References and Notes

(1) For part XII see J. Tsuji, H. Takahashi, and T. Kajimoto, *Tetrahedron Lett.*, 4573 (1973).
(2) O. Hayaishi and K. Hashimoto, *J. Biochem. (Tokyo)*, 37, 371 (1950).
(3) O. Hayaishi, M. Katagiri, and S. Rothberg, *J. Amer. Chem. Soc.*, 77, 5450 (1955); *J. Biol. Chem.*, 229, 905 (1957).
(4) For reviews see (a) A. E. Martell and M. M. Taqui Khan in "Inorganic Biochemistry," Vol 2, G. L. Eichhorn, Ed., Elsevier, New York, N.Y., 1973, p 654; (b) K. Bloch and O. Hayaishi, "Biological and Chemical Aspects of Oxygenases," Maruzen, Tokyo, 1966; (c) R. O. C. Norman and J. R. L. Smith in "Oxidases and Related Redox Systems," Vol. 1, T. E. King, H. S. Mason, and M. Morrison, Ed., Wiley, New York, N.Y., 1965, p 131; (d) O. Hayaishi, ref 4c, p 286; (e) H. S. Mason, *Advan. Enzymol. Relat. Subj. Biochem.*, 19, 79 (1957); (f) G. A. Hamilton, *ibid.*, 32, 55 (1969).
(5) R. R. Grinstead, *Biochemistry*, 3, 1308 (1964).
(6) T. Matsuura, H. Matsushima, S. Kato, and I. Saito, *Tetrahedron*, 28, 5119 (1972).
(7) J. Böeseken and C. L. M. Kerkhoven, *Recl. Trav. Chim. Pays-Bas*, 51, 964 (1932).
(8) J. A. Elvidge, R. P. Linstead, B. A. Orkin, P. Sims, H. Baer, and D. B. Pattison, *J. Chem. Soc.*, 2228 (1950).
(9) J. A. Elvidge, R. P. Linstead, and P. Sims, *J. Chem. Soc.*, 1973 (1953).
(10) J. A. Elvidge and P. D. Ralph, *J. Chem. Soc. C*, 387 (1966).
(11) H. Takahashi, T. Kajimoto, and J. Tsuji, *Syn. Commun.*, 2, 181 (1972).

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Sulfur Dioxide Trapping of Photochemically Generated 1,4-Biradicals

Sir:

The oxidative photoaddition of *p*-benzoquinone (*p*-BQ) to olefins under aerobic conditions to form 1,2,4-trioxanes (**1**) (Scheme I) has recently emerged as a new and general photochemical reaction.[1] This reaction is believed to proceed through the quinone–olefin intermediate, probably the 1,4-biradical, which has traditionally been invoked as the intermediate in oxetane formation.[2] Since these trapping reactions can be realized in surprisingly high yield,[3] we have initiated a program to determine if substances other than oxygen might also efficiently trap biradicals.

