Photoaddition of Ethenes to 1,4-Naphthoquinone: Factors Influencing the Site of Reaction

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1,4-Naphthoquinone undergoes photocycloaddition to a variety of electron donor and electron acceptor ethenes giving spirooxetanes and/or cyclobutane derivatives. The site of addition onto the quinone depends on the electron donor character of the ethene, with the spirooxetane being generally favoured with ethenes of low oxidation potential. 2,3-Dimethylbut-2-ene, the strongest electron donor ethene studied, also gave a novel acyclic addition product involving the ethene moiety of the quinone. The two types of 1,4-naphthoquinone cycloadducts have appreciable *in vitro* cytotoxicity.

The addition of ethenes to the triplet state of 1,4-benzoquinone invariably yields spirooxetanes **1**[1,2] and we have recently reported on the features of this reaction which control its regiochemistry.[3] Photoreaction at the ethene bond of 1,4-benzoquinone giving cyclobutane derivatives has only been observed for its dimerization[4] and its addition to styrene.[2,3] The rarity of this process reflects the 76 kJ mol^{-1} lower energy of the $^3n,\pi^*$ state than the $^3\pi,\pi^*$ state.[5] The energy difference between these two states in 1,4-naphthoquinone is, however, only of the order of 25 kJ mol^{-1}, and from a theoretical investigation of the excited states of 1,4-quinones it has been proposed that several triplet states are involved in the photochemistry of 1,4-naphthoquinone.[5] Indeed, consistent with the ready accessibility of the $^3n,\pi^*$ and $^3\pi,\pi^*$ states in 1,4-naphthoquinone, early reports have indicated that in this case ($2\pi + 2\pi$) cycloaddition of ethenes giving cyclobutane derivatives can compete with spirooxetane formation,[6] and from quenching experiments both processes are deduced to arise from the triplet manifold.[5] It is evident from studies with benzocyclic ethenes including coumarone and isocoumarin and their derivatives,[7] that the site of addition to the quinone is markedly dependent on the detailed structure of the ethene. From the limited data available, it is tempting to suggest that the spirooxetane–cyclobutane ratio increases with increase in the electron donor character of the addend.

Since these early reports, several accounts have appeared describing the photoaddition of various ethenes to 2-methyl-,[8-10] 2,3-dimethyl-,[9] 2,3-diethyl-,[9] 2-methoxy-,[10,11] 2-hydroxy-,[12] 2-chloro-,[13,14] 2-bromo-,[10] 2-bromo-3-methyl-,[10] 2,3-dichloro-,[10,15-17] 2,3-dibromo-,[10,16] and 2-bromo-3-methoxy-,[10,16] 1,4-naphthoquinones[17] and, although the photochemistry of the parent quinone has received some attention,[17-22] the factors which control the site of reaction (*i.e.* at the carbonyl or ethene of the quinone) have remained unclear. Clarification of these aspects became of concern to us since we wished to prepare predictably functionalized derivatives of the 1,4-naphthoquinone–ethene spirooxetanes **2** and cyclobutane adducts **3** for evaluation as anti-cancer agents following our preliminary studies in conjunction with Professor K. Harrap (Royal Cancer Hospital, Sutton, UK) which showed that members of both these series of photoadducts have remarkable *in vitro* cytotoxicity.

