSO_3 at -50°C , which is presumably $\text{MeO(H)P}^+(\text{OH})(\text{OCH}_2\text{CH}_2\text{OH})$ [$\delta^{31}\text{P}$ 22.3 (d, $^1J_{\text{PH}} = 833$ Hz)].²⁰

Interestingly, CDCl_3 solutions of **9** treated with approximately equimolar quantities of CF_3COOH or HFSO_3 at room temperature exhibited ^{31}P NMR spectra indicative of the phosphite product in reaction 6 as shown by comparison under the same conditions with an authentic sample. It thus appears



that the dealkylation mechanism(s) is influenced by rather subtle kinetic and thermodynamic factors which can drastically alter the course of the reaction.

Acknowledgment. J.G.V. would like to express his thanks to the National Science Foundation for support of this work in the form of a grant.

Registry No.—**5**, 24151-47-1; **6**, 69576-69-8; **7**, 69576-70-1; **8**, 69610-98-6; **9**, 69576-71-2; **10**, 69576-72-3; **10** unprotonated form, 69576-77-8; **11**, 69576-73-4; **11** unprotonated form, 69576-78-9; **12**, 21941-55-9; **12** protonated form, 69576-79-0; phosphorus trichloride, 7719-12-2; 2,4-dimethyl-2,4-pentanediol, 24892-49-7; 4,4,6,6-tetramethyl-1,3,2-dioxaphosphorinane 2-oxide, 34883-00-6; trimethyl phosphite, 121-45-9; 1,4-butanediol, 110-63-4; dimethyl phosphonate, 868-85-9; ethylene glycol, 107-21-1; 2-methoxy-1,3,2-dioxaphospholane, 3741-36-4.

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- (19) We thank Mr. Phil Stricklen for this measurement.
- (20) All attempts to protonate $\text{MeOPOCH}_2\text{CH}_2\text{O}$ failed owing to extensive decomposition. Among the many peaks present in the ^{31}P spectrum are two clusters of peaks separated by about 800 Hz whose chemical shift is approximately 25 ppm. This observation is reasonably consistent with the presence of $\text{MeO(H)P}^+(\text{OH})(\text{OCH}_2\text{CH}_2\text{OSO}_2\text{F})$ considering the similar data obtained for $\text{MeO(H)P(O)(OCH}_2\text{CH}_2\text{OH)}$ in HFSO_3 .

Stabilities of Trivalent Carbon Species. 5. Equilibria of Excited Singlet Alcohols and Carbocations¹

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Fluorescence titrations were carried out with four alcohols whose greatly enhanced reactivity to form carbocations in the excited singlet state is predicted by Förster cycle calculations. Analysis of the fluorescence titration of 5*H*-dibenzo[*a,d*]cycloheptatrien-5-ol indicates that the alcohol reacts with acid in the excited singlet state, but not the ground state, at H_R between +1 and -3. Formation of the cation at very low acid concentrations, as predicted by the Förster cycle, is precluded by the short lifetime of the excited singlet alcohol. The behavior of the fluorescence intensities of the alcohol and corresponding cation implies the involvement of another, nonfluorescing species in the excited-state reactions. Preparative photolyses of the cation indicate that its principal photoreactions are hydride transfer and ether formation.

In general, carbocations absorb light at lower energies than their covalent precursors, and consequently the dissociation constant for reaction 1 involving excited singlet species,



calculated from the Förster cycle,³ is greater than that for the ground-state species (see Figure 1). However, Förster cycle calculations may not describe the actual behavior of the ex-

cited species if equilibrium is not established during their lifetimes.⁴ We have examined the fluorescence spectra of several alcohols and their corresponding cations in aqueous sulfuric acid solution in order to establish the chemistry of these species in the first excited singlet state. Table I lists the alcohols which give rise to carbocations which display fluorescent emission, their $\text{p}K_{\text{R}^+}$ values in the ground state, and $\text{p}K_{\text{R}^+}^*$ values calculated from the Förster cycle. Additionally,

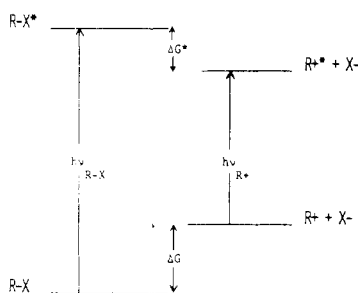


Figure 1. Förster cycle for ionization of R-X. Assuming identical entropies of reaction in the ground and excited states, $\Delta G^* = \Delta G + h\nu_{R^+} - h\nu_{R-X}$. Since $h\nu_{R-X} > h\nu_{R^+}$, ΔG^* is more negative than ΔG .

