Table I. Delayed Trapping of Resin-Bound Benzyne

Starting material	t_1,[a] s	t_2,[b] s	Yield of IIIa (%)
IIb	30[c]	0	99
IIb	30	70	10
IIc		0	99
IIc	70	95	36
IIc	150	220	17

[a] t_1, time at which N_2 evolution ceased. [b] t_2, time at which trapping agent (tetracyclone) was added. [c] Corrected for evolution of CO.

disappearance of all ester carbonyl absorption in the infrared spectrum of the saponified resin. (The absorptions characteristic of the resin-bound carboxylates were observed.)

The prolonged lifetime of the resin-bound aryne was most convincingly demonstrated by the following. Samples of IIb and IIc were treated with 1 equiv of lead tetraacetate in a closed system and N_2 evolution was followed manometrically.[10] Tetracyclone was added to the mixture only after all N_2 evolution had ceased, t_1, and following an additional lag time. The resin esters were saponified, and the product was isolated. Results are shown in Table I. Isolation of IIIa from reactions occurring a full 70 s following the completion of aryne generation reflects a dramatic persistence for the intermediate.

The systematic decrease in yield of IIIa with increasing time lag indicates that a third reaction, other than dimerization, is slowly depleting the aryne concentration. Assuming that this unknown process is operative during the oxidation as well (up to 150 s), the half-life of the aryne is of the order of 50 s for IIc. We have not yet identified the competing pathway.

These results contrast sharply with those of Crowley, Harvey, and Rapoport.[2] They found roughly 58% intraresin anhydride formation between carboxyls on polystyrene with the same degree of cross-linking and extent of functionalization as our own samples.[6] This apparent contradiction may be resolved if site isolation is a phenomenon limited by the time frame. That is, the conformational changes of these polymers may be sufficiently slow that during a period of a hundred seconds a negligible number of reactive sites achieve the proximity required for coupling. Since the arynes undergo irreversible side reactions at a greater rate, no coupling is observed. By contrast, anhydride formation is reversible and may come to equilibrium over a much longer period of time, sufficient time for the polymer chain to exercise all of its conformational degrees of freedom. The probability of close contact between reactive centers may be much greater when averaged over the longer time interval.[11] The effect of viscosity on solution phase kinetics is probably a good analogy. We feel that the word "pseudodilution" is more appropriate than "hyperentropic efficacy"[1] to describe such a phenomenon since its origin is kinetic not thermodynamic (at least for the case of the low-cross-linked polystyrenes). The apparent difference in lifetimes on the two polymers may be related to differences in their mobilities, but clarification of this point will have to await identification of the competing pathway.

We hope that this method will be of value for studying some of the slower reactions of arynes. If so, it would nicely complement the matrix isolation experiments.

Acknowledgments. This work was supported by the U.S. Army Research Office, Grant DAHCO-75-G-0064.

References and Notes

(1) See J. I. Crowley and H. Rapoport, *Acc. Chem. Res.*, **9**, 135 (1976), for a review of the literature.
(2) For example, see J. I. Crowley, T. B. Harvey, and H. Rapoport, *J. Macromol. Sci. Chem.*, **7**, 1117 (1973).
(3) J. Kolc, *Tetrahedron Lett.*, 5321 (1972); O. L. Chapman et al., *J. Am. Chem. Soc.*, **95**, 6134 (1973).
(4) A rate constant of 7 × 10^8 l./(mol s) has been measured in the gas phase, M. E. Schafer and R. S. Berry, *J. Am. Chem. Soc.*, **87**, 4497 (1965).
(5) C. D. Campbell and C. W. Rees, *J. Chem. Soc. C*, 742 (1969).
(6) These samples were prepared[8] from Biobead S-X2, a 2% divinyl benzene cross-linked polystyrene. Functionalization amounted to 0.23 mmol/g.
(7) These samples were prepared[8] from Biobead SM-2, a 15% divinyl benzene cross-linked polystyrene. Functionalization amounted to 0.09 mmol/g.
(8) Preparation of the esters followed the method of R. L. Letsinger et al., *J. Am. Chem. Soc.*, **86**, 5163 (1964).
(9) In each experiment products were isolated following saponification of the esters. Yields reflect the amount of alcohol isolated. All products were characterized by NMR, ir, and mass spectrometry.
(10) The reaction vessel was immersed in a thermostated ultrasonic bath to optimize mass transport rates.
(11) A similar explanation was put forth to explain the time dependence of some intraresin condensation reactions by M. A. Kraus and A. Patchornik, *J. Polym. Sci. Polym. Symp.*, **47**, 11 (1974).