Results and Discussion

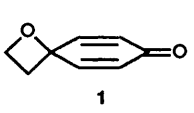
From studies involving the photoadditions of 4- and 6-substituted cyclohex-2-enones to cyclopentene, 2,3-dimethylbut-2-ene, and 2-methylpropene, Desobry and Margaretha have concluded that, apart from the effects of solvent polarity and of substituents on the enone, the site of ethene addition may also be influenced by the 'charge density on the olefinic carbon atom'.[2,3] Indeed, because of the proximity of the energies of the $^3n,\pi^*$ and $^3\pi,\pi^*$ states of 1,4-naphthoquinone, it may be expected that ethenes with low oxidation potentials would react preferentially at the electrophilic oxygen of the excited carbonyl group of the quinone to give spirooxetanes rather than at its ethene bond to yield the cyclobutane isomers. Thus the site of the photocycloaddition would indeed be controlled by the electron donor ability of the ethene. However, Maruyama and co-workers have reported that 1,4-naphthoquinone does not undergo addition to cyclopentene (E_{ox} 1.83 V) or cyclohexene (E_{ox} 1.72 V) in benzene solution but instead is photoreduced to the quinhydrone.[20] Furthermore, they describe the photoproduct from 1,4-naphthoquinone and (*Z*)-cyclooctene (E_{ox} 1.85 V) as the naphthocyclobutene **4** arising from an initial addition at the ethene bond of the quinone. In view of these unexpected results, we have reinvestigated the photoreactions of the quinone in the presence of cyclopentene and cyclooctene and have also studied its additions to acyclic alkenes, styrene and functionalized vinyl compounds. Thus, the photoaddition reactions of 1,4-naphthoquinone have been investigated with ethenes having widely differing electron donor abilities and structures. The results of this study are presented in Table 1. The formation of products was monitored at regular intervals and the reaction was allowed to proceed until no further quinone was consumed, as indicated by absorption spectroscopy: the time for this varied from 7 h (2-methylpropene) to 30 h (acrylonitrile). Termination of product formation before complete consumption of the quinone resulted from the deposition of light-absorbing polymeric matter on the water-cooled Pyrex lamp well, and in some cases much of the starting materials still remained: the chemical yields of the adducts will also depend to some extent on the variable photolabilities of the spirooxetanes.[3] The relative rates of adduct formation were, however, determined in the intial stages of the reactions before occlusion of the lamp well became evident and these values provide a useful comparison of the relative tendencies for each system to give spirooxetanes and/or cyclobutane derivatives.

From the data in Table 1, it would appear that there is no all-embracing relationship between the oxidation potential of the ethene and the relative efficiencies of the cycloadditions to give spirooxetanes (*i.e.* reaction of the $^3n,\pi^*$ state) and cyclobutane derivatives (*i.e.* reaction of the $^3\pi,\pi^*$ state). It is, however, the products and/or adduct formation efficiencies from cyclo-

Table 1 Photocycloadduct formation from 1,4-naphthoquinone and ethenes[a]

Addend	E_{ox}/v	Spirooxetane; rate of formation relative to **5**	Cyclobutane; rate of formation relative to **5**	Total chemical yield (%)[b]
Ethene	2.90	—[c]	**5**; 1.00	28
Oct-1-ene	2.70	1:1 ratio of **6**:**7**;[d] 0.70	**8**;[d] 0.70	60
2-Methylpropene	2.65	1: ratio of **9**:**10**; 2.20	**11**; 3.30	70
3,3-Dimethylbut-1-ene	2.35	1:2 ratio of **12**:**13**;[d] 0.35	**14**;[d] 0.15	22.5
(*Z*)-Cyclooctene	1.85	2:1 ratio of **15**:**16**;[d] 4.05	—[e]	90
Cyclopentene	1.83	—[c]	**17**;[d] 0.35	10
Styrene	1.60	—[c]	2:1 ratio of *exo* **18**:*endo* **18**; 0.85	40
2,3-Dimethylbut-2-ene	1.21	**19**; 1.15. (**20**; 0.80)	—[e]	42 (28)
Vinyl acetate	2.15	*endo* **21**; 0.10	**22**;[d] 0.30	28[f]
Methyl acrylate	3.50 (E_{red}, −2.4)	—	1:3 ratio of *endo* **23**:*exo* **23**; 0.47	26
Acrylonitrile	3.67 (E_{red}, −2.63)	—	**24**;[d] 0.10	5
Ethyl vinyl ether	1.44	**25**;[d] 0.20	**26**;[d] 0.20	8

[a] Benzene as solvent. [b] When no further quinone consumed: values not optimized or corrected for unchanged starting matrials. [c] No spirooxetane detected by ^{1}H NMR spectroscopy. [d] Stereochemistry with respect to the naphthoquinone residue not assigned. [e] No cyclobutane detected by ^{1}H NMR spectroscopy. [f] 12% of approximately equal amounts of the other possible regio- and stereo-isomers of the spirooxetane detected by ^{1}H NMR spectroscopy.



