

Research Fund, administered by the American Chemical Society, the Research Corporation, the National Science Foundation, and the National Institutes of Health.

## References and Notes

- (1) (a) P. Lontie and R. Witters in "Inorganic Biochemistry", Vol. 1, G. L. Eichorn, Ed., Elsevier, Amsterdam, 1973, Chapter 12; (b) J. Peisach, P. Aisen, and W. E. Blumberg, Ed., "The Biochemistry of Copper", Academic Press, New York, N.Y., 1966; (c) F. Ghirelli, Ed., "Physiology and Biochemistry of Haemocyanins", Academic Press, New York, N.Y., 1966; (d) B. L. Vallee and W. E. C. Wacker, "The Proteins", 2d ed, Vol. V, H. Neurath, Ed., Academic Press, New York, N.Y., 1970; (e) R. Osterberg, *Coord. Chem. Rev.*, **12**, 309 (1974).
- (2) For example, it has been suggested that the active site of deoxyhemocyanin contains two Cu(I) atoms each bound by the three to five imidazoles. See (a) A. Ghirelli-Magaldi, International Conference on Copper Proteins, Manziara (Rome), Italy, Sept 22-26 (1974); (b) B. Salvato, A. Ghirelli-Magaldi, and F. Ghirelli, *Biochemistry*, **13**, 4778 (1974).
- (3) Abbreviations used include: DMK, acetone; HDOH, 3,3'-(trimethylenedinitrilo)-di-2-butanedioximate; C<sub>7</sub>H<sub>8</sub>, toluene; 1-Melm, 1-methylimidazole.
- (4) Prepared by condensing 2,3-butanedione monoxime with 1,3-diaminopropane in ethanol at 25 °C which is much simpler than the previously reported procedure: Von E. Uhlig and M. Friedrich, *Z. Anorg. Allg. Chem.*, **343**, 299 (1966).
- (5) This complex has thus far only been isolated in the presence of excess HDOH and even then contains more than the expected amount of Cu. Apparently a second Cu can bind to the two oxime oxygens, similar to the binuclear Cu(II) complex obtained with salicylaldehyde-ethylenediamine: R. M. Countryman, W. T. Robinson, and E. Sinn, *Inorg. Chem.*, **13**, 2013 (1974).
- (6) All complexes isolated gave satisfactory elemental analyses which were submitted to the referees.
- (7) Adding very small amounts of dioxane to a concentrated acetone solution of 2 causes crystallization of the Cu(II) complex which indicates possible complexation of dioxane.
- (8) All electrochemistry was performed with platinum electrodes. The supporting electrolyte used in CH<sub>3</sub>CN was tetraethylammonium perchlorate (TEAP, 0.1 M) but in DMK and CH<sub>2</sub>Cl<sub>2</sub> tetrabutylammonium perchlorate was employed. The reference electrode was a silver wire immersed in a CH<sub>3</sub>CN solution 0.1 M in TEAP and 0.01 M in AgNO<sub>3</sub>, all separated from the bulk of the solution by a sintered glass disk. Potentials are given vs. this Ag|AgNO<sub>3</sub> electrode but note that Ag|0.01 M AgNO<sub>3</sub> + 0.1 M TEAP||0.1 M TEAP vs. the standard hydrogen electrode = 0.54 V.<sup>9</sup>
- (9) (a) H. H. Willard, L. L. Merritt, and J. A. Dean, "Instrumental Methods of Analysis", 4th ed, Van Nostrand Reinhold Co., New York, N.Y., 1965, p 537; (b) R. C. Larson, R. T. Iwamoto, and R. N. Adams, *Anal. Chim. Acta*, **25**, 371 (1961).
- (10) E<sub>pc</sub> = -1.07 V, E<sub>pa</sub> = -0.90 V in CH<sub>3</sub>CN. Excess copper in the sample<sup>5</sup> was plated out as Cu(0) thus providing a clean method for preparing pure solutions of the reduced complex.
- (11) E<sub>pc</sub> = -0.78 V, E<sub>pa</sub> = -0.67 V, in CH<sub>3</sub>CN.
- (12) (a) W. E. Hatfield and R. Whyman, *Transition Met. Chem.*, **5**, 47 (1969); (b) F. H. Jardine, *Adv. Inorg. Radiochem.*, **17**, 115 (1975).
- (13) M. I. Bruce and A. P. P. Ostaszewski, *J. Chem. Soc., Chem. Commun.*, 1124 (1972); M. I. Bruce and A. P. P. Ostaszewski, *J. Chem. Soc., Dalton Trans.*, 2433 (1973).
- (14) M. R. Churchill, B. G. DeBoer, F. J. Rotella, O. M. Abu Salah, and M. I. Bruce, *Inorg. Chem.*, **14**, 2051 (1975).
- (15) C. Mealli, C. S. Arcus, J. L. Wilkinson, T. J. Marks, and J. A. Ibers, *J. Am. Chem. Soc.*, **98**, 711 (1976).
- (16) R. R. Gagné, R. S. Gall, and L. S. Speltz, manuscript in preparation.
- (17) (a) L. Y. Fager and J. O. Alben, *Biochemistry*, **11**, 4786 (1972); (b) J. O. Alben, L. Yen, and N. J. Farrier, *J. Am. Chem. Soc.*, **92**, 4475 (1970).
- (18) Resonance Raman spectra of Cu(II) "blue" copper proteins are interpretable in terms of five coordination, but there are no available data for the Cu(II) proteins: V. Miskowski, S.-P. W. Wang, T. G. Spiro, E. Shapiro, and T. H. Moss, *Biochemistry*, **14**, 1244 (1975).

