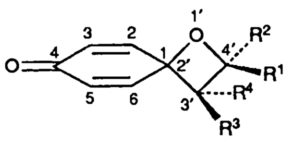
Factors Influencing the Regiochemistry of Spiro-oxetane Formation from the Photocycloaddition of Ethenes to 1,4-Benzoquinone

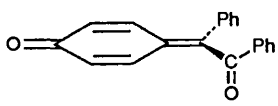
Derek Bryce-Smith, Elizabeth H. Evans, Andrew Gilbert* and Hilary S. McNeill
Chemistry Department, University of Reading, Whiteknights, PO Box 224, Reading, Berkshire, RG6 2AD, UK

The photoadditions of a variety of electron donor and electron acceptor ethenes to 1,4-benzoquinone have been studied. Spiro-oxetanes were formed in each case, though at markedly varying rates. The reactions were not stereoselective. In all cases except that of isopropenyl acetate, the regiochemistry observed was the opposite of that predicted from the relative stabilities of the two possible intermediate 1,4-diradicals and from the known corresponding photoadditions to ketones and aldehydes. A mechanism involving control of the regioselectivity by polar factors resulting from initial electron transfer to the quinone is proposed.

Some years ago we described the first examples of spiro-oxetane 1[1] and quinomethane 2[2] formation from the photocycloaddition of alkenes and alkynes respectively to 1,4-benzoquinone. The access to quinomethanes by this route appeared to be limited to the additions of diphenylacetylene and its derivatives but the spiro-oxetane formation showed the potential of a general process. Other examples of this latter reaction have since been reported but have largely involved complex or somewhat specialized ethenes,[3,4] leaving the simpler systems relatively unexplored. Thus knowledge of the scope of the spiro-oxetane formation and, in particular, the features which may be used to direct and control the regiochemistry of the addition of the ethene to 1,4-benzoquinone is surprisingly limited.



1

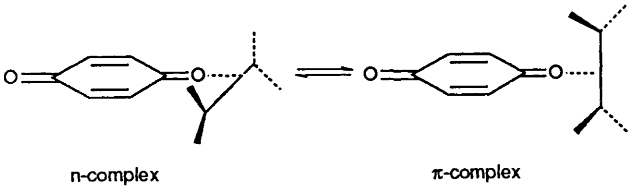


2

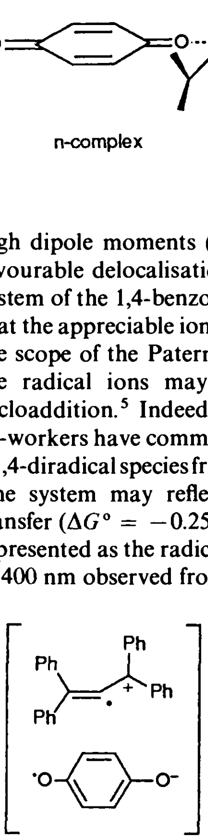
6 $R^1 = R^2 = R^3 = R^4 = H$
7 $R^1 = -C_6H_{13}, R^2 = R^3 = R^4 = H$
8 $R^1 = R^2 = R^4 = H, R^3 = -C_6H_{13}$
9 $R^1 = R^2 = CH_3, R^3 = R^4 = H$
10 $R^1 = R^2 = H, R^3 = R^4 = CH_3$
11 $R^1 = R^2 = R^3 = R^4 = CH_3$
12 $R^1–R^3 = -(CH_2)_3-, R^2 = R^4 = H$
13 $R^1 = R^3 = -(CH_2)_4-, R^2 = R^4 = H$
14 $R^1 = R^3 = -(CH_2)_6-, R^2 = R^4 = H$
15 $R^1 = R^4 = -(CH_2)_6-, R^2 = R^3 = H$
16 $R^1–R^3 = -(CH_2)_2-CH=CH-(CH_2)_2-, R^2 = R^4 = H$
17 $R^1 = R^4 = -(CH_2)_2-CH=CH-(CH_2)_2-, R^2 = R^3 = H$
19 $R^1 = -OC_2H_5, R^2 = R^3 = R^4 = H$
20 $R^1 = -OPh, R^2 = R^3 = R^4 = H$
21 $R^1 = -CO_2CH_3, R^2 = R^3 = R^4 = H$
22 $R^1 = R^4 = H, R^2 = -OC_2H_5, R^3 = CN$
23 $R^1 = R^3 = H, R^2 = -OC_2H_5, R^4 = CN$
27 $R^1 = -OCOCH_3, R^2 = R^3 = R^4 = H$
28 $R^1 = R^2 = R^4 = H, R^3 = -OCOCH_3$
29 $R^1 = R^2 = H, R^3 = CH_3, R^4 = -OCOCH_3$
30 $R^1 = Ph, R^2 = R^3 = R^4 = H$
33 $R^1 = Ph, R^2 = CH_3, R^3 = R^4 = H$
34 $R^1 = Ph, R^2 = H, R^3$ or $R^4 = CH_3$ or H
35 $R^1 = R^3 = Ph, R^2 = R^4 = H$
36 $R^1 = R^4 = Ph, R^2 = R^3 = H$

To account for the experimental features of the Paterno–Büchi reaction (oxetane formation) of carbonyl–ethene systems, it is generally accepted that the involvement of pre-oxetane 1,4-diradicals and exciplexes having charge-transfer character is required, and that the reaction may arise from singlet and/or triplet excited states.[5–7] The need for an excited state complex in the addition reactions of aldehydes and ketones has, however, been questioned and instead it has been proposed that all aspects of oxetane formation can be accommodated by tunnel effect theory.[8]

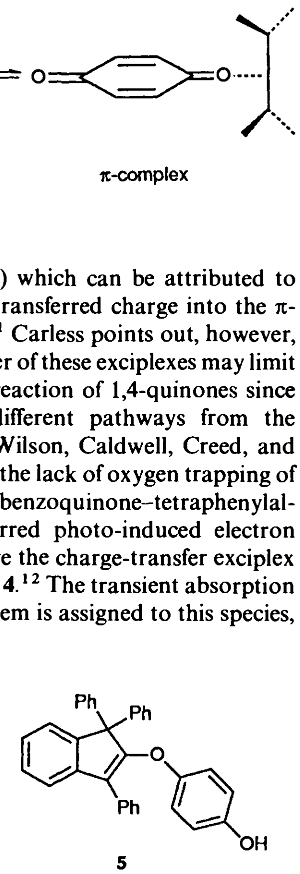
For 1,4-quinones the addition occurs from the $^3n\pi^*$ triplet state,[9] and evidence has been presented for the intermediacy of both excited state complexes of the addends and the pre-oxetane 1,4-diradicals in the addition process.[9,10] It has also been shown by CNDO calculations that 1,4-benzoquinone–ethene systems may form triplet charge-transfer complexes having end-on geometry of type 3: these species are found to have high dipole moments (*ca.* 11 D†) which can be attributed to favourable delocalisation of the transferred charge into the π-system of the 1,4-benzoquinone.[11] Carless points out, however, that the appreciable ionic character of these exciplexes may limit the scope of the Paterno–Büchi reaction of 1,4-quinones since the radical ions may pursue different pathways from the cycloaddition.[5] Indeed recently Wilson, Caldwell, Creed, and co-workers have commented that the lack of oxygen trapping of a 1,4-diradical species from the 1,4-benzoquinone–tetraphenylallene system may reflect a preferred photo-induced electron transfer ($\Delta G^\circ = -0.25$ eV) to give the charge-transfer exciplex represented as the radical ion pair 4.[12] The transient absorption at 400 nm observed from this system is assigned to this species,



3



4



5

---

† 1 D ≈ 3.335 64 × 10^{-30} C m.