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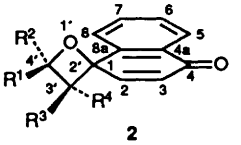

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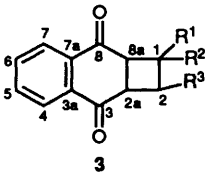

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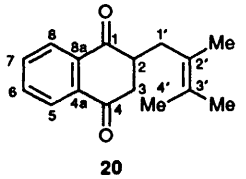
5 $R^1 = R^2 = R^3 = H$
8 $R^1 = [CH_2]_5Me$, $R^2 = R^3 = H$
11 $R^1 = R^2 = Me$, $R^3 = H$
14 $R^1 = CMe_3$, $R^2 = R^3 = H$
17 R^1–$R^3 = -[CH_2]_3-$, $R^2 = H$
18 $R^1 = Ph$, $R^2 = R^3 = H$
22 $R^1 = OCOMe$, $R^2 = R^3 = H$
23 $R^1 = CO_2Me$, $R^2 = R^3 = H$
24 $R^1 = CN$, $R^2 = R^3 = H$
26 $R^1 = OEt$, $R^2 = R^3 = H$
27 $R^1 = C_6H_4$-4-OMe, $R^2 = R^3 = H$
29 $R^1 = R^3 = Ph$, $R^2 = H$

6 $R^1 = [CH_2]_5Me$, $R^2 = R^3 = R^4 = H$
7 $R^1 = R^2 = R^4 = H$, $R^3 = [CH_2]_5Me$
9 $R^1 = R^2 = Me$, $R^3 = R^4 = H$
10 $R^1 = R^2 = H$, $R^3 = R^4 = Me$
12 $R^1 = CMe_3$, $R^2 = R^3 = R^4 = H$
13 $R^1 = R^2 = R^4$, $R^3 = CMe_3$
15 R^1–$R^3 = -[CH_2]_6-$, $R^2 = R^4 = H$
16 R^1–$R^4 = -[CH_2]_6-$, $R^2 = R^3 = H$
19 $R^1 = R^2 = R^3 = R^4 = Me$
21 $R^1 = OCOMe$, $R^2 = R^3 = R^4 = H$
25 $R^1 = OEt$, $R^2 = R^3 = R^4 = H$
28 $R^1 = R^3 = Ph$, $R^2 = R^4 = H$
30 $R^1 = R^3 = H$, $R^2 = OEt$, $R^4 = CN$
31 $R^1 = OEt$, $R^3 = CN$, $R^2 = R^4 = H$
32 $R^1 = OEt$, $R^4 = CN$, $R^2 = R^3 = H$



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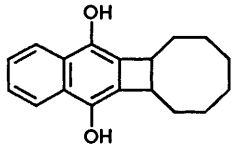

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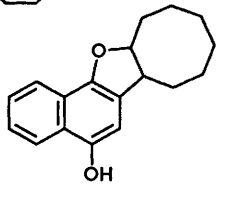

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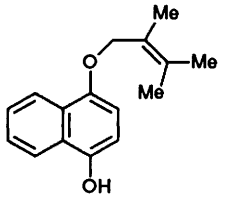

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pentene, styrene and ethyl vinyl ether as the addends that are particularly inconsistent with such a relationship and that are, therefore, anomalous.

