

is interesting to note that the samarium diiodide reduction<sup>14</sup> of **10** affords low yields of **8** and **9** in about a 1:1 ratio but that **9** is the predominant isomer by far in the photoreaction (Table I).<sup>15</sup> No head-to-tail or spiro dimers<sup>15</sup> were detected in this photoreaction. A similar propensity for head-to-head dimerization of thermally generated, unsymmetrical *o*-quinodimethanes has been observed.<sup>16b,17</sup> At present very little can be said about the mechanism of this highly stereospecific photoenol dimerization except to note that the formation of these dimers does not appear to depend upon light intensity (Table I, runs 2 and 3). Thus, this is probably not a photodimerization. Furthermore, these dimers cannot be detected when the photoenols are generated thermally at 80–120 °C from neat cyclobutanol **7**. However, this may be due to the thermal lability of these dimers.<sup>15</sup> Finally, the stilbene **11** is the major of several secondary photoproducts from the known diketone **10**<sup>18</sup> whose photochemistry will be described in a separate publication. The diketone **10** itself seems to arise from the oxidation of the photoenol perhaps through hydrogen abstraction by **3**.<sup>18b,11</sup>

High-intensity irradiation of **1** in the laser-jet apparatus using a single UV argon ion laser beam afforded a significant light intensity dependent increase in the yield of only a single product, anthrone (**4**), at the expense of the other products shown in Scheme II (Table I). The two-photon formation of anthrone (**4**) from **1** has been reported previously in ca. 1% yield.<sup>6</sup> The extremely low yield of this transformation is not only due to the intrinsic inefficiency of its two-photon mechanism but also to the photoreversibility of the formation of the dihydroanthrone tautomer **3** (Scheme I).<sup>6</sup> It might be expected that this photoreversion of **3** to **E-2** might be favored by the high-energy UV photons required to generate **E-2** from **1** but that it might be less favorable with lower energy visible photons which should readily convert the photoenol **E-2** ( $\lambda_{\text{max}} = 417 \text{ nm}$ ) to the dihydroanthrone **3**. In order to test this hypothesis, the laser-jet irradiation of **1** was repeated by using two crossed laser beams (Table I), a UV beam to generate the photoenol **E-2** from **1**, and a visible beam to convert **E-2** to **3**. That this double-beam technique is quite effective is shown by a further substantial enhancement in the yield of anthrone. Since this intensity study was conducted under an inert atmosphere, the enhanced efficiency for the formation of **4** under jet conditions must be due in large part to the high concentrations of hydrogen abstracting species such as radicals and **3**<sup>1</sup>, which will facilitate the oxidation of **3** to **4**.

In conclusion, these studies have served not only to redefine the chemistry of this parent photoenol system but also to provide some indication of the potential of the laser-jet technique as a method for extending high-intensity photochemical phenomena into the realm of synthetic utility.

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**Supplementary Material Available:** X-ray data for **8** and Tables 1–5 listing atomic numbering scheme, X-ray operations, results

(13) See supplementary material paragraph.

(14) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693.

(15) The ratio of **8**:**9** is somewhat variable (see Table I). Control experiments showed that diols **8** and **9** decompose slowly at ca. 50 °C and under the irradiation conditions, as well as partially isomerize into one another upon standing in solution. It could not be determined whether **8** is a primary dimerization product or is formed through the isomerization of **9** during irradiation.

(16) (a) Moss, R. J.; White, R. O.; Rickborn, B. *J. Org. Chem.* **1985**, *50*, 5132. (b) Errede, L. A. *J. Am. Chem. Soc.* **1961**, *83*, 949.

(17) Quinkert, G.; Opitz, K.; Wiersdorff, W. W.; Weinlich, J. *Tetrahedron Lett.* **1963**, 1863.

(18) Huang, R. L.; Lee, H. H. *J. Chem. Soc. C* **1966**, 929. The structure of diketone **10** was also confirmed by an independent synthesis: Wilson, R. M.; Hannemann, K., unpublished results.

and procedure, atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and H-atom coordinates and isotropic thermal parameters (7 pages); Table 6 listing calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