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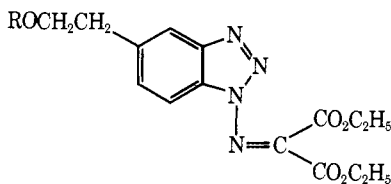
## Pseudodilution, the Solid-Phase Immobilization of Benzyne

Sir:

Among the various advantages associated with solid-phase synthesis, the possibility of maintaining mutual separation of reactive functional groups bound to the same polymer support is particularly attractive. The results of studies directed at determining the extent of such isolation<sup>1</sup> have not been very

encouraging and, in fact, examples of extensive reaction between polymer-bound functional groups have been reported.<sup>2</sup> We have found that the ubiquitous dimerization reaction of benzyne is completely suppressed by attachment of this reactive molecule to a polystyrene resin, thereby extending its lifetime at room temperature to more than a minute.

While benzyne has been isolated as a stable entity in rigid matrices at very low temperature,<sup>3</sup> its lifetime in solution and in the gas phase is limited by dimerization to form biphenylene. This process occurs at a rate approaching diffusion control.<sup>4</sup> In order to determine the effect of polymer immobilization the method of Campbell and Rees<sup>5</sup> for the generation of benzyne was adapted.

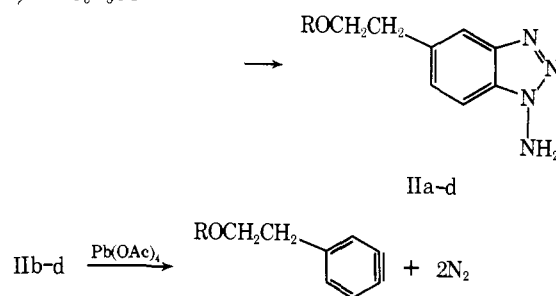


Ia, R = H

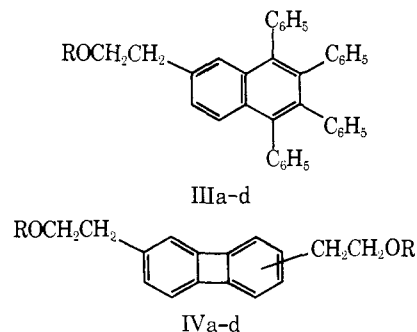
Ib, R =  $\text{P-CO-}$  (ref 6)

Ic, R =  $\text{P-CO-}$  (ref 7)

Id, R = C<sub>6</sub>H<sub>5</sub>CO-



The ketomalonate imine of 6- $\beta$ -hydroxyethyl-1-aminobenzotriazole, Ia, was attached to carboxylated polystyrene resin<sup>8</sup> as the ester Ib. For control experiments the benzoyl ester Id was prepared as well. Deprotection of the amino group was effected by selective hydrolysis with aqueous hydroxylamine. Oxidation of the aminotriazole with lead tetraacetate resulted in rapid evolution of N<sub>2</sub> and formation of characteristic arylene addition products.<sup>9</sup> Thus reaction of Iib in dichloroethane with 1 equiv of lead tetraacetate at 23 °C in the presence of excess tetracyclone, followed by saponification of the resin esters, yielded IIIa (99% based on N<sub>2</sub> evolution).