The low efficiency of oxetane formation from cyclopentene has been previously accounted for in terms of facile hydrogen abstraction by the ^{3}n,π* state of the carbonyl compound from the allylic position to give the stable cyclopentenyl radical.[24] As noted above, the photoreduction of 1,4-naphthoquinone in the presence of this ethene has been earlier described,[20] but the adduct **17** was not reported. While the present cyclopentene anomaly may possibly be accounted for by a preferential hydrogen abstraction reaction, the case of styrene is less readily understood although not entirely unexpected since it is unique among ethenes in giving high proportions of the cyclobutane adduct with 1,4-benzoquinone.[2,3] This feature has yet to be explained but this unexpected addition to the ethene bond in 1,4-naphthoquinone and 1,4-benzoquinone may reflect an orientation of the addends directed by the phenyl group of styrene in an intermediate exciplex. We examined the photoreactions of 1,4-naphthoquinone with 4-methoxystyrene and with (*Z*)-stilbene in an attempt to gain an insight into the factors influencing the additions of phenylethenes to 1,4-quinones. In the former case the cyclobutane adduct **27** was again the sole product, but the addition was slower (relative rate 0.15) compared to the parent styrene and in the latter system the spirooxetane **28** and the cyclobutane **29** were formed with respective relative rates of 0.15 and 0.05. Although addition to the carbonyl is favoured for the stilbene, the formation of any cyclobutane from this system is still unexpected, particularly in view of recent findings that 2-chloro-1,4-naphthoquinone which has a propensity to form cyclobutanes in benzene solution with a variety of ethenes,[13,14] undergoes regio- and stereo-specific addition of (*E*)-stilbene to give the spirooxetane.[25] Similarly, cyclobutane formation from ethyl vinyl ether is surprising in view of the low oxidation potential of the ethene. Acrylonitrile yields the cyclobutane **24** exclusively, and so it may be expected that addition to the ethene bond of the quinone would be further promoted compared to ethyl vinyl ether, in the captodative ethene (*E*)-2-ethoxyacrylonitrile. In this case, however, the reaction occurs solely at the carbonyl group to give the spirooxetanes **30**, **31** and **32** in a respective ratio of 1:10:11 and a total chemical yield of 40% (relative rate 2.15). Such addition is difficult to rationalize in terms of electron donor ability of the ethene, but this regiospecificity and non-stereoselectivity in the spirooxetane formation is also observed in the reaction of this ethene with 1,4-benzoquinone.[3]

With the above exceptions, the data obtained in this study show that for the photoaddition of ethenes to 1,4-naphthoquinone, the formation of the spirooxetanes becomes more favoured with increase in the electron donor ability of the addend (*i.e.* with decrease in the free energy change, ΔG^0, for

electron transfer in the quinone–ethene system). Furthermore, those electron acceptor ethenes (dienophiles) which undergo addition to 1,4-naphthoquinone yield solely the cyclobutane adducts: this also includes the photodimerization of the quinone.[26] Thus the required direction over the site of reaction in these additions can be readily achieved but there are also several other points revealed by this study which require comment.

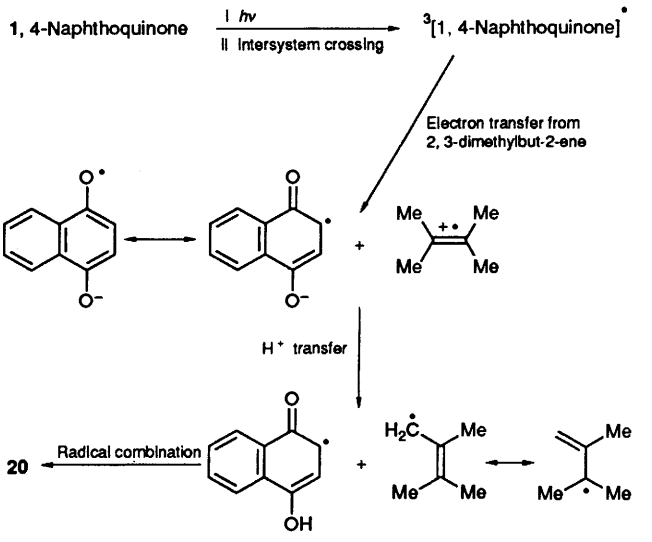
The efficiencies of adduct formation between 1,4-naphthoquinone and the ethenes are appreciably greater than those observed for the corresponding 1,4-benzoquinone systems. The regiochemistries of the spirooxetanes from the addition of the naphthoquinone to 2-methylpropene, 3,3-dimethylbut-1-ene, ethyl vinyl ether and (*E*)-2-ethoxyacrylonitrile are essentially the same as those reported for the benzoquinone additions and are again interpreted in terms of electron transfer to the quinone and control of the attack by the degree and direction of the polarization in the ethene bond.[3] In view of this, it is surprising that the formation of spirooxetanes from vinyl acetate and 1,4-naphthoquinone is regiochemically non-selective whereas the corresponding addition to 1,4-benzoquinone shows a four-fold preference for the 4′-substituted isomer.[3] There is no apparent steric influence to account for this difference but as we have noted previously, the vinyl acetate spirooxetanes in particular, have appreciable photolability which can markedly affect isomer ratios.[3]