Table I. Fluorescence Emission of Alcohols and Carbocations

alcohol	λ , ROH ^a	λ , R ⁺ ^a	pK_{R^+}	$pK_{R^{*+}}$ ^b
1-OH (5 <i>H</i> -dibenzo[<i>a,d</i>]cycloheptatrien-5-ol)	360	550	-3.7	22.7
2-OH (5-phenyl-dibenzo[<i>a,d</i>]cycloheptatrien-5-ol)	360	575	-5.7	22.8
3-OH (9-phenyl-xanthhydrol)		500	1.1	22.3
4-OH (9-phenyl-thioxanthydrol)		540	0.1	25.3

^a Fluorescence maximum, nm. ^b Excited state pK_{R^+} , calculated from average of absorption and fluorescence frequencies and pK_{R^+} .

derivatives of the alcohols 2-OH, 3-OH, and 4-OH with the phenyl rings substituted with chloro, methoxy, methyl, and trifluoromethyl groups were examined and showed behavior similar to the unsubstituted compounds. Alcohols 1-OH and 2-OH display fluorescence emission whose intensity decreases with increasing acid concentration, and all of the cations display emission whose intensity increases with increasing acid concentration. With the exception of 1-OH and 1⁺, the changes in fluorescence spectra match the changes in absorption spectra of the cations and reflect the ground-state equilibria only.

Solutions of 1-OH in acid display fluorescence emission from 1-OH or 1⁺ only. The relative intensities of fluorescence of 1-OH and 1⁺ in a range of sulfuric acid solutions are shown in Figure 2. The change in intensity at high acid concentration corresponds to the formation of the cation in the ground state ($pK_{R^+} = -3.7$). At low acid concentrations ($H_R > -3$), the absorbing species is 1-OH, so the observed emission characteristic of 1⁺ in this region implies that 1-OH undergoes ionization in the excited singlet state to produce the excited singlet 1⁺.

The quenching of 1-OH fluorescence by acid is linearly related to H_3O^+ concentration between 0.1 and 0.5 M. From the slope of the Stern-Volmer plot (1.37) and the fluorescence lifetime (~1 ns), the bimolecular rate constant for quenching is about $1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. In more concentrated acid solution, the rate of quenching increases up to the diffusion limit, where more acid does not increase the quenching and the plateau is observed in the titration curve. At lower acid concentrations, the rate of quenching is less than the rate of fluorescence and quenching is not observed. Thus the greatly enhanced reactivity of the excited singlet alcohol predicted by the Förster cycle cannot be experimentally verified.

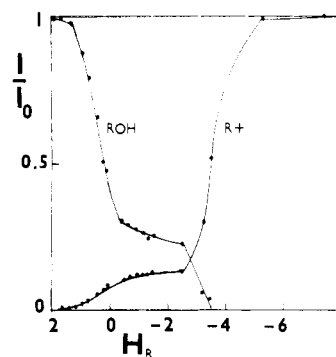
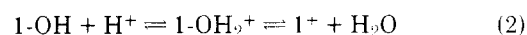


Figure 2. Fluorescence titration of 5*H*-dibenzo[*a,d*]cycloheptatrien-5-ol in sulfuric acid $25 \pm 1^\circ \text{C}$: excitation at 270 nm; emission from alcohol at 360 nm, from cation at 550 nm; alcohol concentration, $2.4 \times 10^{-4} \text{ M}$.

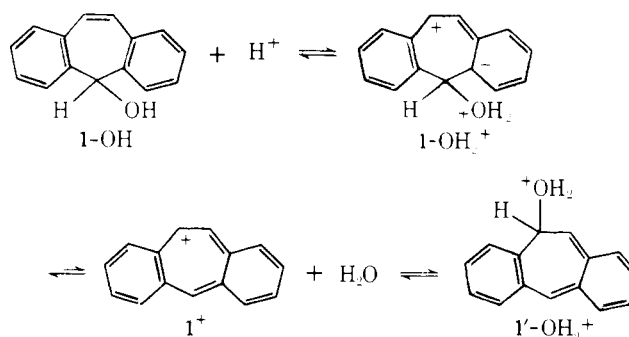
The decrease of the fluorescence intensity of 1-OH parallels the increase of 1⁺ (both curves show inflections at $H_R = 0.3$), but the decrease is more pronounced. If the excited states of 1-OH and 1⁺ were the only species in equilibrium, the sum of their relative intensities would equal 1 at all acid concentrations.⁶ The deviation of this sum from unity implies the presence of at least one other nonfluorescing species reacting with the excited states of 1-OH and 1⁺.

A likely species involved in the conversion of 1-OH to 1⁺ is the conjugate acid 1-OH₂⁺. In the ground state, the presence of this species may be ignored in the determination of pK_{R^+} values because of the rapidity of its formation and conversion to carbocation. In the excited state, however, these reaction velocities may be comparable to excited-state decay. Consider the reaction scheme of excited singlet species as shown in eq 2. Various combinations of rate constants for chemical reactions and decay from excited states leading to inefficient conversion of 1-OH₂⁺ to 1⁺ could account for the observed fluorescence emission.