Table 1 Spiro-oxetane formation from 1,4-benzoquinone and alkenes and cycloalkenes[a]

Addend	E_{ox}/V[17]	Spiro-oxetane	Chemical yield (%)
Ethene	2.90	**6**	5
Oct-1-ene	2.70[18]	**7**:**8** ratio 1:1	25
2-Methylpropene	2.65	**9**:**10** ratio 1:1	30
2,3-Dimethylbut-2-ene	1.21	**11**	40[b]
Cyclopentene	1.83	**12**	1[b]
Cyclohexene	1.72	**13**	10[b]
(*Z*)-Cyclo-octene	1.85	**14**:**15** ratio 3:1	40
(*Z*,*Z*)-Cyclo-octa-1,5-diene	—	**16**:**17** ratio 9:1	25

[a] Benzene solvent. [b] Quinhydrone also formed.

and the 4-hydroxyphenyl indolenyl ether **5** is isolated from reactions in the presence of acid.

Cycloadditions arising from charge-transfer excitation were first reported in the early 1960s[13] and in 1970 we noted that intermediate dipolar species could be intercepted by acid to yield substitution products.[14] In particular, the 1,4-benzoquinone–benzene system which forms a ground state complex showing charge-transfer absorption[15] is photostable, but yields 4-phenoxyphenol (*cf.* **5**) on irradiation in the presence of acid, no doubt *via* protonation of an excited triplet charge-transfer species similar to that proposed in ref. 12.

Our renewed interest in the photoformation of spiro-oxetanes arose from observations made in conjunction with Professor K. Harrap (Royal Cancer Hospital, Sutton, UK) that these compounds have remarkable *in vitro* cytotoxicity and *in vivo* neurotoxicity. This discovery prompted the need for the synthesis of numerous spiro(cyclohexa-2,5-diene-1,2′-oxetan)-4-one derivatives substituted at the 3′- and/or 4′-positions with groups of widely differing functionality. This requirement prompted reappraisal of the mechanistic features of the Paterno–Buchi reaction of 1,4-benzoquinone and the relevance of these to the efficiency and regiochemistry of spiro-oxetane formation.

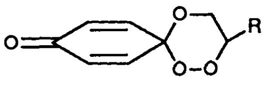
Results and Discussion

In our earlier studies of spiro-oxetane formation[1] we were unable to isolate products from the irradiation of 1,4-benzoquinone in the presence of ethene, styrene and (*E*)-stilbene. These systems were, however, only examined in a quartz apparatus[16] which operated at higher temperatures (*ca.* 80 °C) in the irradiation zone than we have since found desirable. More importantly, we had used unfiltered radiation from a medium pressure mercury lamp. Bunce and Hadley[9] have commented that spiro-oxetanes are unstable 'towards photolysis'; in the present study we note that the adducts do indeed have very variable stabilities under their conditions of formation. We have thus re-examined these quinone–ethene systems using filtered radiation ($\lambda > 300$ nm) and at a temperature less than 25 °C: this gives generally cleaner reactions and more reproducible results, and has enabled us to obtain spiro-oxetanes from the previously unreactive ethenes.

The results from irradiation of 1,4-benzoquinone in the presence of alkenes and cycloalkenes are given in Table 1. The reactions were allowed to proceed until no further quinone was consumed, as indicated by absorption spectroscopy. The yields were not optimized or corrected for unchanged benzoquinone but the values do provide a useful comparison of the relative tendencies for the systems to give spiro-oxetanes. It is apparent from the data for the acyclic alkenes in Table 1 that product formation increases with the electron-donating character of the ethene: this supports the proposed intermediacy of a polar intermediate, possibly an exciplex, in the formation of oxetanes from 1,4-benzoquinone.[9,10]

The effects of solvent polarity on these systems have been examined. The solvent normally employed for preparative experiments is benzene and although the more polar acetonitrile is not recommended, it has been observed that in this solvent the initial rate of spiro-oxetane formation is greater than in benzene. The reaction in acetonitrile soon, however, slows and virtually stops owing to the formation of radiation-absorbing by-products: these are not formed in benzene, in which these reactions may proceed readily to complete consumption of the quinone. The initial enhancement of adduct formation in the more polar solvent is, however, consistent with a mechanism involving polar intermediates. It has been reported that the photoaddition of (*Z*)-cyclooctene to 1,4-benzoquinone occurred more slowly in acetonitrile than in benzene.[9] We find that this is only true for extended irradiations as a result of the above mentioned formation of light-absorbing by-products.

We repeated the reaction of 1,4-benzoquinone with oct-1-ene to confirm the reported 1:1 ratio of regioisomers[1] under more reproducible conditions, since this and the later similar observation with 2-methylbut-1-ene have been used to implicate an exciplex intermediate[9] having the same geometry as that proposed for the benzophenone–but-2-ene system:[19] *cf.* **3**. This excited-state species may then be considered to collapse by bond formation with equal probabilities at either end of a non or weakly polarized ethene thus giving the two oxetane precursor triplet 1,4-diradicals in equal amounts: following spin inversion these cyclise. The same mechanistic feature appears to direct the regiochemistry of the addition of 2-methylpropene to 1,4-benzoquinone but not apparently that of 3,3-dimethylbut-1-ene. It is reported[10] in this case that the 4′- and 3′-*tert*-butyl substituted spiro-oxetanes are formed in a respective ratio of 1:3 which may be presumed to reflect the stabilities of the two precursor 1,4-diradicals and which, furthermore, discounts any suggestion that the 1:1 ratios of the regioisomers reported in this study and earlier[9] arise from a steric repulsive influence on the closure of the 1,4-diradical. However, for the photoaddition of 3,3-dimethylbut-1-ene in the presence of oxygen, although the trioxane **18** formed may initially be presumed to result from trapping of the more stable diradical, the ratio of the spiro-oxetane regioisomers is independent of oxygen pressure.[10] The rationale proposed for this observation was that 'oxygen is trapping an intermediate which occurs before partitioning into the biradical'. Nonetheless it seems from the formation of a 1:3 ratio of the 4′- and 3′-substituted oxetane isomers respectively from 3,3-dimethylbut-1-ene that the regiochemistry of the attack of the quinone onto an ethene within the excited complex may be subject to steric influences.