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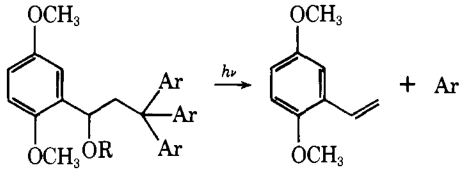
Charge-Transfer-Induced Photosolvolysis of Benzyl Alcohols

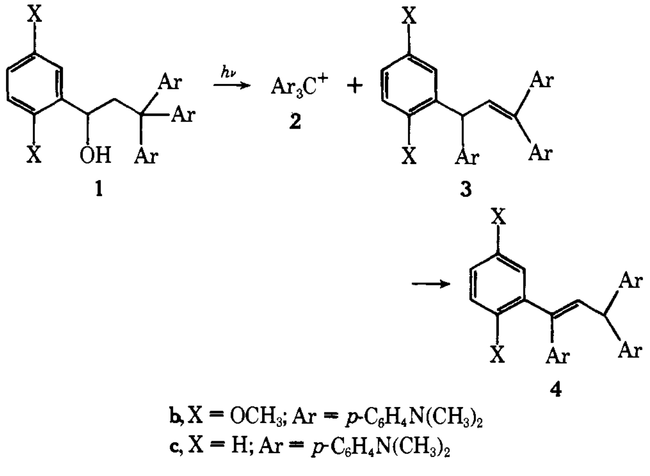
Sir:

A variety of benzyl derivatives including esters, halides, and ammonium and sulfonium salts are known to give products derived from light-induced solvolytic reactions.[1] Electron donating groups at the meta position on the aromatic ring increase the efficiency of the reaction.[2] While studying the fragmentation reactions of the expected intermediate benzyl cations, the benzyl acetate **1a** and alcohol **1b** were prepared.



1a, R = $COCH_3$; Ar = p-$C_6H_4N(CH_3)_2$
1b, R = H; Ar = p-$C_6H_4N(CH_3)_2$

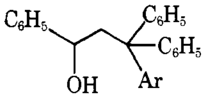
As anticipated, irradiation (254 nm) of **1a** in methanol yielded 2,5-dimethoxystyrene and the blue crystal violet cation. Unexpectedly **1b** likewise yielded these products despite the poor leaving ability of the hydroxyl group.[3] These reactions occurred even when employing light (>300 nm) that was not significantly absorbed by the dimethoxyphenyl chromophore. The methoxy groups were found to be unnecessary, and irradiation of benzyl alcohol **1c** with >300 nm light also gave the crystal violet cation **2**.



b, X = OCH_3; Ar = p-$C_6H_4N(CH_3)_2$
c, X = H; Ar = p-$C_6H_4N(CH_3)_2$

The major products of these reactions (254 or >300 nm) are the rearranged olefins **3c** (38%)[4] and **3b** (40–50%).[4] The structure of **3b** was confirmed by partial conversion to **4b**[4] with butyllithium followed by quenching with methanol, and by oxidation of the two isomers with periodate–permanganate in acetone to give Michler's ketone and 2,5-dimethoxy-4′-dimethylaminobenzophenone,[4] respectively. The position of the double bond in **3c** was assigned by analogy.

The dimethylaminophenyl group was found to migrate in preference to phenyl but migration occurred only when a stabilized carbonium ion could be formed. Irradiation (>300 nm) of **5** produced the rearranged **6** (25%)[4] and irradiation (>300 nm) of **7** yielded unrearranged methyl ether **8** (39%) and the fragmentation product **9** (5%).[4] The lower homologue **10**[5] similarly gave the corresponding methyl ether **11** (60%) plus *p*-dimethylaminostilbene (~1%).[4,5] On replacement of the dimethylaminophenyl group by a dimethylamino group, **12** gave **13** (254 nm) but only in 12% yield.[4,6] Significantly, upon substitution of phenyl for dimethylaminophenyl (**14**) or dimethylcarbinol for the benzylic alcohol group (**15**) related photoproducts were not formed. Likewise 1-phenylethanol failed to undergo photosolvolysis. However, the bond joining the alcohol and arylamine groups was not required, and irradiation (254 or >300 nm) of 0.1 M benzyl alcohol and 0.05 M *N*,*N*-dimethylaniline in methanol gave, albeit slowly, a 86:14 mixture of *o*- and *p*-benzyl-*N*,*N*-dimethylaniline (60%).[4,7]