## Laser-Jet Delayed Trapping: Electron-Transfer Trapping of the Photoenol from 2-Methylbenzophenone<sup>1</sup>

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During the course of the development of the argon ion laser-jet technique for the study of high-intensity photochemistry,<sup>2</sup> it became apparent that the laser jet provided a unique opportunity for the trapping of relatively long-lived photochemical intermediates. Thus, the jet solution containing the photochemical substrate could be passed through the focal region of the laser just before it was injected into a "fountain" of a solution containing the trapping agent. Through the partitioning of the photochemical and trapping steps in this way, it should be possible to employ unusual trapping agents that would quench the formation of the photointermediate or would themselves initiate undesired photochemistry, if they were present during the irradiation phase. One can estimate on the basis of the parameters of the current jet apparatus<sup>3</sup> that photochemical intermediates with lifetimes of about  $10^{-2}$  s or greater should be amenable to trapping by this delayed trapping technique. The *E*-photoenol **1** derived from 2-methylbenzophenone (**2**) (Scheme I) would seem to be an ideal candidate for this type of trapping experiment since it is known to have a lifetime of several seconds.<sup>4</sup> In this report, we describe the first application of this laser-jet delayed trapping technique<sup>5</sup> and the unusual photoenol chemistry observed during the course of this study.

The *E*-photoenol **1** and related species are readily trapped in Diels–Alder reactions such as the first reaction shown in Table I.<sup>6</sup> The reactions listed in Table I have been studied under both photochemical (conventional and jet) and thermal conditions.<sup>7</sup> A distinct limitation of the delayed trapping technique is that only a single pass through the laser beam is possible. Once quenched in the "fountain", the solution cannot be recycled. Thus, even though the reactions are quite clean, the conversion usually is only

(1) Presented at the XI IUPAC Symposium on Photochemistry, Lisbon, Portugal, July 21–Aug 1, 1986.

(2) Wilson, R. M.; Hannemann, K.; Peters, K.; Peters, E.-M. *J. Am. Chem. Soc.*, preceding paper in this issue.

(3) A jet nozzle diameter of 100  $\mu\text{m}$  provides a laminar stream velocity of about  $4.25 \text{ m}\cdot\text{s}^{-1}$  and a residence time in the laser focal region of about 25  $\mu\text{s}$ . In the experiments described here, the laser beam is focused about 5 mm above the trapping solution which affords a delay time of about 1 ms between irradiation and quenching in the trapping solution.

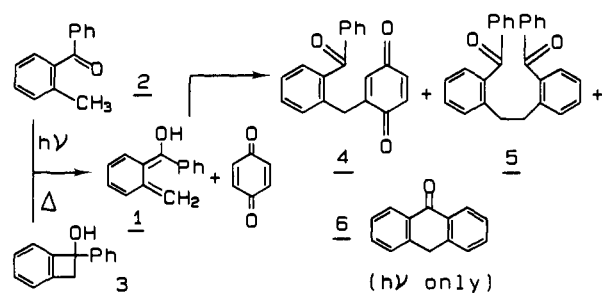
(4) (a) Sammes, P. G. *Tetrahedron* **1976**, *32*, 405 and references therein. (b) Wilson, R. M. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1985; Vol. 7, Chapter 5 and references therein. (c) Haag, R.; Wirz, J.; Wagner, P. J. *Helv. Chim. Acta* **1977**, *60*, 2595.

(5) We thank a referee for calling our attention to the fact that this delayed trapping laser-jet technique is the liquid-phase analogue of the classical gas-phase lead mirror delayed trapping of methyl radicals: Paneth, F.; Hofeditz, W. *Ber. Dt. Chem. Ges.* **1929**, *62*, 1335.

(6) (a) Arnold, B. J.; Sammes, P. G.; Wallace, T. W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 415. (b) Nerdel, F.; Brodowski, W. *Chem. Ber.* **1968**, *101*, 1398.

(7) All products of these trapping experiments were either identical with authentic material or had spectral properties which were consistent with the proposed structures: maleic anhydride adduct, ref 6b; naphthoquinone adduct, mp 175 °C dec, IR (KBr) 3420, 1675, 1660  $\text{cm}^{-1}$ ; **4**, yellow oil, IR ( $\text{CCl}_4$ ) 1665, 1600, 1580  $\text{cm}^{-1}$ ; **5**, mp 106–107 °C, IR (KBr) 1655, 1600, 1580  $\text{cm}^{-1}$ ; **7**, mp 60–64 °C, IR (KBr) 3300–3100, 1770, 1710, 1695, 1655  $\text{cm}^{-1}$ ; **8**, mp 184–185 °C, IR (KBr) 1725  $\text{cm}^{-1}$ ; **9**, mp 117–120 °C, IR (KBr) 3440, 1670, 1660  $\text{cm}^{-1}$ ; **10**, yellow oil, IR (KBr) 1670, 1660, 1600  $\text{cm}^{-1}$ .