Sulfur dioxide is known to be an efficient radical trapping agent[4] which forms polymeric sulfones[5] and unstable sulfinic acids[6] in radical reactions with olefins and hydrocarbons. Farid[7] has reported that 1,4-biradicals generated photochemically through intramolecular γ-hydrogen abstraction in *tert*-butylquinones can be trapped by sulfur dioxide to yield labile sulfinic acids. Therefore, we have examined the photochemistry of *p*-BQ in the presence of sulfur dioxide and olefins that are known to form trioxanes in trapping experiments with oxygen.
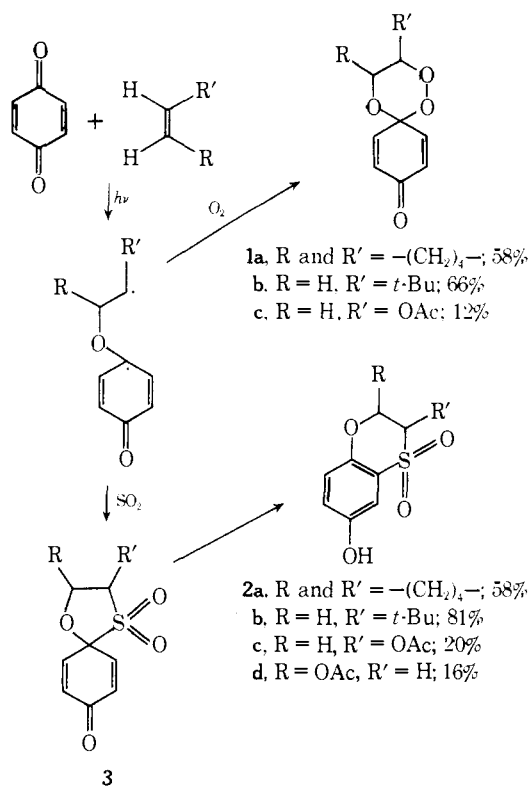
The trioxanes **1a–c** can be isolated following argon ion laser irradiations[8] of the appropriate *p*-BQ–olefin mixture in carbon tetrachloride solution under an atmosphere of high pressure oxygen (159 psi). Cyclohexene affords **1a**, bp 95° at 10^{-6} mm, *tert*-butylethylene affords **1b**, mp 78.4–78.7°,[1c] and vinyl acetate affords a mixture of trioxanes from which **1c** can be isolated as a viscous oil[9] (Scheme I).[10] The structure of trioxane **1b** has been established by oxygen-18 labeling studies.[1c] Trioxanes **1a** and **1c** both exhibit the characteristic dienone patterns in the nmr spectra as well as the appropriate number of signals for protons on carbon bearing oxygen. In **1c** the methylene protons are deshielded by 0.4–0.5 ppm relative to the methylene protons in the unstable isomer which indicates that the methylene protons in **1c** are adjacent to the more highly deshielding peroxide linkage.[11]

Argon ion laser irradiation for 20 min of the same *p*-BQ–olefin mixtures in a 10–20% carbon tetrachloride solution of sulfur dioxide at −11° affords the following sulfones: from cyclohexene, **2a**, mp 171.0–173.9°; from *t*-butylethylene, **2b**, mp 254.0–255.3°; and from vinyl acetate, **2c** and **2d**, mp 182.9–184.5° and 164.1–169.2°, respectively. All of these substances were 1:1:1 adducts of *p*-BQ, sulfur dioxide, and olefin as judged by their molecular ions and elemental analysis. They all exhibited strong hydroxyl absorption in the infrared as well as the characteristic intense sulfone bands in the 1295–1270 and 1135–1130-cm^{-1} regions. The nmr spectra each displayed very similar patterns in the aromatic region consisting of a one-proton doublet at low field (δ 7.3–7.1 ppm, J = 2–3 Hz), and a complex two-proton signal at higher field (δ 7.1–6.95 ppm). These data are only consistent with the proposed 7-hydroxy-4,1-benzoxythian 1,1-dioxide ring system. The location of the acetoxyl and *tert*-butyl substituents follows from the nmr spectra and the predominance of the McLafferty rearrangement observed in the mass spectrum of **2b**.[12]

Clearly, biradical trapping by sulfur dioxide closely parallels trapping by oxygen. The two differ in that the sulfur dioxide series affords rearranged products. Presumably, sulfur dioxide trapping leads initially to the spirosulfone **3** which undergoes a dienone–phenol rearrangement to **2**. This rearrangement must be extremely facile, since it has not been possible to detect **3**. Perhaps the excess sulfur dioxide, which is required in order to realize efficient trapping, serves as a Lewis acid[13] catalyst for this rearrangement. Dienones such as **3** would be expected to rearrange very readily with the sulfonyl group undergoing migration.[14]

These results demonstrate that biradical trapping is not peculiar to oxygen, but in fact may be a general technique of broad synthetic utility. Finally, it must be noted that sulfur dioxide offers several distinct advantages over oxygen as a trapping agent for biradicals that have been generated photochemically. It is much easier to obtain the requisite

Scheme I

1a, R and R' = –(CH₂)₄–; 58%
 b. R = H, R' = *t*-Bu; 66%
 c. R = H, R' = OAc; 12%

2a. R and R' = –(CH₂)₄–; 58%
 b. R = H, R' = *t*-Bu; 81%
 c. R = H, R' = OAc; 20%
 d. R = OAc, R' = H; 16%

3

high concentration of the trapping agent without using high pressure equipment, if sulfur dioxide is the trapping agent. Furthermore, the sulfones that are formed are not particularly sensitive to ultraviolet radiation as are the peroxides formed in oxygen trapping experiments. Therefore, while an argon laser source with an output of about 2 W accelerates the rate of formation of the sulfones by a factor of about 70 over a conventional ultraviolet light source, the sulfones can easily be isolated from uncomplicated reaction mixtures using a conventional 3600 Å light source.

