be a very general one.[17] It is capable of giving quantitative information on the energetics of strong hydrogen bonding which will allow a better evaluation of the importance of intramolecular processes in the gas phase and solution.[18]

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[17] Beauchamp has reported that proton bound dimerization of dimethoxyalkanes (but not dihydroxyalkanes) is inhibited by intramolecular hydrogen bond formation (ref 3c). All of our diaminoalkanes formed proton bound dimers from 10^{-4} to 10^{-3} Torr with equal facility. This further supports Beauchamp's conclusion that a nonbridging hydrogen is needed for dimerization.

[18] The solution thermodynamic data for protonation of diaminoalkanes in water indicate that intramolecular hydrogen bonding is not important and that inductive effects are felt strongly for short chain lengths. The long chain diamines behave in solution nearly like analogous *n*-alkylamines.

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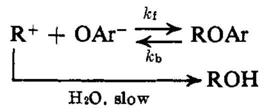
Interaction of Phenols with the Tri-*p*-anisylmethyl Cation

Sir:

The effects of ionic and nonionic solutes upon the rate and equilibrium constants for the attack of water upon the tri-*p*-anisylmethyl cation (R^+) have been explained in terms of ion pairing and changes in solvent structure.[1,2] In extending earlier work,[2] we used phenoxide ions as nucleophiles by taking hydroxide ion in an excess of the phenol, so that the phenoxide ion concentration was that of the initial hydroxide ion. The concentrations of phenoxide ions were 3×10^{-3} *M* and of phenol 0.06–0.25 *M*. (All the rate measurements were made using a Durrum-Gibson stopped flow spectrophotometer.[2]) The reaction gives an equilibrium mixture of R^+ and ROAr which in a few seconds gives the thermodynamically stable ROH (*cf.* the reaction of R^+ with azide ion[2]).



The rate constants fit eq 1, where k_f^0 is the rate constant extrapolated to zero phenol.[3]

$$\log (k_f/k_f^0) = a[\text{ArOH}] \qquad (1)$$

The values of k_f^0, a, and the equilibrium constant $K = k_f/k_b$ are given in Table I. Values of k_f and K for the reaction of R^+ with other anionic nucleophiles are included for comparison.

This stabilization of R^+ by phenols is confirmed by the observation that phenols decrease the reactivity of R^+ toward water, and increase the equilibrium formation of R^+ in dilute acid, as measured by $-H_R$.[4]

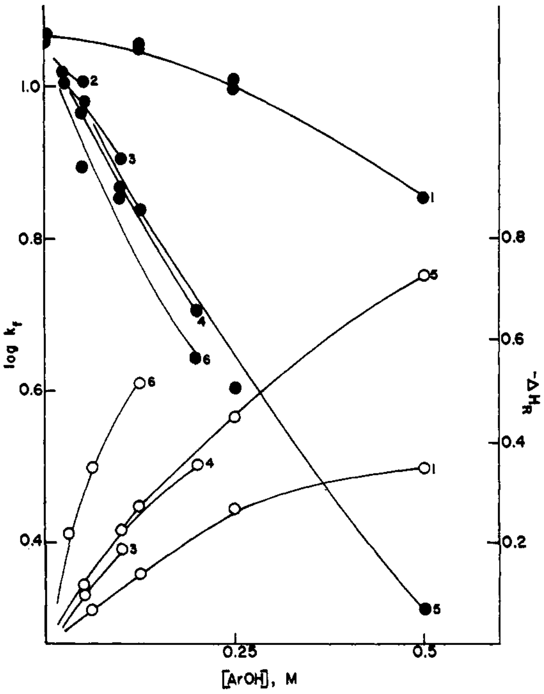


Figure 1. Inhibition of the reaction of R^+ and water at 25.0° by phenols (left-hand scale, solid points), and increase of $-H_R$ by phenols (right-hand scale, open points). Substituents: (1) none; (2) *p*-Me; (3) *p*-OMe; (4) *m*-OME; (5) *m*-OH; (6) 3,5-$(OH)_2$.

Table I. Reaction of Tri-*p*-anisylmethyl Cation with Phenoxide Ions and Other Anionic Nucleophiles[a]

Nucleophile	k_f, l. mol^{-1} sec^{-1}	a[b]	K, l. mol^{-1}
$C_6H_5O^-$	1.05×10^5	-1.0	1.6×10^4
p-$MeC_6H_4O^-$	2.5×10^5		
p-$MeOC_6H_4O^-$	4.25×10^5	-2.1	2.4×10^4
m-$MeOC_6H_4O^-$	1.42×10^5		2.3×10^3
OH^-	8.2×10^3[c]		Large
N_3^-	5×10^6[c]		6.6×10^4
CN^-	2.7×10^3[d]		Large

[a] In water at 25.0°. [b] For reaction of ArO^- and R^+ in the presence of ArOH, eq 1. [c] Reference 2. [d] Measured using the methods described in ref 2.