Contrary to the present findings, irradiation of 1,4-naphthoquinone and (*Z*)-cyclooctene in carbon tetrachloride solution has been previously reported to yield the naphthocyclobutene **4** as the sole product.[20] We have shown that the discrepancy between the two sets of results does not arise from a solvent effect and that the mixture of spirooxetanes **15** and **16** is also the product in carbon tetrachloride solution with none of **4** being detected by ^{1}H NMR spectroscopy at 20% conversion of the quinone. However, we would not recommend this solvent in these systems, particularly for the extended periods of irradiation used in ref. 20 since this procedure leads to a variety of secondary products not observed in benzene solution. It is also possible that in the earlier work the spirooxetanes rearranged to the dihydrobenzofuran **33** and that this was mistakenly assigned structure **4**: certainly the ^{1}H NMR spectrum was recorded under conditions (*i.e.* CF_3CO_2H–$CDCl_3$ solution) which would promote this rearrangement.[1a]

The formation of **20** from 1,4-naphthoquinone and 2,3-dimethylbut-2-ene is unexpected and to our knowledge such acyclic addition at the ethene bond of a quinone is unprecedented, although we note that the 1,4-naphthoquinone–dioxane system is reported to give the substituted quinone on irradiation.[27] We rationalize the present process as shown in Scheme 1 in terms of photoinduced electron transfer from the donor ethene to the quinone followed by proton transfer from the radical cation to the radical anion and combination of the resulting radicals. It is, however, surprising that in such a pathway neither products from the semiquinone radical anion (*e.g.* the aryl ether **34**) nor those which involve the tertiary rather than the primary allylic radical site are observed.

To summarize, from the present study it is apparent that in 1,4-naphthoquinone–ethene systems there is, at least for alkenes, a useful relationship between the ease of electron transfer from the ethene to the quinone and the type of reaction observed (*i.e.* acyclic addition < spirooxetane formation < cyclobutane formation with increase in oxidation potential of the ethene and hence ΔG^0 values for electron transfer): a similar relationship is well-known for the photoreactions of ethenes with benzene and its derivatives.[28]

Finally we note that the 1,4-naphthoquinone–ethene cyclobutane adduct **5** has been previously synthesised using the reaction of the dianion of dimethyl cyclobutane-1,2-dicarboxylate with dimethyl phthalate at −75 °C for 13 h.[29] We feel that the present photochemical route offers a more straightforward and practical synthesis of **5** and its derivatives and thereby gives a ready access to the derived naphthocyclobutenes.



Scheme 1 Reaction of 1,4-naphthoquinone with 2,3-dimethylbut-2-ene

Experimental

The photochemical and analytical methods employed in this study are the same as those described in ref. 3. Irradiations were of 1,4-naphthoquinone (0.066 mol) (freshly recrystallized from benzene–charcoal) and the ethene (0.066 mol) in azeotropically dried AR grade benzene solution (150 cm^3). For the reactions with 2,3-dimethylbut-2-ene and 4-methoxystyrene, the solutions (150 cm^3) comprised 0.009 and 0.03 mol, respectively, in each reactant. 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 0.1 mol). Irradiations were terminated when it was assessed chromatographically and spectroscopically that no further quinone was being consumed.

The work-up procedure involved removal of the ethene and solvent by rotary evaporation under vacuum, and separation of the residual 1,4-naphthoquinone and the adducts by 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. Isomer ratios of the adducts were assessed from the ^{1}H NMR spectral data of the crude mixtures. Product yields were estimated in a similar way and do not take into account unchanged starting materials. The spectral features which allow the photoproducts to be assigned spirooxetane or cyclobutane structures are well documented (*e.g.* see references 1 and 2) and hence only those data of structural relevance are presented here. The ^{1}H NMR spectra were recorded of $CDCl_3$ solutions with tetramethylsilane as the internal reference at 220 MHz unless otherwise stated and the coupling constants are in Hz. The infrared spectra were obtained from liquid films unless otherwise stated.