18 R = C(CH$_3$)$_3$
32 R = Ph

It may therefore be deduced that while there are many examples of the addition of alkenes to aromatic and aliphatic carbonyl compounds in which the regioisomer ratios reflect relative stabilities of intermediate 1,4-diradicals,[5,6,7] the regiochemistry of oxetane formation of the same addends with 1,4-benzoquinone is controlled and directed within a species which is a precursor of the 1,4-diradical. Furthermore, partitioning of the 1,4-diradical between reaction possibilities can be markedly dependent on the particular system. Thus, while significant

Table 2 Spiro-oxetane formation from 1,4-benzoquinone and electron-donor and -acceptor ethenes[a]

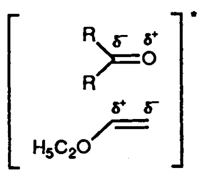
Ethene	E_{ox}/V[17]	Spiro-oxetane	Chemical yield (%)
Ethyl vinyl ether	1.44	**19**	4[b]
Phenyl vinyl ether	1.75	**20**	5[c]
Acrylonitrile	3.67 (E_{red}, −2.63)	—	—
Methyl acrylate	3.50 (E_{red}, −2.4)	**21**	2
(*E*) 3-Ethoxyacrylonitrile	—	**22**:**23** ratio 1:1	30

[a] Benzene solvent. [b] Reaction terminated after short exposure times since the oxetane was very photolabile under its conditions of formation. [c] Minor amounts of the enol ether cyclobutane dimer also formed.

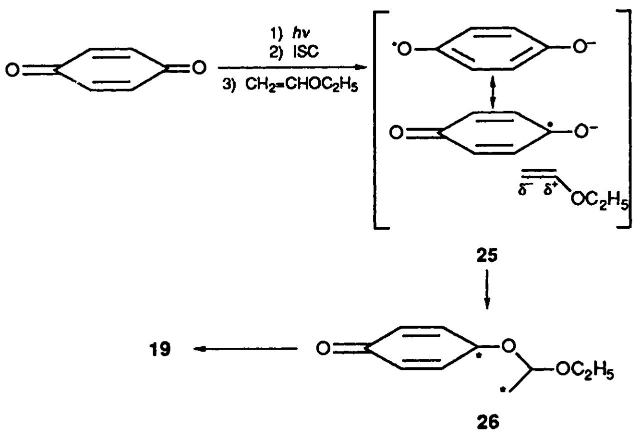
amounts of by-products arise by internal disproportionation in this species from the reaction of acetone with 2,3-dimethylbut-2-ene,[20] in contrast these products are not observed from the 1,4-quinone reaction which instead gave good conversions into the spiro-oxetane.

The correlation between the electron donor ability of cyclic alkenes and their ease of oxetane formation with carbonyl compounds has received comment from Guildford–Jones.[7] However, since only cyclopentene and cyclohexene follow this trend, the appreciable differences observed in the reactivities of the cyclic alkenes towards the $^3n\pi^*$ state of 1,4-benzoquinone are more realistically seen to arise from the effects associated with ring size. The low efficiency of the cyclopentene and cyclohexene additions may then be considered to result from competitive H-abstraction by the excited quinone leading to the ready formation of the corresponding allyl radicals: these have a higher degree of resonance stabilization than the corresponding non-planar species from (*Z*)-cyclooctene.[21] Hence hydrogen abstraction from the cyclooctene will occur less readily than spiro-oxetane formation if the latter is relatively insensitive to ring size. In the previous accounts of the reaction with cyclooctene, stereoisomer formation was not considered.[1,9] The *cis*- and *trans*-fused spiro-oxetane isomers are, however, both formed and hence the addition is presumed, as for the but-2-enes as addends,[9] to involve the triplet pre-oxetane 1,4-diradical in which bond rotation occurs. As expected, there is a much lower tendency for rotation of the bond to occur during the addition of the more rigid (*Z*,*Z*)-cycloocta-1,5-diene.

Control of the regiochemistry of the addition of 1,4-benzoquinone to ethenes thus appears to occur in a precursor of the 1,4-diradical intermediate (presumably an exciplex) and is not necessarily influenced by the relative stabilities of the 1,4-diradicals themselves. To investigate whether the electronic characteristics of substituents on the ethene (*i.e.* polarity of the ethene bond) can be used to manipulate the regiochemistry by influencing the site of attack of the quinone carbonyl group within the exciplex, we examined the photoaddition of 1,4-benzoquinone to ethyl vinyl ether, phenyl vinyl ether, acrylonitrile, methyl acrylate, and the captodative ethene, (*E*)-3-ethoxyacrylonitrile. The results are presented in Table 2. The specific (or at least highly selective) formation of the 4′-ethoxy-substituted oxetane isomer from 1,4-benzoquinone and ethyl vinyl ether contrasts with the preferred formation of the 3′-isomer from photoadditions of this ethene to benzophenone and to acetone.[22] This latter preference reflects both the stabilities of the 1,4-diradicals and the orientation that may be expected for the addends in an exciplex **24**. We considered the possibility that the regiochemistry of the benzoquinone addition is governed by the conformation within a ground-state complex, but could obtain no evidence for this from UV–VIS or ^{1}H NMR spectroscopy.[23] A more promising possibility is that the addition proceeds by photoinduced electron transfer from the ethyl vinyl ether to the quinone to give a radical-ion pair of the type described as a 'charge-transfer exciplex' and for which direct evidence has been obtained recently in a 1,4-benzoquinone system.[12] Such a species as **25** may be expected to combine to give the triplet 1,4-diradical **26** which, following spin inversion, gives the observed 4′-ethoxy isomer. Change of solvent from benzene to acetonitrile increased the rate of formation of **19** by *ca.* 50%, but only during short irradiation periods, for the reasons given above. Unfortunately the photolability of the spiro-oxetane prevented its synthesis in other than small amounts. However, as described in ref. 12, for the 1,4-benzoquinone–tetraphenylallene system, increased solvent polarity would also be expected to promote decay of the 'charge-transfer exciplex' to give the quinone radical anion and the enol ether radical-cation particularly since the two electron donors have closely similar reported oxidation potentials (E_{ox}, tetraphenylallene = 1.45 V;[24] E_{ox}, ethyl vinyl ether = 1.44 V[17]). The implication is that these species combine to give the 1,4-diradical prior to solvent separation and spin inversion. The same directing factors also, not surprisingly, operate for the phenyl vinyl ether addition since again only the 4′-phenoxy spiro-oxetane was detected.



