# Laser-induced Formation of 1,2,4-Trioxans: the trapping of Oxetan Precursors with Molecular Oxygen

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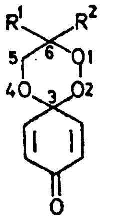
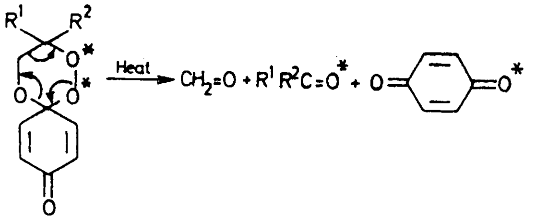
*Summary* The formation of 1,2,4-trioxans by laser irradiation of *p*-benzoquinone and olefins under aerobic conditions has been shown to be a general reaction which proceeds through an intermediate quinone–olefin adduct.

Two examples of 1,2,4-trioxans arising from the aerobic irradiation of *p*-quinones in the presence of an olefin have been reported.[1,2] In an effort to establish the scope and the mechanism of this unusual reaction we have examined the oxidative photoaddition of *p*-benzoquinone to a variety of olefins. We report here the results of oxidative photoadditions to unsymmetrical olefins.



(1) $R^1 = H; R^2 = Ph$
(2) $R^1 = R^2 = Ph$
(3) $R^1 = H, R^2 = Bu^t$

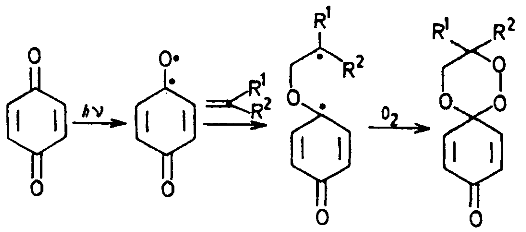
In all cases the *p*-benzoquinone was excited with a 6 W argon ion laser† in order to facilitate the isolation of the trioxan products.[2] Styrene, 1,1-diphenylethylene, and t-butylethylene afforded the trioxans (**1**), m.p. 126·2—126·4° (**2**), m.p. 131·4—131·6°, and (**3**), m.p. 78·4—78·7°, respectively. Each of these trioxans was accompanied by varying amounts of the expected oxetans and oxetan-derived products. Only small amounts of these oxetan products were observed with the phenyl olefins, the major products being the trioxans (**1**) (56%) and (**2**) (42%). In the case of the t-butylethylene a mixture of two isomeric oxetans (69%) predominated over the trioxan (**3**) (25%) in reactions conducted under 1 atm. of oxygen. However, the oxetan formation was drastically suppressed when the reaction was conducted under 11 atm. of oxygen (oxetans, 26%; trioxan, 66%).



Scheme

The substitution of the trioxan rings in the 6-position rather than the 5-position has been demonstrated both in degradation studies and an $^{18}O_2$ labelling study. In a control experiment *p*-benzoquinone was shown not to undergo carbonyl oxygen exchange with $^{18}O_2$ upon irradiation in the absence of olefin.[3] Preparation of (**1**), (**2**), and (**3**) in a 50% enriched $^{18}O_2$ atmosphere followed by pyrolysis of the isolated trioxans yielded three carbonyl-fragmentation products in each case. These products were analysed by mass spectrometry and found to contain the $^{18}O$ in the $R^1R^2C{=}O$ compound (47—50%) and the *p*-benzoquinone (23—26%) (see Scheme).‡ These results are only in accord with a 6-substituted trioxan in which 89% or more of the oxygen-18 is distributed between the peroxide oxygens.

Not only do these results verify the structures of the trioxans, but they also demonstrate that the oxygen is incorporated without significant scrambling with the quinone oxygens. When coupled with the observation that each of these unsymmetrical olefins produces only a single trioxan, these labelling results indicate that the trioxans arise through the trapping of an initial quinone–olefin adduct by molecular oxygen. Furthermore, this adduct must be a surprisingly long-lived species ($10^{-7}$—$10^{-6}$ s) which is very probably the more stable quinone–olefin biradical usually associated with oxetan formation.



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† A Coherent Radiation Model 53A argon ion laser with lines at 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) was used.

‡ Accurate values for the oxygen-18 analyses have been submitted to the Chemical Society. Molecular oxygen in the mass spectrometer prevented the determination of oxygen-18 incorporated into formaldehyde.

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[2] E. J. Gardner, R. H. Squire, R. C. Elder, and R. M. Wilson, *J. Amer. Chem. Soc.*, 1973, **95**, 1693; R. M. Wilson, E. J. Gardner, R. C. Elder, R. H. Squire, and L. R. Florian, *J. Amer. Chem. Soc.*, 1974, **96**, 2955.

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