1,4-*Naphthoquinone–Ethene*.—1,2-*Dihydrocyclobuta*[b]-*naphthalene*-3,8(2aH,8aH)-*dione* **5**. M.p. 100–101 °C; δ_H 8.18 (4-H, 7-H, dd, $J_{4,5}$, $J_{7,6}$ 6.6; $J_{4,6}$, $J_{7,5}$ 2.2), 7.80 (5-H, 6-H, dd), 3.7 (2a-H, 8a-H, m), 2.7 (*endo* 1-H, *endo* 2-H, m) and 2.35 (*exo* 1-H, *exo* 2-H, m); δ_C(22.5 MHz) 197.69 (C-3, C-8), 135.29 (C-3a, C-7a), 134.29 (C-4, C-7), 127.40 (C-5, C-6), 43.96 (C-2a, C-8a) and 26.14 (C-1, C-2); ν_{max}(KBr disc)/cm^{-1} 1680s and

1580m (Found: C, 77.4; H, 5.4. $C_{12}H_{10}O_2$ requires C, 77.39; H, 5.42%).

1,4-*Naphthoquinone–Oct*-1-*ene*.—4′- and 3′-*Hexylspiro*-[*naphthalene*-1,2′-*oxetan*]-4(1H)-*one* **6** *and* **7**. Compound **6** δ_H(60 MHz) 8.21–7.40 (4 aromatic H's, overlapping with 2-H, d, $J_{2,3}$ 11.0), 6.43 (3-H, d), 5.0–4.45 (4′-H br m), 3.80–3.05 (*endo* 3′-H and *exo* 3′-H, br m) and 1.65–0.80 (13 H, hexyl chain, m); ν_{max}/cm^{-1} 1680s and 960s (Found: M$^+$, 270.1610. Calc. for $C_{18}H_{22}O_2$: *M*, 270.1614). Compound **7**, δ_H(60 MHz), 8.30–7.40 (4 aromatic H, m; overlapping with 2-H, d, $J_{2,3}$ 11.5), 6.25 (3 H, d), 4.92 (*endo* 4′-H, dd, $J_{endo4',exo4'}$, 8.5, $J_{endo4',3'}$, 6.5), 4.50 (*exo* 4′-H, dd, $J_{exo4',3'}$, 6.5), 3.70–2.80 (3′-H, overlapping m's) and 1.85–0.70 (13 H, hexyl chain, m); ν_{max}/cm^{-1} 1680s and 960s (Found: M$^+$, 270.1613. Calc. for $C_{18}H_{22}O_2$: *M*, 270.1614).

1-*Hexyl*-1,2-*dihydrocyclobuta*[b]*naphthalene*-3,8(2aH,8aH)-*dione* **8**, δ_H(60 MHz) 8.15–8.05 (4-H, 7-H, dd, $J_{4,5}$ $J_{7,6}$ 17.5, $J_{4,6}$ $J_{7,5}$ 8.5), 7.80–7.65 (5-H, 6-H, dd), 3.60–3.20 (2a-H, 8a-H, m), 2.75–2.15 (*exo* and *endo* 2-H, *exo* and/or *endo* 1-H, m) and 1.40–0.70 (13 H, hexyl chain, m); ν_{max}/cm^{-1} 1680s and 1595m (Found: M$^+$, 270.1612. Calc. for $C_{18}H_{22}O_2$: *M*, 270.1614).

1,4-*Naphthoquinone*–2-*Methylpropene*.—Isomers **9** and **10** were not fully separated despite extensive chromatography. The ^{1}H NMR spectrum of the mixture of **9** and **10** was assigned by comparison with those of the two spirooxetanes from the addition of 2-methylpropene to 1,4-benzoquinone:[3] *m*/*z* 214 (M$^+$); δ_H 8.2–7.7 (4 aromatic H, dd, *J* 7 and 1) 7.75–7.40 (4 aromatic H, m), 7.55 (2-H, dd, $J_{2,3}$ 10), 7.40 (2-H, dd, $J_{2,3}$ 10), 6.33 (3-H, dd), 6.32 (3-H, dd), 4.56 (4′-Ha,b of isomer **10**, s), 1.72 (3′-Ha,b of isomer **9**, s), 1.25 (2 × Me of isomer **9**, s) and 0.75 (2 × Me of isomer **10**, s); ν_{max}/cm^{-1} 1678s and 953m.