24 R = CH_3 or Ph



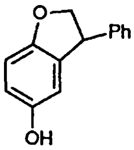
There is no precedent for oxetane formation with methyl acrylate as the addend. The reported photoadditions of acrylonitriles to ketones to give cyanooxetanes occur with regio- and stereo-specificity; and in contrast with other Paterno–Büchi reactions, the direction of any charge transfer is from the excited carbonyl compound to the ethene:[25] such charge transfer is most unlikely to occur from 1,4-benzoquinone, and the very low yields of spiro-oxetanes probably reflect a weak interaction between the addends. Nonetheless the reaction with methyl acrylate is again highly regioselective, if not specific, but it is the 3′- rather than the 4′-methoxycarbonyl- substituted spiro-oxetane which is formed: this may appear surprising in view of the specific opposite regiochemistry for the addition of the acrylonitriles to ketones.[25] In these cases, however, the reaction arises from the S_1 state of the ketone and is considered to involve nucleophilic (Michael) attack of the carbonyl carbon onto the more positive end of the electron acceptor ethene.[5] Direct attack of the 1,4-benzoquinone onto the methyl acrylate to give the more stable 1,4-diradical can account for the observed regiochemistry of the spiro-oxetane **21** but would require the electrophilic oxygen of the excited quinone to react at the more electron deficient site of the ethene. An alternative explanation is that photoexcited 1,4-benzoquinone and methyl acrylate form an exciplex which has a degree of charge transfer from the ethene to the quinone. Collapse of this species would again lead to the more stable 1,4-diradical and the spiro-oxetane isomer with regiochemistry alternative to that of the ethyl vinyl ether addition, as observed. This proposal is supported by the initial *ca.* 50% increase in the rate of the spiro-oxetane formation from methyl acrylate when the reaction is carried out in acetonitrile rather than benzene.

Thus it appears that the regiochemistry and regioselectivity of the photocycloaddition of ethenes to 1,4-benzoquinone to give spiro-oxetanes is decided by the preferred mode of bond formation within the species (probably a charge-transfer exciplex) which precedes formation of the 1,4-diradical. This appears to be controlled by the degree and direction of polarization in the ethene bond which results from the electronic nature of its substituents. For (*E*)-3-ethoxyacrylonitrile the ethene bond is strongly polarized and the addition occurs to give **22** and **23** in a 1:1 ratio and in good yield with regiospecificity in the direction expected from the above considerations. Ethenes which are not strongly polarized are attacked at each end of the C=C bond with equal probability (*e.g.* 2-methylpropene).

To examine this point further, we compared the regiochemistry of spiro-oxetane formation from vinyl acetate (E_{ox} = 2.15 V), 2-methylpropene (E_{ox} = 2.65 V) and ethyl vinyl ether (E_{ox} = 1.44 V). Similar studies with allyl methyl ether, methyl vinylacetate, and methyl but-3-enoate were intended to demonstrate the effect of reducing the electronic effects of substituents on the ethene bond by interposing a methylene group.

The respective ratio of the 4′- to 3′-substituted spiro-oxetanes (**27** and **28**) from vinyl acetate varied from 4:1 (15% conversion) to 2.2:1 (50% conversion), thereby reflecting photostability differences of the two isomers. This increased preference for formation of the 4′-isomer **27** compares with the 1:1 ratio of oxetanes from 2-methylpropene, and is consistent with control of the regiochemistry by the degree and direction of polarity in the ethene bond. The same regioselective preference for the acetal structure has been observed by Adam and co-workers for the addition of 1,4-benzoquinone to several unsaturated lactones on UV–VIS laser irradiation.[26] Methyl-substituted vinylacetates were also examined in this reaction, and with one exception the 4′-acetoxy spiro-oxetane was favoured over the 3′-isomer in ratios of *ca.* 2:1. The exception was isopropenyl acetate which surprisingly gave only the 3′-acetoxy-3′-methyl oxetane **29**. Formation of this isomer is wholly consistent with control of the regiochemistry by the relative stabilities of the 1,4-diradicals and/or dipolar interactions without charge transfer within an intermediate of the type depicted in **24**, but it is contrary to that expected from control by the electron donor character of the ethene. At present the cause of this anomaly is not known. The yields of oxetanes from the allyl compounds were low (5%), but each gave the 4′- and 3′-regioisomers with low selectivities (*i.e.* allyl methyl ether, 1:1; methyl vinylacetate, 1:1.3; and methyl but-3-enoate, 2:1) more resembling those from non-polarized ethenes, such as 2-methylpropene. These observations further support the postulated importance of ethene bond polarity in the control of the regioselectivity of spiro-oxetane formation.

Finally, we consider oxetane formation from 1,4-benzoquinone and phenylethenes (styrenes). Wilson *et al.* have reported that using an argon laser radiation source and in the absence of oxygen, styrene undergoes photoaddition to 1,4-benzoquinone to give the 4′-phenyl substituted spiro-oxetane **30** and, surprisingly, the dihydrobenzofuran **31**.[10] In the Experimental section of their paper, however, there is no reference to the formation of **31** under these conditions, although the oxetane **30** is fully characterised (20%) and a second adduct (16%) is tentatively described as 7-phenylbicyclo[4.2.0]oct-3-ene-2,6-dione. Under one atmosphere of oxygen, the major product (56%) is the trioxane **32**, and **30** and **31** were isolated in 9 and 5% yields respectively. In view of the uncertainty concerning the formation of **31**, and our earlier failure to isolate products from this system,[1] we have re-examined the 1,4-benzoquinone–styrene reaction in benzene solution under atmospheres of nitrogen and oxygen and using filtered radiation (λ > 300 nm). Under nitrogen, the previous results[10] were largely confirmed. The formation of cyclobutane adducts from styrenes and 1,4-benzoquinone will be considered fully elsewhere, but attempts to detect the dihydrobenzofuran **31** either chromatographically or spectroscopically failed. However, the important feature of this reaction is that the major product is the oxetane **30** with regiochemistry not reflecting formation from the more stable 1,4-diradical. Solutions degassed under oxygen gave the trioxane **32** and the 4′-phenylspiro-oxetane **30** in a ratio closely similar to that earlier reported,[10] but the dihydrobenzofuran **31** was again not detected. The fomation of **30** from styrene (E_{ox} = 1.59 V) is consistent with the other results described here in that there is a relationship between the regiochemistry of the isolated oxetane and the electron-donating ability of the ethene. However, at least for the styrene–1,4-benzoquinone system, both possible 1,4-diradicals appear to be formed. The precursor of **30**, analogous to **26** appears to cyclize too rapidly for oxygen trapping to compete, while the more stable diradical readily forms the trioxane. The fate of this latter 1,4-diradical in the absence of oxygen remains a matter of speculation. It has been reported that this species yields the dihydrobenzofuran **31** which we cannot detect under our conditions. Nevertheless, even under argon laser irradiation **31** is only a minor product and is formed in amounts which clearly do not reflect the relative concentrations of the two pre-oxetane 1,4-diradicals formed under oxygen. It thus appears that although the more stable 1,4-diradical can be trapped by oxygen, in nitrogen degassed solution its major reaction is regression to starting materials. This conclusion, if correct, suggests the need for a degree of caution in drawing mechanistic deductions from isomer ratios alone.