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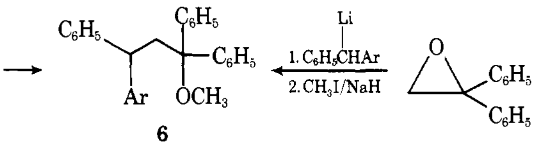

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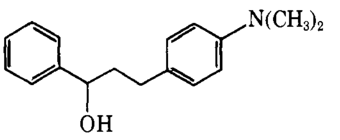

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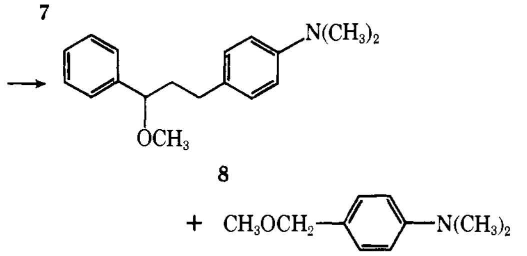

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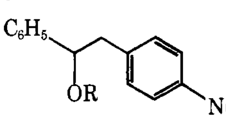
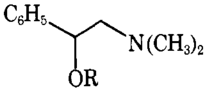
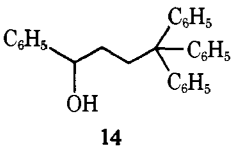


10, R = H
11, R = CH_3



12, R = H
13, R = CH_3



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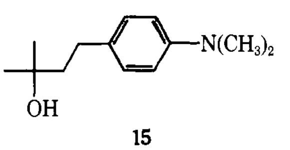


15

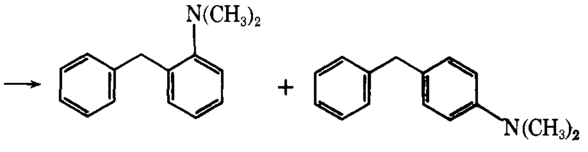
These observations appear to be uniquely consistent with photochemical formation of carbonium ions which undergo subsequent substitution, rearrangement, or fragmentation reactions. Fragmentation occurs only when the departing carbonium ion is stabilized by one or more dimethylaminophenyl groups. Only this group was observed to migrate and only when greater charge stabilization was achieved. The ortho:para ratio observed in the benzyl alcohol-*N*,*N*-dimethylaniline reaction was unexpectedly high but was identical with the ratio of these products (86:14) found when benzyl cation was prepared by adding phenyldiazomethane to 0.05 M *N*,*N*-dimethylaniline hydrochloride in methanol.

Table I. Ultraviolet Absorption Maxima in Methanol

	Compound [Ar = *p*-$C_6H_4N(CH_3)_2$]	λ_{max}, nm (ϵ, l. mol^{-1} cm^{-1})	
	p-CH_3Ar	252 (13 000)	302 (1900)
15	$(CH_3)_2COHCH_2CH_2Ar$	252 (12 300)	301 (1520)
7	$C_6H_5CHOHCH_2CH_2Ar$	254 (14 200)	302 (1560)
10	$C_6H_5CHOHCH_2Ar$	256 (15 800)	301 (1750)
5	$C_6H_5CHOHCH_2CAr(C_6H_5)_2$	262 (15 000)	300 (sh)
1c	$C_6H_5CHOHCH_2CAr_3$	263	300 (sh)
12	$C_6H_5CHOHCH_2N(CH_3)_2$	258 (~250)[a]	[a]
14	$C_6H_5CHOHCH_2C(C_6H_5)_3$	260 (970)	

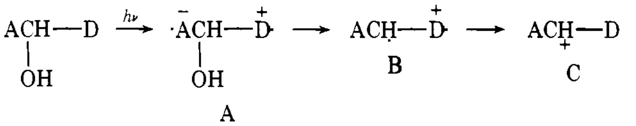
[a] Concentration dependent, tailing to 310 nm.