1,1-*Dimethyl*-1,2-*dihydrocyclobuta*[b]*naphthalene*-3,8(2aH,-8aH)-*dione* **11**, δ_H 8.18–8.05 (4-H, 7-H, dd, $J_{4,5}$ $J_{7,6}$ 6 and $J_{4,6}$ $J_{7,5}$ 3.3), 7.8 (5-H, 6-H, dd), 3.55 (1-H, m), 3.38 (10-H, br d, $J_{2a,8a}$ 8), 2.5 (*endo* 2-H, overlapping dd, J_{gem} $J_{endo2,2a}$ 8), 2.25 (*exo* 2-H, dd, $J_{exo2,2a}$ 5), 1.38 (Me, s) and 0.95 (Me, s); ν_{max}/cm^{-1} 1683s and 1597m (Found: M$^+$, 214.0994. Calc. for $C_{14}H_{14}O_2$: *M*, 214.0990).

1,4-*Naphthoquinone*–2,3-*Dimethylbut*-1-*ene*. Isomers **12** and **13** were not fully separated despite extensive chromatography. Compound **12**, *m*/*z* 242 (M$^+$); δ_H 8.20–8.0 (2 aromatic H, m), 7.75–7.35 (2 aromatic H, m), 7.64 (2-H, d, $J_{2,3}$ 11.5), 6.38 (3-H, d), 4.64 (4′-H, m), 3.0 (*endo* 3′-H, overlapping dd, $J_{endo3',exo3'}$ 11, $J_{endo3',4'}$ 10), 2.52 (*exo* 3′-H, dd, $J_{exo3',4'}$ 6.5) and 1.1 (9 H, s, CMe_3); ν_{max}/cm^{-1} 1660s and 950s. Compound **13**, *m*/*z* 242 (M$^+$); δ_H 8.20–8.0 (2 aromatic H, m), 7.75–7.35 (2 aromatic H, m), 7.62 (2 H, d, $J_{2,3}$ 11.5), 6.40 (3-H, d), 4.86 (*endo* 4′-H, $J_{endo4',exo4'}$ 11, $J_{endo4',3'}$ 6.5), 4.68 (*exo* 4′-H, m), 3.34 (3′-H, overlapping dd) and 0.84 (9 H, s, CMe_3); ν_{max}/cm^{-1} 1660s and 950 m.

1-tert-*Butyl*-1,2-*dihydrocyclobuta*[b]*naphthalene*-3,8(2aH,8aH)-*dione* **14** m.p. 47.5–49 °C δ_H 8.2–8.0 (4-H, 7-H, m), 7.9–7.6 (5-H, 6-H, m), 3.6–3.2 (1-H, 10-H, overlapping m's), 2.6–2.2 (11-H, *endo* 12-H, *exo* 12-H, overlapping m's) and 0.85 (9 H, s, CMe_3); ν_{max}(KBr disc)/cm^{-1} 1680s and 1600m (Found: M$^+$, 242.1307. Calc. for $C_{18}H_{18}O_2$; *M*, 242.1302).

1,4-*Naphthoquinone*–(Z)-*Cyclooctene*.—*Spiro*(*naphthalene*-1,2′-*perhydrocyclooct*[b]*oxet*)-4(1H)-*one* **15**, δ_H 8.15–7.95 (2 aromatic H, m), 7.75–7.35 (2 aromatic H, m), 7.53 (2-H, d, $J_{2,3}$ 9.5), 6.43 (3-H, d), 4.83 (4′-H, 7 lines, *J* 14.3, 8.8 and 4.4), 3.1–2.85 (3′-H, m) and 2.30–0.85 (12 H on hexane bridge); ν_{max}/cm^{-1} 1665s and 956s (Found: M$^+$, 268.1461. Calc. for $C_{18}H_{20}O_2$: *M*, 268.1458).

Compound **16** not completely separated from **18** despite extensive chromatography: *m*/*z* 268 (M$^+$); δ_H 8.15–7.95 (2 aromatic H, m), 7.80–7.35 (2 aromatic H, m), 7.64 (2-H, d, $J_{2,3}$ 10.1), 6.26 (3-H, d), 5.1 (4′-H, 7 lines, *J* 14.5, 7.5 and 3.0), 3.08–2.88 (3′-H, m) and 2.30–0.82 (12 H on hexane bridge); ν_{max}/cm^{-1} 1665s and and 956s.