31

The photoaddition of other carbonyl compounds to styrenes markedly favours formation of the regioisomer from the more stable of the two pre-oxetane 1,4-diradicals.[27] We have,

Table 3 Spiro-oxetane formation from 1,4-benzoquinone and phenylethenes[a]

Ethene	Spiro-oxetane	Chemical yield (%)
Styrene	**30**	20
α-Methylstyrene	**33**	8
β-Methylstyrene	**34**	14
(*E*)-Stilbene[b]	**35**:**36** ratio 1:2[c]	18

[a] Benzene solvent. [b] Irradiation filtered by means of a nitrite–biphthalate solution (λ = 400 nm)[1]. [c] Same ratios of oxetane stereoisomers from (*Z*)-stilbene.

therefore, examined the photoreactions of 1,4-benzoquinone in the presence of methylstyrenes and the (*Z*)- and (*E*)-stilbenes. These results and those with styrene are presented in Table 3. For the α- and β-methylstyrenes formation of the 4'-phenyl substituted oxetanes is greatly preferred, as with styrene itself. The observation that (*Z*) and (*E*) stilbenes gave identical ratios of oxetane stereoisomers with 1,4-benzoquinone is wholly consistent with bond rotation in intermediate pre-oxetane 1,4-diradicals: (*Z*)- and (*E*)-but-2-enes behave similarly.[9]

To summarize, the central finding of this study is that although 1,4-benzoquinone resembles simple aldehydes and ketones in forming oxetanes by photocycloaddition of various ethenes, the regiochemistry is in most cases the opposite of that expected. It is proposed that this difference reflects polar influences on the regiochemistry resulting from the strong electron acceptor character of the quinone.

Experimental

Photochemical and Analytical Methods.—Irradiations were carried out on freshly recrystallized 1,4-benzoquinone (0.097 mol) (from benzene–charcoal) and the ethene (0.097 mol) in azeotropically dried AR-grade benzene solution (150 cm^3). The photochemical source comprised a 125 W medium-pressure mercury arc inside a water-cooled Pyrex immersion well: this was placed in a Pyrex vessel containing the benzene solution of the reactants. For experiments using radiation of wavelength longer than 400 nm, the water cooling was replaced by a cooled, recirculated nitrite–biphthalate filter solution.[1] The solutions were degassed under nitrogen prior to irradiation. The reactions involving ethene and 2-methylpropene were first flushed with nitrogen and then sealed under the required ethene (approximately 0.15 mol). Irradiation periods varied from 3 to 48 h with reactions being terminated when it was assessed chromatographically that no further quinone was being consumed; or that, as for the spiro-oxetane from ethyl vinyl ether, the product had reached a photostationary-state concentration.

The two work-up procedures employed were (*a*) the irradiated solution was shaken with 0.1 mol dm^{-3} sodium hydroxide solution (50 cm^3), washed with water (50 cm^3), dried over anhydrous magnesium sulphate, and the solvent and ethene removed by rotary evaporation under vacuum; and (*b*) the ethene and solvent were removed from the irradiated solution by rotary evaporation under vacuum and the 1,4-quinone by vacuum sublimation. In both cases the crude product was analysed chromatographically and spectroscopically to ensure that no change had occurred during the separation and purification of the product(s): the latter procedure involved flash chromatography using ICN silica 32–63 (Park Scientific Ltd.) with mixtures of freshly distilled diethyl ether and light petroleum (b.p. 30–40 °C) as the eluent.

The effect of solvent (benzene, acetonitrile and carbon tetrachloride) on the reactions was assessed chromatographically from irradiation of solutions (6.5×10^{-3} mol of each reactant) in Pyrex tubes (10 cm^3 capacity) using a 'merry-go-round' apparatus and the above water-cooled lamp; it was also monitored by the disappearance of the quinone absorption in the 400–480 nm region and the appearance of the spiro-oxetane from solutions (30 cm^3) of the 1,4-quinone (5.5×10^{-4} mol) and ethene (7.5×10^{-4} mol) irradiated with an array of six 150 W quartz–halogen lamps.

NMR spectra were recorded on a Joel FX90Q, a Bruker WM250 or a Bruker WH400 (SERC Spectrometer Service, Warwick) instrument with tetramethylsilane as an internal reference and in CDCl$_3$ solution. IR spectra were obtained using a Perkin Elmer 881 spectrophotometer and accurate mass data were recorded at the SERC Mass Spectrometry Service Centre, Swansea, after purity assurance by TLC (Camlab Polygram G/UV precoated sheets). Elemental analyses were determined by Medac Ltd., Brunel University.

The isomer ratios of the spiro-oxetanes were assessed from the ^{1}H NMR spectral data of the crude product mixtures. Yields of the photoadducts are based on the amounts of the spiro-oxetane(s) present in the crude product (estimated by ^{1}H NMR spectroscopy) and do not take into account the unchanged starting materials.

Spiro-oxetanes.—The spectral features which allow the photoproducts of 1,4-benzoquinone and ethenes to be assigned spiro-oxetane structures are given in references 1, 9 and 10. Only the structurally relevant data are, therefore, presented here. All coupling constants are in Hz, and unless otherwise stated the IR spectral data were obtained from liquid films.

Spiro(cyclohexa-2,5-diene-1,2'-oxetan)-4-one **6**.—δ_H 7.28 (2-H, 6-H, d, $J_{2,3}$, $J_{6,5}$ 11), 6.10 (3-H, 5-H, d), 4.68 (4'-H, t, $J_{3',4'}$ 7.5) and 2.80 (3'-H, t); ν_{max}/cm^{-1} 1670s and 970m (Found: M$^+$, 136.0524. Calc. for $C_8H_8O_2$: *M*, 136.0522).

4'-Hexylspiro(cyclohexa-2,5-diene-1,2'-oxetan)-4-one **7**.—δ_H 7.5–7.0 (2-H, 6-H, m), 6.36–6.05 (3-H, 5-H, m), 4.95 (4'-H, m), 3.1–2.4 (3'-H$_{a,b}$, m) and 2.0–1.0 (13 H, hexyl chain); ν_{max}/cm^{-1} 1665s and 977m [Found: M$^+$, 220.1464. Calc. for $C_{14}H_{20}O_2$: M, 220.1458].

3'-Hexylspiro(cyclohexa-2,5-diene-1,2'-oxetan)-4-one **8**. δ_H 7.5–7.0 (2-H, 6-H, m), 6.2–6.0 (3-H, 5-H, m), 4.90–4.35 (4'-H$_{a,b}$ two dd, J_{gem} 8, $J_{3',4'}$ 6), 3.4–3.0 (3'-H, m) and 1.8–0.8 (13 H, hexyl chain); ν_{max}/cm^{-1} 1665s and 980m (Found: M$^+$, 220.1460. Calc. for $C_{14}H_{20}O_2$: *M*, 220.1458).