$C_6H_5N(CH_3)_2$ + $C_6H_5CH_2OH$



The photochemical reaction apparently requires both an electron acceptor (phenyl) and donor (dimethylamino). Sensitization by energy transfer is excluded at least in the reaction of benzyl alcohol with *N*,*N*-dimethylaniline since both the singlet (95 kcal/mol) and triplet (76 kcal/mol)[8] energies of *N*,*N*-dimethylaniline are lower than those of benzyl alcohol, E_s = 110 kcal/mol and E_T = 82 kcal/mol.[9] The short wavelength ultraviolet absorption maxima of **2a**, **5**, **7**, and **10** (Table I) reveal bathochromic shifts relative to *N*,*N*-dimethyltoluidine. This apparent charge-transfer absorption suggests the possibility of a singlet reaction. An observation that up to 0.2 M benzyl alcohol fails to observably quench *N*,*N*-dimethylaniline fluorescence is not in disagreement since the photoreaction of these compounds was very inefficient. Moreover a triplet intermediate appears unlikely since neither 0.2 M 3,3,4,4-tetramethyldiazetidene 1,2-dioxide[10] nor 0.08 M piperylene quenched the reactions of *N*,*N*-dimethylaniline with like concentrations of benzyl alcohol.[11]

In these reactions the complexed (or free) phenyl radical anion (A) presumably expels hydroxide ion to give a benzyl radical (B). This species is reoxidized by the electron deficient donor to give a ground state carbonium ion (C). The closest analogy for this process is SRN1[12] displacement at electron deficient benzylic carbon.[13] This analogy differs from the present observations in that the benzyl radical is not oxidized to a cation but reacts with a nucleophile to give a radical anion. Thus a unique feature in the present reaction is back transfer of an electron from the benzyl radical (B → C), a process that might be anticipated by consideration of the relative electronegativities of nitrogen and carbon. This process, in effect, inverts the charge on phenyl from negative to positive during the course of the reaction.[14] The synthetic utility of the reaction is under investigation.



$$\underset{\displaystyle OH}{ACH}\!-\!D \xrightarrow{h\nu} \cdot\overset{-}{\underset{\displaystyle OH}{ACH}}\!-\!\overset{+}{D}\cdot \longrightarrow \underset{\displaystyle B}{AC\dot{H}\!-\!\overset{+}{D}\cdot} \longrightarrow \underset{\displaystyle C}{AC\overset{}{\underset{+}{H}}\!-\!D}$$

References and Notes

(1) V. B. Ivanov, V. L. Ivanov, and M. G. Kuzmin, *Mol. Photochem.*, **6**, 125 (1974); S. J. Cristol and G. C. Schloemer, *J. Am.Chem. Soc.*, **94**, 5916 (1972); V. Lillis, J. McKenna, J. M. McKenna, and I. H. Williams, *J. Chem. Soc., Chem. Commun.*, 473, 474 (1974); A. L. Maycock and G. A. Berchtold, *J. Org. Chem.*, 35, 2532 (1970).

(2) H. E. Zimmerman and V. R. Sandel, *J. Am. Chem. Soc.*, **85**, 915 (1963); J. W. Chamberlin, *J. Org. Chem.*, **31**, 1658 (1966); D. A. Jaeger, *J. Am. Chem. Soc.*, **97**, 902 (1975).

(3) Photosolvolysis of a cyclopropylcarbinol has previously been reported; S. S. Hixson and J. Borovsky, *J. Chem. Soc., Chem. Commun.*, 607 (1975).

(4) All new compounds had satisfactory elemental analyses and NMR spectra. Except for **3** and **4** new photoproducts were compared with samples synthesized by unambiguous procedures. Photochemical yields were calculated taking into account recovered starting material.

(5) S. S. Jenkins, J. S. Buck, and L. A. Bigelow, *J. Am. Chem. Soc.*, **52**, 4495 (1930).

(6) M. Tiffeneau and E. Fourneau, *Bull. Soc. Chim. Fr.*, **14** (43), 971 (1913).

(7) D. A. Archer, H. Booth, and R. D. Stangroom, *J. Chem. Soc. C*, 2276 (1970).

(8) Y. Gondo and Y. Kanda, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **5**, 133 (1964).

(9) The triplet energy for benzyl alcohol was assumed to differ insignificantly from that of toluene (E_T = 82 kcal/mol); D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

(10) E. F. Ullman and P. Singh, *J. Am. Chem. Soc.*, **94**, 5077 (1972).

(11) The absence of quenching by the diazetidene, a radical-chain inhibiter, militates against a possible radical chain reaction.

(12) J. K. Kim and J. F. Bunnett, *J. Am. Chem. Soc.*, **92**, 7463, 7464 (1970).

(13) N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975); G. A. Russell and W. C. Danen, *J. Am. Chem. Soc.*, **88**, 5663 (1966); **90**, 347 (1968).

(14) Photosolvolysis of a benzyl ether bearing a ferrocenyl group may proceed by a similar path; C. Baker and W. M. Horspool, *J. Chem. Soc., Chem. Commun.*, 1236 (1972).