Scheme I

Table I. Trapping of the *E*-Photoenol 1 of 2-Methylbenzophenone (2)

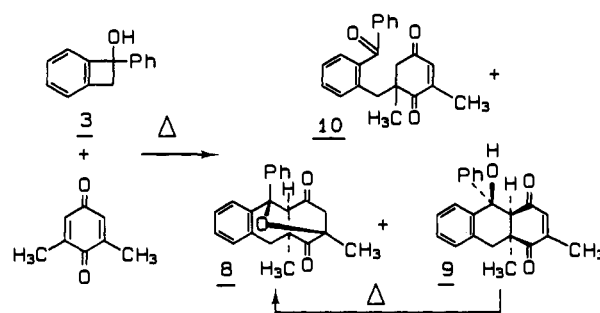
trapping agent ( $E_R^a$ ) <sup>a</sup>	reaction conditions	products, % yield <sup>b</sup> (% conversion)
(1) maleic anhydride, (-0.92 V)*	jet <sup>c</sup>	60–80 (10–15)
	$\Delta, d, e$ 8 h	75
(2) 1,4-naphthoquinone (-0.64 V)	$\Delta, d, f$ 8 h	80; 2, 17
(3) 2,6-dimethyl 1,4-benzoquinone (-0.61 V)	$\Delta, d$ 8 h	8, 61; 9, 6; 10, 5; 2, ~25
(4) 1,4-benzoquinone (-0.47 V)	jet <sup>c, g</sup>	4, 60; 5, 6; 6, 19 (14)
	$\Delta, d$ 6 h	4, 47; 5, 5; 6, 0; 2, 15
	jet <sup>c</sup>	7, 10 (~10)
(5) PTAD (+0.06 V)	Rayonet, <sup>h</sup> 15 h	7, 43 (75)
	$\Delta, d, i$ 3 h	7, 0

<sup>a</sup>Reduction potentials are reported vs. Ag/AgCl electrode in CH<sub>3</sub>CN and are reversible unless noted otherwise (\*). <sup>b</sup>Yields in the photochemical reactions are based on unreacted 2. Yields in the thermal reactions are based on isolated materials, except for 2 which was determined by NMR analysis of the crude reaction mixture. <sup>c</sup>Irradiation conducted in benzene with all UV lines of an argon ion laser (334–364 nm, 2.8 W). See also ref 2. A nozzle diameter of 50  $\mu$ m increases conversion to about 20% but requires a much higher head pressure. <sup>d</sup>The *E*-photoenol 1 was generated from 3 in refluxing toluene as shown in Schemes I and II. <sup>e</sup>For lactone from 3, see ref 6a, and from maleic anhydride-photoenol adduct, see ref 6b. <sup>f</sup>Conventional photochemistry produced the same adduct as the major of about four reaction products. <sup>g</sup>Only traces of 4 are formed when benzoquinone and 2 are irradiated together in a single pass through the focused UV lines of the laser. Conventional photochemistry using the visible laser lines (458–514 nm) produced traces of 4 and using the UV lines produced 4 in reaction mixtures that were much more complex than those obtained by the delayed trapping method. <sup>h</sup>A Rayonet photochemical reactor with 350-nm lamps was used. No reaction occurred using the visible laser lines. <sup>i</sup>The failure to observe trapping is due to rapid PTAD decomposition under these conditions.

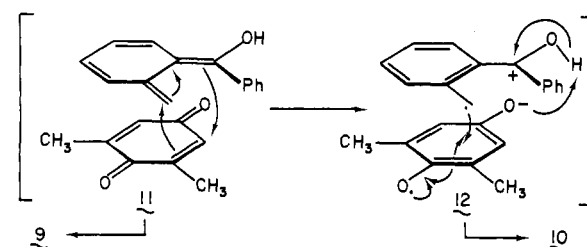
about 10–20%. Fortunately, in the cases described here, an alternative method is available for generating the photoenol 1 through the thermal ring cleavage of the cyclobutanol 3.<sup>8</sup> This thermal method usually affords the same or closely related trapping products to those observed in the photochemical trapping experiments and, thus, provides an ideal control as well as substantially larger quantities of trapping products.