3',3'- *and* 4',4'-*dimethylspiro(cyclohexa-2,5-diene-1,2'-oxetan)-4-one* (**9** and **10**).—Isomers **9** and **10** were not fully separated despite extensive chromatography.

9: *m*/*z* 164 (M$^+$); δ_H 7.12 (2-H, 6-H, d, $J_{2,3}$, $J_{6,5}$ 5.0), 6.0 (3-H, 5-H, d), 2.6 (3'-H$_{a,b}$, s) and 1.38 (two CH$_3$, s); ν_{max}/cm^{-1} 1660s and 980m.

10: *m*/*z* 164 (M$^+$); δ_H 7.28 (2-H, 6-H, d, $J_{2,3}$, $J_{6,5}$ 5.0), 6.18 (3-H, 5-H, d), 4.38 (4'-H$_{a,b}$, s) and 1.25 (two CH$_3$, s); ν_{max}/cm^{-1} 1660s and 980m.

3',3',4',4'-*Tetramethylspiro(cyclohexa-2,5-diene-1,2'-oxetan)-4-one* **11**.—M.p. 104–105 °C; δ_H 7.2 (2-H, 6-H, d, $J_{2,3}$, $J_{6,5}$ 8.5), 6.1 (3-H, 5-H, d), 1.52 (two CH$_3$, s) and 1.20 (two CH$_3$, s); δ_C (22.5 MHz) 184.88 (C-4), 150.16 (C-2, C-6), 128.11 (C-3, C-5), 86.17 (C-1), 80.05 (C-4'), 49.75 (C-3'), 26.92 (CH$_3$ on C-4') and 21.92 (CH$_3$ on C-3'); ν_{max}(Nujol)/cm^{-1} 1670s and 980m (Found: C, 75.0; H, 8.4. $C_{12}H_{16}O_2$ requires C, 74.95; H, 8.39%).

Spiro(cyclohexa-2,5-diene-1,2'-perhydrocyclopent[b]*oxet)-4-one* **12**.—*m*/*z* 176 (M$^+$); δ_H 8.18–7.75 (2-H, 6-H, m), 7.70–7.40 (3-H, 5-H, m), 5.90–5.45 (5a'-H, m), 3.60–3.15 (2a'-H, m) and 3.1–1.2 (6 H, 3'-H$_2$, 4'-H$_2$, 5'-H$_2$); ν_{max}/cm^{-1} 1675s and 980m.

Spiro(cyclohexa-2,5-diene-1,2′-perhydrobenz[b]oxet)-4-one **13**.—δ_H 7.43–7.10 (2-H, 6-H, m), 6.38–6.0 (3-H, 6-H, m), 5.20–4.85 (6a′-H, m), 3.25–2.80 (2a′-H, m) and 2.2–1.2 (8 H, 3′-H_2, 4′-H_2, 5′-H_2, 6′-H_2); ν_{max}/cm^{-1} 1670s and 970m (Found: M^+, 190.098. Calc. for $C_{12}H_{14}O_2$: *M*, 190.099).

Spiro(cyclohexa-2,5-diene-1,2′-perhydrocyclooct[b]oxet)-4-one.—Analytical and some spectral data for the spiro-oxetane from this system have been previously published;[1] more detailed spectral data are now reported.

cis-*Isomer* **14**: δ_H 7.39 (6-H, dd, $J_{6,5}$ 9.6, $J_{6,2}$ 2.9), 7.0 (2-H, dd, $J_{2,3}$ 9.6), 6.26 (5-H, dd, $J_{5,3}$ 2.0), 6.12 (3-H, dd), 4.85 (8a′-H, m), 2.95 (2a′-H, m) and 2.41–0.85 (12 H, 3′- to 8′-H_2); δ_C(22.5 MHz) 185.32 (C-4), 150.03 (C-6), 146.30 (C-2), 129.04, (C-5), 127.70 (C-3), 78.32 (C-8a′), 85.65 (C-1), 52.62 (C-2a), 38.53, 29.58, 28.88, 28.18, 26.56 and 25.64 (C-3′ to C-8′ bridge).

trans-*Isomer* **15**: (not fully separated from **14**) δ_H 7.26 (2-H, dd, $J_{2,3}$ 9.9, $J_{2,6}$ 2.9), 7.15 (6-H, dd, $J_{6,5}$ 9.9) 6.26 (3-H, dd, $J_{3,5}$ 2.0), 6.12 (5-H, dd), 4.85 (8a′-H, m), 2.95 (2a′-H, m) and 2.40–0.85 (3′- to 8′-H_2); ν_{max}/cm^{-1} 1670s and 970m.

cis-*Spiro(cyclohexa-2,5-diene-1,2′-2a′,3′,4′,7′,8′,8a′-hexahydro-2′H-cyclooct[b]oxet)-4-one* **16**.—δ_H 7.38 (6-H, dd, $J_{6,5}$ 9.5, $J_{6,2}$ 2.5), 6.94 (2-H, dd, $J_{2,3}$ 9.5), 6.26 (5-H, dd, $J_{5,3}$ 2.0), 6.13 (3-H, dd), 5.78–5.50 (5′-H, 6′-H, m) 4.85 (8a′-H, m), 3.10 (2a′-H, m) and 2.4–1.3 (8 H, 3′-, 4′-H_2 7′-, 8′-H_2); δ_H(22.5 MHz) 186.84 (C-4), 149.79 (C-6), 146.21 (C-2), 130.04 (C-6′), 129.30 (C-5) 128.74 (C-5′), 127.93 (C-3), 83.30 (C-1), 78.43 (C-8a′), 50.88 (C-2a′), 34.30, 24.87, 23.73 and 21.05 (C-3′, C-4′, C-7′, C-8′); ν_{max}/cm^{-1} 1670s and 970m (Found: M^+, 216.1150. Calc. for $C_{14}H_{16}O_2$: 216.1146).

trans-*Isomer* **17** (not fully separated from **16**): δ_H 7.24 (6-H, dd, $J_{6,5}$ 9.5, $J_{6,2}$ 2.5), 7.15 (2-H, dd, $J_{2,3}$ 9.5), 6.25 (5-H, dd, $J_{5,3}$ 2.0), 6.15 (3-H, dd) remainder of the spectrum essentially the same as that of **16**.

4′-Ethoxyspiro(cyclohexa-2,5-diene-1,2′-oxetan)-4-one **19**.—δ_H 7.21 (6-H, dd, $J_{6,5}$ 9.8, $J_{6,2}$ 3.0), 7.09 (2-H, dd, $J_{2,3}$ 9.9), 6.10 (3-H, 5-H, two overlapping dd, $J_{3,5}$ 2.0), 5.5 (4′-H, dd, $J_{4',3a'}$ 3.95, $J_{4',3'b}$, 5.75), 3.82 (1 H, CH_2, dq, *J* 9.55 and 7.10), 3.55 (1 H, CH_2, dq, *J* 9.55 and 7.10), 3.0 (3-H_b, *cis* to OEt, dd, J_{gem} 12.5), 2.64 (3′-H_a, *trans* to OEt, dd) and 1.25 (CH_3, t); ν_{max}/cm^{-1} 1670s and 930m (Found: M^+, 180.0780. Calc. for $C_{10}H_{12}O_3$: *M*, 180.0783).