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References and Notes

(1) (a) D. Creed, H. Werbin, and E. T. Strom, *J. Amer. Chem. Soc.*, **93**, 502 (1971); (b) R. M. Wilson, E. J. Gardner, R. C. Elder, R. H. Squire, and L. R. Florian, *ibid.*, **96**, 2955 (1974); (c) R. M. Wilson and S. W. Wunderly, *J. Chem. Soc., Chem. Commun.*, 461 (1974).
(2) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968); J. M. Bruce, *Quart. Rev., Chem. Soc.*, **21**, 405 (1967).
(3) Styrene and p-benzoquinone under 159 psi of oxygen afford 1 (R = H, R' = Ph) in 94% yield upon irradiation with an argon ion laser, unpublished results, R. M. Wilson and S. W. Wunderly.
(4) A. Good and J. C. J. Thynne, *Trans. Faraday Soc.*, **63**, 2708, 2720 (1967).
(5) F. S. Dainton and K. J. Ivin, *Proc. Roy. Soc., Ser. A*, **212**, 96, 207 (1952).
(6) C. C. Badcock, H. W. Sidebottom, J. G. Calvert, G. W. Reinhardt, and E. K. Damon, *J. Amer. Chem. Soc.*, **93**, 3115 (1971); H. W. Sidebottom, C. C. Badcock, J. G. Calvert, B. R. Rabe, and E. K. Damon, *ibid.*, **93**, 3121 (1971).
(7) S. Farid, *Chem. Commun.*, 73 (1971).
(8) A Coherent Radiation Laboratories Model 53A argon ion laser was used in this work. This laser emits with a maximum power of about 6 W in the following lines: 514.5 nm (2.5 W), 501.7 (0.5), 496.5 (0.7), 488.0 (1.5), 476.5 (0.6), and 457.9 (0.2).
(9) All attempts to resolve this mixture by silica gel chromatography led to the complete and selective destruction of a very unstable trioxane isomer; whereupon, it becomes possible to isolate the stable isomer 1c in pure form by trap-to-trap distillation at 10⁻⁶·mm.
(10) All new substances reported here afforded satisfactory elemental analysis and exhibited spectroscopic properties in accord with the structures proposed.
(11) This assignment of structure is supported by degradative studies which shall be reported in detail later.
(12) R. Smakman and Th. J. de Boer, *Org. Mass Spectrom.*, **3**, 1561 (1970).
(13) L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, **73**, 4169 (1951); J. Grundnes, S. D. Christian, V. Cheam, and S. B. Farnham, *ibid.*, **93**, 20 (1971); M. M. Rogic' and J. Vitrone, *ibid.*, **94**, 8642 (1972).
(14) J. N. Marx, J. C. Argyle, and L. R. Norman, *J. Amer. Chem. Soc.*, **96**, 2121 (1974).

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**Solvolysis of the 2-Aryl-5-methyl-2-norbornenyl p-Nitrobenzoates. Evidence for π Participation as a Factor in the Variation of the Rates and Products with Increasing Electron Demand at the Cationic Center**

Sir:

The exo:endo rate ratio in the solvolysis of the 2-aryl-5-methyl-2-norbornenyl p-nitrobenzoates (1 and 2) increases

1

2
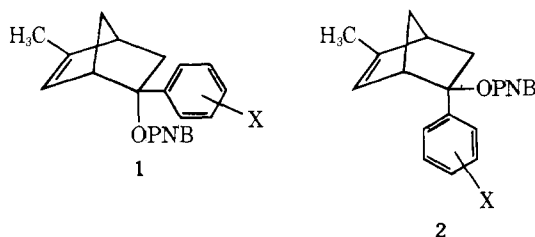
as the electron demand of the 2-aryl substituent is increased. Moreover, the reaction products reveal increasing involvement of the double bond. These results indicate that the double bond activated by the 5-methyl substituent is strongly involved in the solvolysis, in contrast to the behavior of the parent 2-aryl-2-norbornenyl derivative[1] (3 and 4).