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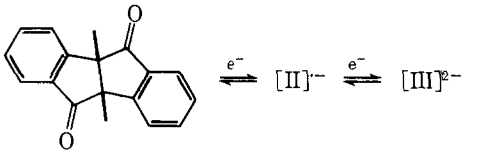
Symmetry vs. Fluxionality, a Radical Anion with Borderline Properties

Sir:

Electrochemical reduction of the diketone I (*cis*-10,11-dimethyldiphensuccindan-9,12-dione) proceeds via two reversible, one-electron steps at half-wave potentials of −1.75 and −2.23 V vs. Ag|AgCl.[1] This report concerns the spectroscopic properties of the radical anion II which reveal some unusual and interesting structural properties.



I

The electron paramagnetic resonance spectrum of II exhibits splittings consistent with four pairs of equivalent protons with hyperfine constants of 2.65, 2.55, 1.3, and 0.2 G. The absence of detectable hyperfines for the methyls effectively rules out structure IIa. The remaining choices, rapidly equilibrating species IIc and IIc′ and the fully symmetrical structure IIb, where the dotted lines denote a strong homoconjugative interaction, are equally consistent.

Further insight was provided by the infrared spectrum. An infrared solution cell was modified to include the components of a three-electrode electrochemical cell. The working electrode consisted of a 80-mesh platinum grid fitted between the NaCl windows.[2] Excellent potential control was achieved with Nernstian equilibrium established within 3 min of commencing electrolysis The spectrum of II, obtained at −1.85 V, is shown in Figure 1.[3] (Upon repolarization of the electrode to −1.0 V the spectrum of I was regenerated.) Table I presents the relevant absorptions of a series of representative carbonyl compounds and their respective radical anions.

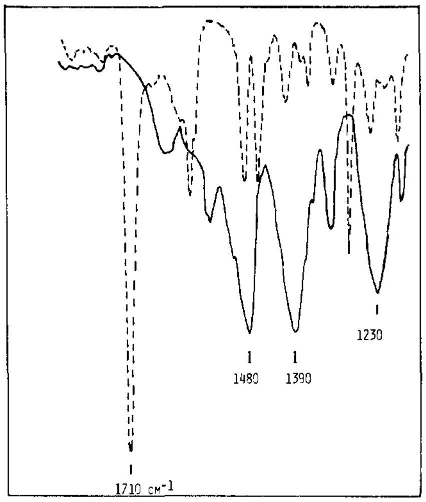
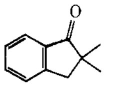
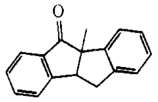
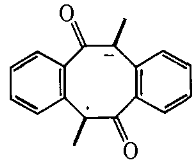


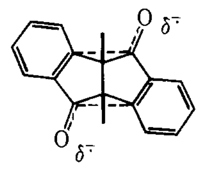
Figure 1. The infrared spectra of I (dotted line) and II (solid line) obtained in dimethyl-d_6 sulfoxide with 0.4 M $(CH_3)_4NPF_6$.

Table I. Infrared Absorptions of Carbonyl Radical Anions

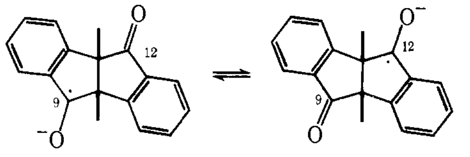
Compound	*E* vs. Ag/AgCl (v)	ν_{CO} (cm^{-1})	$\nu_{CO\cdot^-}$ (cm^{-1})
9-Fluorenone	−1.22	1695	1540
1,4-Naphthoquinone	−0.63	1660	1510
	−2.08	1710	1548
	−2.02	1710	1544



IIa



IIb



IIc IIc′

The most striking features of the spectrum of II are: (i) the absence of absorption at 1710 cm^{-1} characteristic of the neutral carbonyl, and (ii) three strong yet broad absorptions at frequencies much lower than those observed for the monoketone anion radicals of Table I. (The latter have only a single strong band in this region.)

Structure IIb might be expected to have a C–O stretching mode as low as 1480 cm^{-1}, but the other two bands and the broadness are difficult to rationalize for this structure. Alternatively, if the fluxional motion of the equilibrating pair IIc ⇌ IIc′ is rapid enough to influence the vibrational states of the system, the anomolous features of the spectrum may be accommodated.

Hush's theory for mixed-valence equilibria is relevant to understanding the dynamic properties of IIc.[4] In this view, the potential surface which includes IIc and IIc′ is derived from the weak interaction of two zeroth-order surfaces which