4′-Phenoxyspiro(cyclohexa-2,5-diene-1,2′-oxetan)-4-one **20**.—δ_H 7.2–6.7 (5 H, phenyl, 2-H, 6-H, overlapping m), 6.2–5.9 (3-H, 5-H, 4′-H, overlapping m) and 3.0–2.6 (2 H, 3′-$H_{a,b}$, m); ν_{max}/cm^{-1} 1670s and 930m (Found: M^+, 228.0779. Calc. for $C_{14}H_{12}O_3$: *M*, 228.0783).

Methyl 4-oxo(spirocyclohexa-2,5-diene-1,2′-oxetane)-4′-carboxylate **21**. δ_H 7.22 (2-H, 6-H, m), 6.25 (3-H, 5-H, m), 5.05 (4′-H_a, *cis* to CO_2CH_3, dd, J_{gem} 9.9, $J_{4',3'}$, 6.6), 4.72 (4′-H_b, *trans* to CO_2CH_3, dd, $J_{4',3'}$, 6.5), 4.0 (3′-H, overlapping dd) and 3.75 (CH_3, s); ν_{max}/cm^{-1} 1720, 1675, 980 and 930 (Found: M^+, 194.0595. Calc. for $C_{10}H_{10}O_4$: *M*, 194.0576).

trans-4′-Ethoxy-4-oxospiro(cyclohexa-2,5-diene-1,2′-oxetane)-3′-carbonitrile **22**.—M.p. 119–121 °C; δ_H 7.44 (2-H, dd, $J_{2,3}$ 10.2, $J_{2,6}$ 3.0), 6.98 (6-H, dd, $J_{6,5}$ 10.2), 6.36 (3-H, dd, $J_{3,5}$ 2.0), 6.28 (5-H, dd), 5.58 (4′-H, d, $J_{4',3'}$ 5.7), 4.20 (3′-H, d) 3.74 (1 H, CH_2, dq, *J* 9.6 and 7.2), 3.74 (1 H, CH_2, dq, *J* 9.6 and 7.2) and 1.36 (CH_3, t, *J* 7.2); δ_C 183.91 (C-4), 145.41 (C-2), 144.56 (C-6), 130.26 (C-3, C-5), 112.76 (CN), 97.81 (C-4′), 70.05 (C-1), 65.10 (CH_2), 40.25 (C-3′) and 15.15 (CH_3); ν_{max}(Nujol)/cm^{-1} 2220w, 1670s and 940m (Found: C, 64.4; H, 5.4; N, 6.85. $C_{11}H_{11}NO_3$ requires C, 64.37; H, 5.40; N, 6.83%).

cis-*Isomer* **23**: δ_H 7.24 (2-H, dd, $J_{2,3}$ 12.9, $J_{2,6}$ 3.1), 7.06 (6-H, dd, $J_{6,5}$ 12.9), 6.40 (3-H, dd, $J_{3,5}$ 2), 6.26 (5-H, dd), 5.65 (4′-H, d, $J_{4',3'}$ 4.2), 3.76 (3′-H, d), 3.88 (1 H, CH_2, dq, *J* 6.0 and 4.5), 3.72 (1 H, CH_2, dq, *J* 6.0 and 4.5) and 1.32 (CH_3, t, *J* 6.0); δ_C 83.84 (C-4), 145.38 (C-6), 143.83 (C-2), 129.61 (C-3, C-5), 113.90 (CN), 99.88 (C-4′), 74.03 (C-1), 65.44 (CH_2), 41.35 (C-3′) and 15.14 (CH_3); ν_{max}/cm^{-1} 2220w, 1670s and 940m (Found: M^+, 205.0735. Calc. for $C_{11}H_{11}NO_3$: *M*, 205.0783).

4-Oxospiro(cyclohexa-2,5-diene-1,2′-oxetan)-4′-yl (**27**) *and -3′-yl* **28** *Acetate*.—Isomers **27** and **28** were not fully separated despite extensive chromatography. Enriched mixtures in each showed the following: δ_H 7.35–7.10 (2-H, 6-H, m, both isomers), 6.50 [4′-H, **27**, dd, $J_{4',3'(trans)}$ 6, $J_{4',3'(cis)}$ 4], 6.35–6.15 (3-H, 5-H, m, both isomers), 5.54 [3′-H, **28**, dd, $J_{3',4'(trans)}$ $J_{3',4'(cis)}$ 6.5], 4.88 (4′-H_a, **28**, dd, J_{gem} 8), 4.72 (4′-H_b, **28**, dd), 3.20 [3′-H_a, **27**, dd, J_{gem} 13, $J_{4',3'(trans)}$ 6], 2.81 [3′-H_b, **27**, dd, $J_{4',3'(cis)}$ 4], 2.17 (CH_3, **27**, s) and 2.07 (CH_3, **28**, s); ν_{max}/cm^{-1} 1750s, 1670s and 980m.

3′-Methyl-4-oxospiro(cyclohexa-2,5-diene-1,2′-oxetan)-3′-yl Acetate **29**.—δ_H 7.4–6.8 (2-H, 6-H, m), 6.35–6.20 (3-H, 6-H, m), 4.90 (4′-H_a, d, $J_{4',4b'}$ 8), 4.5 (4′-H_b, d), 2.0 (OCH_3) and 1.78 (CH_3); ν_{max}/cm^{-} 1750s, 1670s and 970m (Found: M^+, 208.0725. Calc. for $C_{11}H_{12}O_4$: *M*, 208.0732).

4′-Phenylspiro(cyclohexa-2,5-diene-1,2′-oxetan)-4-one.—Spectral data for **30** are closely simlar to those reported in ref. 10.

6′-Phenylspiro(cyclohexa-2,5-diene-1,3′-1′,2′,4′-trioxan)-4-one **32**. ^1H NMR and IR spectral data identical with those reported in ref. 10; δ_C 184.69 (C-4), 140.27 (C-6), 138.65 (C-2), 132.27 (Ph), 129.74 (C-1), 128.96 (C-5), 127.20 (C-3), 81.68 (*C*-Ph) and 64.38 (CH_2).

4′-Methyl-4′-phenylspiro(cyclohexa-2,5-diene-1,2′-oxetan)-4-one **33**.—δ_H 7.4 (5 H, Ph, br s), 7.25 (6-H, dd, $J_{6,5}$ 10, $J_{6,2}$ 2), 6.90 (2-H, dd, $J_{2,3}$ 10), 6.18 (5-H, dd, $J_{3,5}$ 1.5), 6.00 (3-H, dd), 2.95 (3′-$H_{a,b}$, d, J_{gem} 9) and 1.80 (CH_3, s); ν_{max}/cm^{-1} 1670s and 980m (Found: M^+, 226.098. Calc. for $C_{15}H_{14}O_2$: *M*, 226.099).