3

4
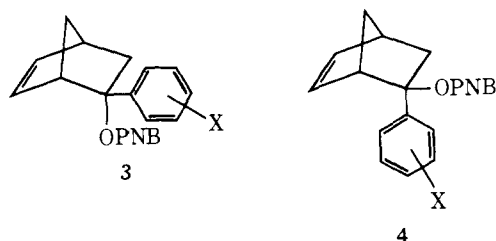
The tool of increasing electron demand has been applied as a test for π and σ participation in a number of systems. The results confirm the presence of such participation in 7-aryl-*anti*-norbornenyl,[2] arylcyclopropylmethylcarbinyl,[3] and 3-aryl-3-nortricyclyl.[4] However, the data indicate the absence of such participation in the solvolysis of 2-aryl-2-norbornenyl[1] (3 and 4) and 2-aryl-2-norbornyl[5] (5 and 6) derivatives.

5

6
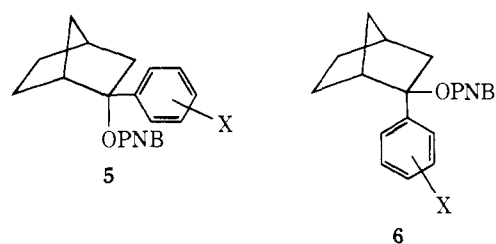
It has been suggested that tertiary benzylic cations are so stable that participation could be detected only in systems where such participation is of very large magnitude,[6] such as the *anti*-norbornenyl[2] and the cyclopropylcarbinyl systems.[3,4] Accordingly, we undertook to activate the double bond of 3 and 4 moderately in order to test whether with such activation the tool of increasing electron demand could detect moderate participation. (We are also seeking to increase the electron demand at the cationic center of 3 and 4 in the hope of establishing the incursion of π participation by such means.)

Table I. Rates of Solvolysis of 5-Methyl-2-aryl-2-norbornenyl p-Nitrobenzoates in 80% Acetone at 25.0°

Substituent in 2-aryl[a]	Isomer	Rate constant $10^6 k_1$, sec⁻¹	ΔH^*, kcal mol⁻¹	ΔS^*, eu	k_1^{5-Me}/k_1^{5-H}[b]	Exo:endo rate ratio
p-CH₃O	2[c]	3000[d]			1.19	354
	1[e]	8.48			1.05	
p-H	2[f]	9.18			7.4	1260
	1[g]	7.28 × 10⁻³[h]	26.4	−7.2	1.21	
p-CF₃	2[i]	0.0794[i]			26	6700
	1[j]	1.19 × 10⁻⁵[h]	30.4	−6.4	0.93	

[a] All new compounds gave spectral and microanalytical data consistent with the proposed structure. [b] Values of k_1^{5-H} (3 and 4) from ref 1. [c] Benzoate. ROBz, liquid; $k_1^{25°}$ = 1.44 × 10⁻⁴ sec⁻¹; ROH mp 68–69°. [d] Rate constant for p-nitrobenzoate estimated by multiplying the rate constant for the benzoate by the factor 20.8⁵. [e] ROPNB mp 112–113° dec; ROH bp 108–110° (0.02 mm). [f] ROPNB mp 116–118°; ROH bp 90° (0.03 mm). [g] ROPNB mp 109–110°; $k_1^{100°}$ = 69.3 × 10⁻⁶ sec⁻¹, $k_1^{75°}$ 5.07 × 10⁻⁶ sec⁻¹; ROH bp 82° (0.12 mm). [h] Value calculated from data at other temperatures. [i] Value calculated from values for p-H and p-MeO using the equation log (k/kH) = ρσ⁺ (ref 9). [j] ROPNB mp 155°; $k^{150°}$ = 62.5 × 10⁻⁶ sec⁻¹, $k_1^{125°}$ = 6.16 × 10⁻⁶ sec⁻¹; ROH bp 103° (0.15 mm).