Photo-induced Cycloaddition of Tetra-substituted *p*-Quinones to Diphenylketen

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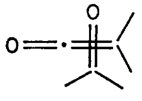
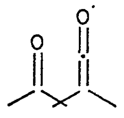
Summary Photo-induced cycloadditions of the tetra-substituted *p*-quinones duroquinone, chloranil, and 9,10-anthraquinone to diphenylketen afford two types of adducts: the 1-oxaspiro[3.5]nona-5,8-diene-2,7-diones (**3**) and bicyclo[4.2.0]octa-5-ene-2,4,7-triones (**4**).

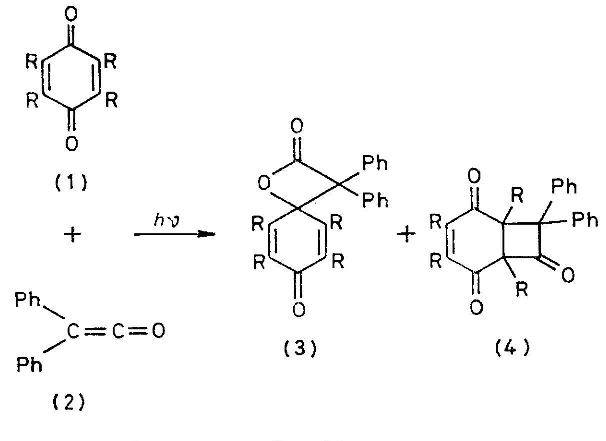
The mono adduct, 3,3-diphenyl-1-oxaspiro[3.5]nona-5,8-diene-2,7-dione of *p*-benzoquinone and diphenylketen has been isolated by Staudinger and Bereza.[1] However, tetra-substituted quinones, such as duroquinone, chloranil, and 9,10-anthraquinone, do not react with keten at room temperature.[1]



$[\pi 2_s + \pi 2_a]$



$[\pi 2_s + \pi 2_s]$



SCHEME. **a**; R = Me
b; R = Cl
c; RR = -[CH=CH]$_2$-

In principle, ketens are ideal as the $\pi 2_a$ components in concerted thermal $[\pi 2_s + \pi 2_a]$ cycloadditions.[2] For reactions with quinones, this mode of addition should be affected by steric interactions between the keten and the quinone substituents. The photochemically allowed $[\pi 2_s + \pi 2_s]$ process, however, would be expected to involve a different geometric approach with smaller steric repulsion.

We describe here the photo-induced cycloadditions of sterically hindered *p*-quinones to diphenylketen. The results presently obtained are the first examples of photoreactions of carbonyl functions with diphenylketen.

A benzene solution of duroquinone (**1a**) and diphenylketen was irradiated by a high pressure mercury lamp with a Pyrex filter. Two crystalline products were obtained by t.l.c. separation. The major adduct shows two carbonyl i.r. absorptions at 1825 and 1635 cm^{-1} indicating the presence of oxetan-2-one and cyclohexadienone groups and was assigned the oxaspirononadienedione structure (**3a**), m.p. 165—166·5 °C (decomp.), 49% yield, δ (CDCl$_3$) 1·39 (q, J 0·1 Hz, 2Me), 1·86 (q, J 0·1 Hz, 2Me), and 7·1—7·5 (m, 2Ph). The minor adduct has cyclobutanone (ν 1790 cm^{-1}) and cyclohexenedione (1660 cm^{-1}) units and was assigned the bicyclo-octenetrione structure (**4a**), m.p. 135—137 °C, 25%, δ (CDCl$_3$) 1·37 (s, Me), 1·40 (s, Me), 1·61 (q, J 0·1 Hz, Me), 1·74 (q, J 0·1 Hz, Me), and 7·1—7·8 (m, 2Ph). The photoreaction of (**1a**) with (**2**) in chloroform afforded (**3a**) and (**4a**) in 42 and 12% yields, respectively. The reaction was also examined in the presence of pyrene (quencher of the $^3\pi,\pi^*$ state of duroquinone), but the distribution of products was unchanged: (**3a**) 15% and (**4a**) 8%, although the yields had decreased.

The photoreaction of chloranil (**1b**) with (**2**) afforded the spiro-oxetanone (**3b**); m.p. 176—184 °C (gradual decomp.), 38% yield, ν 1850 and 1682 cm^{-1}, δ 7·2—7·7 (m, Ph), with recovery of chloranil (10%). The bicyclo compound (**4b**) could not be isolated.

9,10-Anthraquinone (**1c**) and (**2**) in chloroform were irradiated to give the adduct (**3c**); m.p. 190—196 °C (decomp.), 53% yield, ν 1830 and 1680 cm^{-1}, δ 7·0—7·3 (m, 16H) and 8·2—8·4 (m, 2H) with recovery of (**1c**) (39%).

When the maximum amounts of the adducts (**3**) are present, the photoreactions should be stopped for separation by t.l.c., because these types of spiro-oxetanones are known to decompose on prolonged irradiation.[3]

p-Quinones afford cycloadducts such as oxetans and/or cyclobutanes upon irradiation in the presence of olefins.[4] Both types of cycloadducts (**3**) and (**4**) are formed from the $^3\pi,\pi^*$ excited states of the quinone[5] because of the absence of solvent and quenching effects. Therefore, the predominant formation of oxetanone may be explained by the extent of dipole–dipole interactions between the $^3\pi,\pi^*$ excited states of the carbonyl groups of quinones and the ground state of diphenylketen.

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