Some examples of this behavior are shown in Figure 1. In 3 *M* HCl or $HClO_4$, where the equilibrium is wholly toward R^+, added phenols shift the broad maximum of R^+ at 482 nm slightly toward larger wavelengths.[6] With 1 *M* resorcinol $\Delta\lambda_{max} = +7$ nm and with 0.063 *M* phloroglucinol $\Delta\lambda_{max} \sim +2$ nm. Phenols have only a small effect on the protonation of *p*-nitroaniline, and cyclohexanol (up to 0.1 *M*) does not increase $-H_R$. (However, H_R is affected by relatively high concentrations of many nonionic solutes.[1])

Electron-donating substituents in the phenols increase both their ability to stabilize R^+ and the nucleophilicity of the phenoxide ions (Figure 1 and Table I).

There is extensive evidence for interactions between cations and aromatic compounds,[7] and it has been suggested that π complexes are intermediates in aromatic

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[1] M. J. Postle and P. A. H. Wyatt, *J. Chem. Soc., Perkin Trans. 2*, 474 (1972).

[2] C. A. Bunton and S. K. Huang, *J. Amer. Chem. Soc.*, **94**, 3536 (1972).

[3] Hydrogen bonding between phenol and phenoxide ion could reduce the nucleophilicity of the latter, although it is probably unimportant in water. It does not explain the effects on H_R or on the reaction with water, and leads to the prediction that inhibition of the phenoxide ion reaction should increase with increasing phenol acidity in disagreement with experiment.

[4] For discussions of acidity functions, see ref 5.

[5] R. H. Boyd in "Solute–Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 3.

[6] These shifts are similar to that of +8 nm given by 1 *M* NaOTos, for which $\Delta H_R = -0.65$, and which strongly inhibits reactions of R^+ with H_2O and OH^-.

[7] E. J. F. Duynstee and E. Grunwald, *Tetrahedron*, **21**, 2401 (1965); J. Gordon and R. L. Thorne, *J. Phys. Chem.*, **73**, 3643, 3652 (1969); J. J. Brooks, W. Rhine, and G. D. Stucky, *J. Amer. Chem. Soc.*, **94**, 7346 (1972).

electrophilic substitution.[8] In addition, similar interactions are believed to be responsible for the catalysis of the acetolysis of fluorenyl tosylates by phenanthrene.[9] All the evidence suggests that there is some binding of the cation with the aromatic π system rather than a chance encounter, and the ability of phenols to stabilize R^+ is greater than that of simple univalent electrolytes (Figure 1 and ref 2 and 10). Neighboring group participation by aryl substituents is often interpreted in terms of intermediate phenonium ions,[11] but interactions between the π system and the forming carbocation may be important.

Despite their low basicities, phenoxide and thiophenoxide ions[12] are excellent nucleophiles toward triarylmethyl cations, and interactions between the cation and the aromatic π system of the nucleophile may be important, although formally, one could also regard this high reactivity of phenoxide ion as an α effect, which is the high nucleophilicity observed when an atom having unshared electrons is adjacent to the reaction center. However, the reactions of thiophenoxide ion were with stable triarylmethyl dye cations, where the importance of nucleophile–cation ion pairing and general base catalysis has been postulated.[13] Slow proton transfers do not appear to be of great importance in reactions of the tri-*p*-anisylmethyl cation.[1,2,13]

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[8] G. Olah, *Accounts Chem. Res.*, **4**, 240 (1971); *cf.* J. H. Ridd, *ibid.*, **4**, 248 (1971).

[9] A. K. Colter, S. S. Wang, G. H. Megerle, and P. S. Ossip, *J. Amer. Chem. Soc.*, **86**, 3106 (1964); A. K. Colter, F. F. Guzik, and S. H. Hui, *ibid.*, **88**, 5754 (1966).

[10] C. A. Bunton, J. H. Crabtree, and L. Robinson, *J. Amer. Chem. Soc.*, **90**, 1258 (1968).

[11] D. J. Cram, *J. Amer. Chem. Soc.*, **86**, 3767 (1964); J. M. Harris, F. L. Schadt, P. v. R. Schleyer, and C. J. Lancaster, *ibid.*, **91**, 7508 (1969).

[12] C. D. Ritchie, *Accounts Chem. Res.*, **5**, 348 (1972), and references cited.

[13] E. A. Hill and W. J. Mueller, *Tetrahedron Lett.*, 2565 (1968).