The results from the trapping of 1 with various trapping agents under photochemical and thermal conditions are outlined in Table

Scheme II



Scheme III



I. The trapping with benzoquinone has been examined most thoroughly, and products observed are shown in Scheme I. The only trapping product observed is the quinone 4. Products 5 and 6 are typical of the high-intensity photochemistry of 2.<sup>2</sup> *N*-Phenyltriazolinedione (PTAD) is known to react efficiently with enol species,<sup>9</sup> yet it apparently has not been employed successfully in the trapping of photoenols.<sup>9a</sup> That PTAD can be utilized for this purpose is demonstrated by the formation of 7 in the delayed trapping of 1. Even though 7 can be formed more conveniently under conventional photochemical conditions, the jet trapping unequivocally demonstrates that 7 arises from the trapping of 1 and not from methyl hydrogen abstraction by excited PTAD.

As indicated in Table I, two modes of photoenol trapping seem to occur, the known Diels–Alder mode (entries 1 and 2) and a new mode which formally involves only reaction at the methyl substituent of 2 (entries 4 and 5).<sup>10</sup> Only in the case of trapping with 2,6-dimethylbenzoquinone (entry 3 and Scheme II) were both modes of reaction observed. In this interesting example, the major product 8 results from the usual photoenol Diels–Alder reaction followed by ether formation through conjugate addition of the endo-hydroxyl group of 9 to enedione double bond. This pathway was confirmed by heating the primary Diels–Alder adduct 9 under the trapping reaction conditions to form 8 exclusively. This control experiment also excludes the possibility that the third product, the triketone 10, comes from a retro-aldol reaction of 9. Finally it should be noted that in both modes of reaction, the benzophenone methyl substituent becomes bonded to the more highly substituted quinone carbon. This regiochemistry is completely consistent with the least hindered endo geometry for the Diels–Alder reaction of the *E*-photoenol 1 (11 in Scheme III) but is inconsistent with a radical addition to the quinone which would be expected to occur at the least substituted quinone carbon.<sup>11</sup> Finally, it appears that the two modes of trapping correlate with the reduction potentials of the trapping agents (Table I, trapping agents listed in order of increasing reduction potential) and that the transition between these modes occurs at about –0.60 V, which is not an unreasonable value for the oxidation of the photoenol 1.

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(10) An apparently related reaction has been observed between the photoenol of 2-methylacetophenone and 4-cyanopyridine to form 4-(2-benzoylbenzyl)pyridine; Morrocchi, S., personal communication.

(11) Jacobsen, N.; Torsell, K. *Acta Chem. Scand.* **1973**, 27, 3211. Jacobsen, N.; Torsell, K. *Liebigs Ann. Chem.* **1972**, 763, 135.

(8) (a) Adam, G.; Andrieux, J.; Plat, M. *Tetrahedron Lett.* **1981**, 22, 3181. (b) Horner, L.; Subramaniam, P. V.; Eiben, K. *Liebigs Ann. Chem.* **1968**, 714, 91.

On the basis of these observations, it seems likely that the same type of Diels-Alder donor-acceptor complex (**11**) is involved in both trapping modes (Scheme III). For the more powerful acceptors, the degree of electron transfer might become sufficiently high to favor complex collapse via proton transfer and radical coupling (**12**) rather than the more conventional [4 + 2] cycloaddition pathway (**11**). The exact timing of these steps is not certain, but the radical coupling step would either have to occur first or very rapidly following proton transfer in order to afford the regiochemistry observed for **10**.<sup>12</sup>

In summary, this work has not only served to demonstrate the feasibility of the laser-jet delayed trapping technique for intercepting long-lived photochemical intermediates but also has provided evidence which indicates that photoenols function in the previously unrecognized capacity of effective electron donors.

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(12) In the case of **10**, the methyl substituent blocks tautomerization to the hydroquinone which apparently occurs in the trapping with benzoquinone itself. This hydroquinone in turn could be oxidized by the excess benzoquinone trapping agent to form the isolated trapping product **4**.

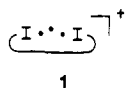
### Formation of Intramolecular Radical Cations with an Iodine-Iodine $2\sigma/1\sigma^*$ Three-Electron Bond in the Oxidation of 1,*n*-Diiodoalkanes

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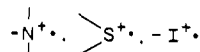
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Radical cations of the general type



