Substituent Effects on the Rates of Alkyne–Quinone Photoaddition

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Summary Evidence for bonding at an electrophilic site on excited-state quinone is presented.

ALKYNE photoaddition to 2-methoxy-1,4-naphthoquinone yields cyclobutene adducts (I).[1,2] Methylphenylacetylene provides a single isomer of structure (Ia).[2] Analogous selectivity has been observed with 2-methyl-1,4-naphthoquinone.[3] This orientation suggests that initial bonding occurs at C-3 of these quinones, as in (II), and may be attributed to diradical stability.[2,3] Alternatively, these results may reflect the electronic state of reactive quinone which determines the site of bonding. We report on a kinetic study of diphenyl, *p*-methoxy, and *p*-cyanodiphenylacetylene photoaddition to 2-methoxy-1,4-naphthoquinone, which provides information pertinent to this question.

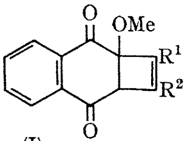
In each experiment, two alkynes competed for the quinone. Relative rates were determined by the expression, $k_A/k_{A'} = \log(A_t/A_0)/\log(A'_t/A'_0)$, where k_A is the rate of alkyne A disappearance.[4] Alkyne ratios were obtained at various times t by g.l.c. (internal standard); adduct ratios (n.m.r.) provided a check on the proper stoicheiometry. Each unsymmetrical alkyne yielded both isomeric adducts which were separated and identified by chemical and spectral means; isomer ratios, which remained constant on extended irradiation, were determined by n.m.r.

The results (Table) indicate a small preference for adduct (Ic), and insensitivity to the cyano-substituent. These findings are in contrast to the high selectivity with methylphenylacetylene and, by themselves, suggest a nearly concerted process of weakly electrophilic quinone. However, this data is also consistent with initial bonding at C-3, whereby the transition state reflects both the radical character of (II) and the polarity indicated in partially bonded (III). The relative insensitivity to the cyano-group is explicable in these terms, since radical stabilization is expected to favour (IIe), whereas charge separation is better accommodated in (IIIf). Both radical and polar factors enhance (IIc) formation. The low selectivity [(Ic)—(Id)] is attributed to inefficient interaction at a developing vinyl radical.† This means of polar contribution, which reflects quinone electrophilicity, has analogy in ground-state radical processes.[5] Alternative polar factors have been considered in related photoadditions.[6,7]

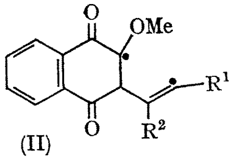
Relative rates of adduct formation[a]

Adduct	Benzene	Acetonitrile
(Ic)	5·1 ± 0·3	3·1 ± 0·3
(Id)	2·3 ± 0·3	1·9 ± 0·3
(Ie)	0·9 ± 0·2	1·0 ± 0·2
(If)	0·7 ± 0·2	0·8 ± 0·2

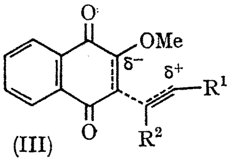
[a] Relative to (Ib) in each solvent after correction for its statistical advantage.



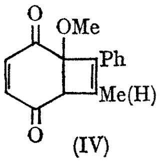
(I)



(II)



(III)



(IV)

a; R^1=Ph, R^2=Me b; R^1=R^2=Ph
c; R^1=C_6H_4·OMe-*p*, R^2=Ph
d; R^1=Ph, R^2=C_6H_4·OMe-*p*
e; R^1=C_6H_4·CN-*p*, R^2=Ph
f; R^1=Ph, R^2=C_6H_4·CN-*p*

Analogously, photoaddition of methylphenylacetylene (or phenylacetylene) to methoxy-*p*-benzoquinone yields adduct (IV).[2,8] Thus, reaction occurs at a site clearly less electrophilic in ground-state quinone than the alternative C=C. Consequently, we propose that these quinones react in excited-states, which are electrophilic at C-3. This conclusion is in accord with a recent hypothesis on C=O *vs.* C=C photoaddition to quinones.[9]

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† For this reason, photoaddition of *p*-methoxystilbene is expected to proceed with more pronounced orientational selectivity, although many geometric isomers are possible.

[1] S. P. Pappas and N. A. Portnoy, *J. Org. Chem.*, 1968, **33**, 2200.
[2] S. P. Pappas, B. C. Pappas, and N. A. Portnoy, *J. Org. Chem.*, 1969, **34**, 520.
[3] S. Farid, W. Kothe, and G. Pfundt, *Tetrahedron Letters*, 1968, 4147.
[4] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, 1959, p. 173.
[5] R. Breslow, "Organic Reaction Mechanisms," W. A. Benjamin, New York, 1966, pp. 220—227.
[6] E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, 1964, **86**, 5570.
[7] B. D. Challand and P. de Mayo, *Chem. Comm.*, 1968, 982, and references therein.
[8] S. P. Pappas and B. C. Pappas, *Tetrahedron Letters*, 1967, 1597, and unpublished results.
[9] J. A. Barltrop and B. Hesp, *J. Chem. Soc.* (*C*), 1967, 1625.