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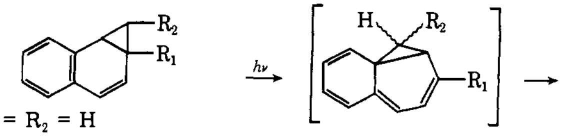
Selectivity in the Excited State Rearrangements of Homobenzotropilidenes

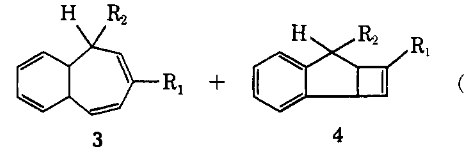
Sir:

The photochemistry of benzonorcaradienes[1a-f] and benzotropilidenes[1d-g,2] has been of general interest in recent years. A major process in benzonorcaradiene photochemistry involves a formal 1,5-sigmatropic shift with eventual production of either a 1,2-benzotropilidene[1c,e] or a 2,3-benzobicyclo[3.2.0]hepta-2,6-diene (eq 1),[1c,f,3] while the photochemistry of benzotropilidenes is dominated by 1,7-group migration (eq 2).[4]

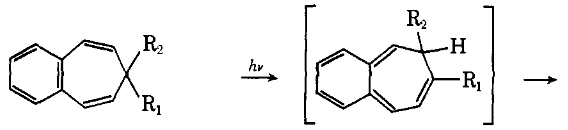


1a, $R_1 = R_2 = H$
b, $R_1 = CO_2CH_3$; $R_2 = H$
c, $R_1 = CN$; $R_2 = H$
d, $R_1 = H$; $R_2 = CH_2CO_2CH_3$

2

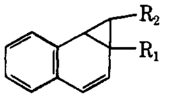


3 4 (1)



5a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CO_2CH_3$
c, $R_1 = CO_2CH_3$; $R_2 = H$
d, $R_1 = R_2 = CH_3$
e, $R_1 = CH_3$; $R_2 = CH_3$

6



7 (2)

Aside from the intrinsic interest in the photochemistry of homo systems,[5] there existed rearrangement possibilities in 1,2-homo-3,4-benzotropilidenes which are formally analogous to high efficiency processes in both benzonorcaradienes and benzotropilidenes.[6] We wish to report here the highly selective, facile photoisomerization of homobenzotropilidenes **8a** and **8b** to the corresponding 4,5-benzobicyclo[4.2.0]octa-2,4-dienes **9a** and **9b**.

Irradiation of **8a** in cyclohexane at 300–330 nm through Pyrex led to rapid formation of a single product at low conversion (10–15%). Extended irradiation produced naphthalene and several uncharacterized compounds in addition to this initially formed material. The major product was isolated by vpc and its structure established as **9** by comparison of its nmr spectrum with that of 4,5-benzobicyclo[4.2.0]octa-2,4-diene (**9a**).[7,7a] To obtain additional evidence on the

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[1] (a) E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1458 (1967); (b) J. S. Swenton and A. J. Krubsack, *ibid.*, **91**, 786 (1969); (c) G. W. Gruber and M. Pomerantz, *ibid.*, **92**, 4004 (1970); (d) D. M. Madigan and J. S. Swenton, *ibid.*, **92**, 7515 (1970); *Tetrahedron*, **28**, 2703 (1972); (e) D. M. Madigan and J. S. Swenton, *J. Amer. Chem. Soc.*, **93**, 6316 (1971); (f) M. Kato, M. Kawamura, Y. Okamoto, and T. Muva, *Tetrahedron Lett.*, 1171 (1972); (g) H. Dürr and H. Kober, *ibid.*, 1255 (1972).

[2] (a) M. Pomerantz and G. W. Gruber, *J. Amer. Chem. Soc.*, **89**, 6798, 6799 (1967); **93**, 6615 (1971); (b) K. A. Burdett, D. H. Yates, and J. S. Swenton, *Tetrahedron Lett.*, in press.

[3] Whether 1,2-benzotropilidenes or benzobicyclo[3.2.0]hepta-2,6-dienes are produced is dependent upon the particular system. For a discussion, see ref 1e.

[4] Recently, it has been noted that a 1,3-hydrogen shift in the parent 3,4-benzotropilidene competes with the more common 1,7 process to the extent of ~10%.[2b]

[5] For an interesting series of papers in homofulvene photochemistry, see: (a) T. Tabata and H. Hart, *Tetrahedron Lett.*, 4929 (1969); (b) H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, **92**, 3474 (1970); (c) N. K. Hamer and M. Stubbs, *Chem. Commun.*, 1013 (1970), and references cited therein.

[6] The quantum efficiency of the **1b** → **3b** reaction is 0.45–0.35, while we have observed that the efficiencies of 1,7 shifts in five different 3,4-benzotropilidenes are always >0.5.

[7] A. M. Braun, *J. Org. Chem.*, **35**, 1208 (1970).

(7a) Note Added in Proof. Recently [P. Crews and J. Beard, *J. Org. Chem.*, **38**, 522 (1973)] 7,8-benzobicyclo[4.2.0]-2,7-octadiene (i) has been isolated instead of **9a** from the benzyne-cyclohexadiene reaction. This compound was presumably thermally converted to **9a** in the previous study. To exclude this thermal rearrangment in our work, we have examined the crude nmr spectrum of the irradiation of **8a** and find no evidence for i in our reaction.