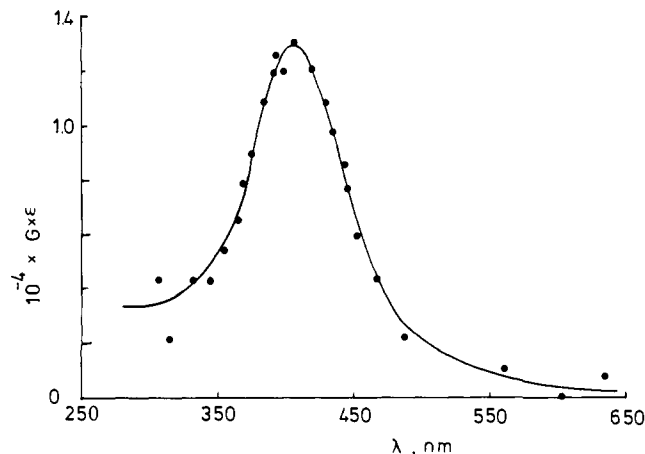
have been identified as transients in the  $\cdot\text{OH}$ -induced oxidation of 1,*n*-diiodoalkanes in aqueous solutions. They are the first examples for an intramolecular cationic  $2\sigma/1\sigma^*$  three-electron bond between two monovalent hetero atoms.

Radical cations derived from organic compounds and containing  $2\sigma/1\sigma^*$  three-electron bonds have been subject to many experimental and theoretical investigations in recent years.<sup>1,2</sup> Generally such bonds can be formed via interaction of an unpaired (usually p-electron of an oxidized tri-, di-, or monovalent hetero atom, e.g.,



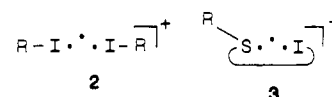
with the free electron pair of a second (identical or different) hetero atom. Alternatively such bonds may result from addition of an electron to an already existing  $\sigma$ -bond. The electronic structure of these three-electron bonds is characterized by the combined effect of two bonding  $\sigma$ -electrons and one antibonding, i.e., bond-weakening  $\sigma^*$ -electron.

Three-electron bond formation, in principle, is possible intermolecularly between hetero atoms located in different molecules



**Figure 1.** Optical absorption spectrum of **1a**, measured immediately after a 1-2  $\mu\text{s}$  pulse given to an  $\text{N}_2\text{O}$  saturated, pH 3, aqueous solution of  $2 \times 10^{-5}$  M 1,3-diiodopropane.

or intramolecularly if both interacting hetero atoms belong to the same molecule. The latter generally requires a favorable conformation for sufficient orbital overlap. Intramolecular three-electron bonds of high stability are particularly found between multibridged tri- and divalent hetero atoms, e.g., upon reduction of tricyclic hydrazonium dications<sup>3</sup> or oxidation of bicyclic dithia compounds.<sup>4</sup> Despite all these many examples it was not until recently that we could report on the first three-electron bonded radical cations in liquid phase which involve monovalent hetero atoms, namely



The intermolecular radical cations **2** were generated in the  $\cdot\text{OH}$  radical induced oxidation of alkyl iodides in acidic (pH < 4) aqueous solution<sup>5</sup> and exist in the equilibrium



The intramolecular species **3** results from a corresponding oxidation of 1-iodo-*n*-alkylthioalkanes provided that sulfur-iodine p-orbital overlap is sufficiently facilitated by a suitable steric arrangement.<sup>6</sup>

The only group of three-electron bonded radical cations which has so far evaded experimental verification in liquid environment is that with intramolecular interaction of two monovalent halogen atoms. Even low temperature, solid matrix ESR experiments with neat 1,2-diiodo- and 1,2-dibromoethane could not provide unambiguous identification of such species.<sup>7</sup> In the present study we now report on the first observation of intramolecular radical cations of type **1** on the basis of their optical absorptions.

Figure 1 exhibits the transient optical absorption spectrum recorded upon pulse radiolysis of an  $\text{N}_2\text{O}$  saturated, pH 3, aqueous solution containing  $2 \times 10^{-5}$  M 1,3-diiodopropane. It shows a broad band with a maximum at 405 nm. The absorption decays exponentially with  $t_{1/2} = 150 \mu\text{s}$ . Simultaneous time-resolved conductivity experiments revealed the formation of a positively charged transient with corresponding kinetic characteristics.<sup>8</sup> It can thus be concluded that our intermediate is a radical cation. Its yield amounts to  $G = 2.9$  or ca. 50% of the initial  $\cdot\text{OH}$  radicals as calculated from the conductivity data. The pH dependence of the yield shows essentially the same characteristics as for the

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(7) Mishra, S. P.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1492.

(8) In acid solution the generation of a radical cation plus an associated  $\text{OH}^-$  ion, followed by  $\text{OH}^- + \text{H}^+$  neutralization leads to a decrease in conductance. For analysis of such experimental data see, for example, ref 5.

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