3′-Methyl-4′-phenylspiro(cyclohexa-2,5-diene-1,2′-oxetan)-4-one **34**.—Mixture of stereoisomers not separated: δ_H 7.5–7.1 (7 H, Ph, 2-H, 5-H, overlapping m), 6.35 (5-H, dd, $J_{5,6}$ 7, $J_{5,3}$ 1), 6.25 (3-H, dd), 5.45 (4′-H, br s), 3.10 (3′-H, overlapping q) and 1.15 (CH_3, d); ν_{max}/1670s and 980m.

cis- **35** *and* trans-*3′,4′-diphenylspiro(cyclohexa-2,5-diene-1,2′-oxetan)-4-one*. Isomers **35** and **36** were not completely separated despite extensive chromatography. **35** δ_H 7.6–7.2 (12 H, 2 × Ph, 2-H, 6-H, overlapping m), 6.25 (5-H, dd, $J_{5,6}$ 10, $J_{5,3}$ 1.5), 6.10 (3-H, dd, $J_{3,2}$ 10), 5.53 (4′-H, d, $J_{4',3'}$ 9) and 4.51 (3′-H, d); ν_{max}/cm^{-1} 1675s and 970m. **36** δ_H 7.6–7.2 (12 H, 2 × Ph, 2-H, 6-H, overlapping m), 6.28 (4′-H, d, $J_{4',3'}$ 8.5), 6.25 (3-H, d, $J_{3,2}$ 10), 6.10 (5-H, d, $J_{5,6}$ 10) and 4.39 (3′-H, d); ν_{max}/cm^{-1} 1670s and 980m.

Acknowledgements

The Cancer Research Campaign is thanked for financial support. We are grateful for the award of a postdoctoral fellowship (to E. H. E.) and a research assistantship (to H. S. M.).

References

1 D. Bryce-Smith and A. Gilbert, *Proc. Chem. Soc.*, 1964, 87; D. Bryce-Smith, A. Gilbert and M. G. Johnson, *J. Chem. Soc. C*, 1967, 383.
2 D. Bryce-Smith, G. I. Fray and A. Gilbert, *Tetrahedron Lett.*, 1964, 2137; H. E. Zimmermann and L. Craft, *Tetrahedron Lett.*, 1964, 2131.
3 W. M. Horspool, 'Enone Cycloadditions and Rearrangements: Photoreactions of Dienones and Quinones' in *Specialist Periodical*

Report on Photochemistry, Royal Society of Chemistry, 1970–1990, vols. 1–21 inclusive.

4 K. Maruyama and A. Osuka, 'Recent Advances in the Photochemistry of Quinones,' in *The Chemistry of Quinonoid Compounds Vol. II*, ed. S. Patai and Z. Rapport, Wiley, 1988, 759.

5 H. A. J. Carless in *Synthetic Organic Photochemistry*, ed. W. M. Horspool, Plenum Press, New York, 1984, 425.

6 D. R. Arnold, *Adv. Photochem.*, 1968, **6**, 301; H. A. J. Carless, *Photochemistry in Organic Synthesis*, ed. J. D. Coyle, The Royal Society of Chemistry, Special Publication No. 57, 1986, 95.

7 G. Jones, *Organic Photochemistry*, ed. A. Padwa, Marcel Dekker, New York, 1981, vol. 5, p. 1.

8 L. G. Arnaut and S. J. Formoshino, *J. Photochem.*, 1987, **39**, 13.

9 N. J. Bunce and M. Hadley, *Can. J. Chem.*, 1975, **53**, 3240.

10 R. M. Wilson, S. W. Wunderly, T. F. Walsh, A. K. Musser, R. Outcalt, F. Geiser, S. K. Gee, W. Brabender, L. Yerino, T. T. Conrad and G. A. Tharp, *J. Am. Chem. Soc.*, 1982, **104**, 4429.

11 R. M. Wilson, R. Outcalt and H. H. Jaffe, *J. Am. Chem. Soc.*, 1978, **100**, 301.

12 K. A. Schnapp, R. M. Wilson, D. M. Ho, R. A. Caldwell and D. Creed, *J. Am. Chem. Soc.*, 1990, **112**, 3700.

13 D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 1962, 2675 and references therein; R. Robson, P. W. Grubb and J. A. Barltrop, *J. Chem. Soc.*, 1964, 2153.

14 D. Bryce-Smith, R. Deshpande, A. Gilbert and J. Grzonka, *Chem. Commun.*, 1970, 561.

15 L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, 1953, **75**, 3776.

16 D. Bryce-Smith, J. A. Frost and A. Gilbert, *Nature* (*London*), 1967, **213**, 1121.

17 J. Mattay, *Tetrahedron*, 1985, **41**, 2405.

18 Oxidation potential calculated from the ionisation potential by the formula given in L. L. Miller, G. D. Nordblom and E. A. Mayeda, *J. Org. Chem.*, 1972, **37**, 916.

19 R. A. Caldwell, G. W. Sovocool and R. P. Gatewski, *J. Am. Chem. Soc.*, 1973, **95**, 2549.

20 H. A. J. Carless, *J. Chem. Soc., Perkin Trans. 2*, 1974, 834.

21 P. Borrell and J. Sedlar, *Trans. Faraday Soc.*, 1970, **66**, 1670.

22 S. H. Schroeter and C. M. Orlando, *J. Org. Chem.*, 1969, **34**, 1181.

23 D. Bryce-Smith, B. E. Connett and A. Gilbert, *J. Chem. Soc. C*, 1968, 816; D. Bryce-Smith, A. Gilbert and H. M. Tyrrell, *J. Chem. Soc. Chem. Commun.*, 1974, 699.

24 G. Schlegel and H. J. Schafer, *Chem. Ber.*, 1983, **116**, 960.

25 J. A. Barltrop and H. A. J. Carless, *J. Am. Chem. Soc.*, 1972, **94**, 1951; J. A. Barltrop and H. A. J. Carless, *Tetrahedron Lett.*, 1968, 3901.

26 W. Adam, U. Kliem and V. Lucchini, *Liebigs Ann. Chem.*, 1988, 869; W. Adam, U. Kliem, T. Mosandl, E-M. Peters, K. Peters and H-G. von Schnering, *J. Org. Chem.*, 1988, **53**, 4986; W. Adam, U. Kliem, E-M. Peters, K. Peters and H-G. von Schnering, *J. Prakt. Chem.*, 1988, band 330, 391.

27 H. A. J. Carless, A. K. Maitra and H. S. Trivedi, *J. Chem. Soc. Chem. Commun.*, 1979, 984.

Paper 1/02638K
Received 3rd *June* 1991
Accepted 19th *June* 1991