In the absence of trapping agents, behavior of the resin-bound and solution-phase arynes differed greatly. Oxidation of Iid in concentrations as low as 0.006 M provided the two isomeric biphenylenes IVd as the only isolable product (65% yield). By contrast, oxidation of Iib, followed by saponification of the product yielded no detectable amount of the corresponding dimer alcohols, IVa. A yield as low as 0.3% would have been detected. The possibility that resin-bound dimers were formed but resisted saponification was ruled out by the

Table I. Delayed Trapping of Resin-Bound Benzynes

Starting material	$t_1,^a$ s	$t_2,^b$ s	Yield of IIIa (%)
I Ib	30 <sup>c</sup>	0	99
I Ib	30	70	10
I Ic		0	99
I Ic	70	95	36
I Ic	150	220	17

<sup>a</sup>  $t_1$ , time at which N<sub>2</sub> evolution ceased. <sup>b</sup>  $t_2$ , time at which trapping agent (tetracyclone) was added. <sup>c</sup> 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 I Ib and I Ic were treated with 1 equiv of lead tetraacetate in a closed system and N<sub>2</sub> evolution was followed manometrically.<sup>10</sup> Tetracyclone was added to the mixture only after all N<sub>2</sub> 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 I Ic. We have not yet identified the competing pathway.

These results contrast sharply with those of Crowley, Harvey, and Rapoport.<sup>2</sup> 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.<sup>6</sup> 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.<sup>11</sup> 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"<sup>11</sup> 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.

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## References and Notes

- See J. I. Crowley and H. Rapoport, *Acc. Chem. Res.*, **9**, 135 (1976), for a review of the literature.
- For example, see J. I. Crowley, T. B. Harvey, and H. Rapoport, *J. Macromol. Sci. Chem.*, **7**, 1117 (1973).
- J. Kolc, *Tetrahedron Lett.*, 5321 (1972); O. L. Chapman et al., *J. Am. Chem.*

*Soc.*, **95**, 6134 (1973).

- A rate constant of  $7 \times 10^8$  l./mol s has been measured in the gas phase, M. E. Schafer and R. S. Berry, *J. Am. Chem. Soc.*, **87**, 4497 (1965).
- C. D. Campbell and C. W. Rees, *J. Chem. Soc. C*, 742 (1969).
- These samples were prepared<sup>8</sup> from Blobead S-X2, a 2% divinyl benzene cross-linked polystyrene. Functionalization amounted to 0.23 mmol/g.
- These samples were prepared<sup>8</sup> from Blobead SM-2, a 15% divinyl benzene cross-linked polystyrene. Functionalization amounted to 0.09 mmol/g.
- Preparation of the esters followed the method of R. L. Letsinger et al., *J. Am. Chem. Soc.*, **86**, 5163 (1964).
- 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.
- The reaction vessel was immersed in a thermostated ultrasonic bath to optimize mass transport rates.
- 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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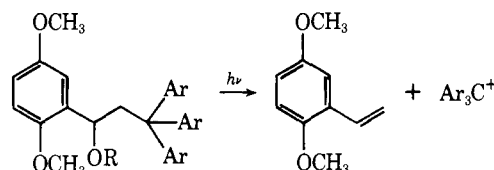
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## Charge-Transfer-Induced Photosolvolysis of Benzyl Alcohols

Sir:

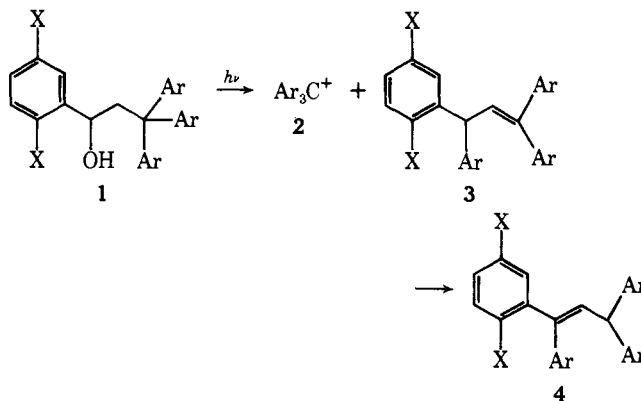
A variety of benzyl derivatives including esters, halides, and ammonium and sulfonium salts are known to give products derived from light-induced solvolytic reactions.<sup>1</sup> Electron donating groups at the meta position on the aromatic ring increase the efficiency of the reaction.<sup>2</sup> While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



**1a**, R = COCH<sub>3</sub>; Ar = *p*-C<sub>6</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>2</sub>

**1b**, R = H; Ar = *p*-C<sub>6</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>2</sub>

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.<sup>3</sup> 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<sub>3</sub>; Ar = *p*-C<sub>6</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>2</sub>

**c**, X = H; Ar = *p*-C<sub>6</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>2</sub>