Another nonfluorescing species⁷ which may be considered is the isomeric alcohol 1'-OH. HMO calculations for the excited singlet state of 1⁺ show maximum positive charge at carbons 9 and 10, in contrast to carbon 5 in the ground state, and attack by water at these positions would yield 1'-OH or its conjugate acid. Charge distribution in the excited state has been useful in rationalizing products of photosubstitution reactions.⁸ Structural formulas which approximately represent charge distributions in the excited singlets 1-OH₂⁺ and 1⁺ are shown in Scheme I. The positive oxygen in 1-OH₂⁺ stabilizes the negative charge on the adjacent benzene ring. The relation of the singlet state to the charge transfer structure, such as depicted for 1-OH₂⁺, has been discussed in connection with the enhanced acidity and basicity typical of excited singlets.⁹ The diversion of 1⁺ to 1'-OH can account for the small relative fluorescence of 1⁺ compared to the

Scheme I



quenching of fluorescence of 1-OH. The scheme as shown is rather complex for species with short lifetimes (τ 1-OH, ~ 1 ns, ethanol; τ 1⁺, 40 ns, 98% H₂SO₄), but not unreasonably so.^{8,10}

Preparative scale photolyses of mixtures of 1-OH and 1⁺ in varying concentrations of acid failed to yield products derived from 1'-OH, which is not surprising because 1'-OH should revert to the more stable 1-OH rapidly in acid. The major photolysis products are the ether 1-O-1 and the hydride transfer products, dibenzocycloheptatriene and dibenzotroponone. Irradiation with a sunlamp through Pyrex ensures absorption by the cation rather than by the alcohol, and the excited cation undergoes bimolecular reactions with the alcohol to produce the products mentioned. The nature of the excited species is not known, but because the reaction mixture was well stirred without excluding oxygen, a triplet species is unlikely. A vibrationally excited ground-state cation or excited singlet may be the photoactive species. Hydride transfer between cation and alcohol and ether formation are known to be ground-state reactions of tropylium ions,¹¹ but in control experiments only 1-OH could be recovered from solutions identical with those which were irradiated but which were left in the dark.

Experimental Section

Materials. Aldrich Chemical Co. 5*H*-dibenzo[*a,d*]cycloheptatrien-5-ol (1-OH) was recrystallized from benzene. The other alcohols were obtained from reactions of phenylmagnesium bromide with the appropriate ketones: 2-OH from dibenzo[*a,d*]cycloheptatrien-5-one (Aldrich); 3-OH from xanthone (Eastman); 4-OH from thioxanthone, prepared by the method of Davis and Smiles.¹² All melting points agreed with literature values. Sulfuric acid solutions were prepared by diluting J. T. Baker reagent grade acid with distilled water. Acid concentrations were determined with a Photovolt digital pH meter for dilute concentrations and by titrations with standardized KOH solution for concentrated solutions. Acid concentrations were converted to H_R values by means of Deno's tables.¹³

Fluorescence Titrations. Solutions of the alcohols were prepared in absolute ethanol, and 1-mL aliquots were diluted to 100 mL with the appropriate aqueous sulfuric acid solution. Immediately after the solution was prepared, the fluorescence emission spectrum was recorded with a Farrand spectrofluorometer fitted with 5-nm slits, a Honeywell recorder, an IP 28 photomultiplier, and a thermostated cell compartment maintained at 25 ± 1 °C. Absorption titrations were similarly determined with a Cary 14 spectrophotometer. The ground state pK_{R^+} values agreed with literature values, indicating that the presence of 1% ethanol has little effect on the H_R scale in this acidity range.

Fluorescence Lifetimes. Fluorescence lifetimes were kindly measured by Dr. R. F. Chen, using apparatus described previously.¹⁴

Photolysis of 1-OH. In a typical reaction, 1 g of 1-OH was mixed

with 150 mL of 5 N H₂SO₄ in a 500-mL Pyrex flask. The mixture was filtered to remove undissolved alcohol, and the orange solution was stirred and irradiated with a 250-W G.E. sunlamp for 30 min. Ether extraction, followed by neutralization, drying (MgSO₄), and evaporation, yielded a yellow solid. The solid was dissolved in methylene chloride and slurried with Fisher neutral alumina (80% reaction product-20% alumina). The solvent was evaporated, and the mixture was added to a column of alumina in petroleum ether. Development of the column with petroleum ether-methylene chloride yielded, in order, the following compounds: dibenzo[*a,d*]cycloheptatriene, dibenzo[*a,d*]cycloheptatrienyl ether, dibenzo[*a,d*]cycloheptatrien-5-one, and unreacted 1-OH. The compounds were identified by comparison with authentic samples.

Acknowledgments. Partial support for this work was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society. Dr. Raymond F. Chen, National Heart Institute, measured the fluorescence lifetimes, and Dr. N. C. Chinh carried out some of the photolysis experiments.

Registry No.—1-OH, 10354-00-4; 2-OH, 55090-29-4; 3-OH, 596-38-3; 4-OH, 6630-80-4.

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