1,4-*Naphthoquinone–Cyclopentene*.—2,3,3a,9b-*Tetrahydro*-1H-*cyclopenta*[3,4]*cyclobutanaphthalene*-4,9(3bH,9bH)-*dione* **17** m.p. 106–107 °C δ_H 7.95–7.65 (5-H, 8-H, m) 7.63–7.15 (6-H, 7-H, m), 3.7 (3b-H, 9a-H, m), 2.92–2.5 (9b-H, 3a-H, m) and 1.98–1.04 (6 H of propane bridge, m); ν_{max}(KBr disc)/cm^{-1} 1680s and 1580m (Found: C, 79.63; H, 6.21. $C_{15}H_{14}O_2$ requires C, 79.62; H, 6.24%).

1,4-*Naphthoquinone–Styrene*.—An adduct between 1,4-naphthoquinone and styrene has been mentioned previously[20] but no structural information was presented. *exo*-1-Phenyl-1,2-dihydrocyclobuta[*b*]naphthalene-3,8(2aH, 8aH)-dione **18**, m.p. 78.5–79.5 °C δ_H 8.2–8.1 (4-H, 7-H, m), 7.85 (5-H, 6-H, dd, $J_{5,4}$ $J_{6,7}$ 4.8, $J_{5,7}$ $J_{6,4}$ 4.4), 7.35–7.25 (5 aromatic H, m), 3.92–3.75 (2a-H, 8a-H, m), 3.60–3.45 (1-H, m) and 2.93–2.65 (*endo* and *exo* 12-H, m); ν_{max}(KBr disc)/cm^{-1} 1679s and 1587m (Found: C, 82.40; H, 5.36. $C_{18}H_{14}O_2$ requires C, 82.42; H, 5.38%). *endo*-**18**, m.p. 161–162.5 °C; δ_H 8 1 (7-H, dd, $J_{7,6}$ 6.6, $J_{7,4}$ 2.2) 7.82 (4-H, dd, $J_{4,5}$ 6.6), 7.76–7 58 (5-H, 6-H, m), 7.5–7.3 (5 aromatic H, m), 4.23 (1-H, br overlapping ddd, $J_{1,8a}$, $J_{1,exo2}$ 9, $J_{1,endo2}$ 10.5), 4.00 (8a-H, overlapping dd with fine splittings $J_{8a,2a}$, $J_{8a,1}$ 9, $J_{8a,2}$ 2 and 0.8), 3.75 (2a-H, overlapping ddd, $J_{2a,exo2}$ 9, $J_{2a,endo2}$ 8) and 3.04–2.7 (*endo* 2-H, *exo* 2-H, m); ν_{max}(KBr disc)/cm^{-1} 1670s and 1584m (Found: C, 82.30; H, 5.40. $C_{18}H_{14}O_2$ requires C, 82.42; H, 5.38%).

1,4-*Naphthoquinone*–2,3-*Dimethylbut*-2-*ene*.—3′,3′,4′,4′-*Tetramethylspiro*[*naphthalene*-1,2′-*oxetan*]-4(1H)-*one* **19**, δ_H 8.0 (2 aromatic H, m), 7.75–7.20 (2 aromatic H, m; 2-H, d, $J_{2,3}$ 5), 6.3 (3-H, d), 1.62 (CH_3, s), 1.58 (CH_3, s), 1.15 (CH_3, s) and 0.8 (CH_3, s); ν_{max}/cm^{-1} 1665s and 980s (Found: M$^+$ 242.1272. Calc. for $C_{16}H_{18}O_2$: *M*, 242.1302).

2-(2,3-*Dimethylbut*-2-*enyl*)*naphthalene*-1,4(2H,3H)-*dione* **20** m.p. 99–100 °C, δ_H 8.05 (2 aromatic H, m), 7.75 (2 aromatic H, m), 3.26–3.10 (2 H, m), 3.08 (3-Ha, dd, J_{gem} 16.3, $J_{3,.2}$ 5.4), 2.80 (3-Hb, dd, $J_{3b.2}$ 8.4), 2.60 (1′-Ha, dd, J_{gem} 13.8, $J_{1'a.2}$ 5.6), 2.45 (1′-Hb, dd, $J_{1'b.2}$ 9.2), 1.78 (CH_3, s), 1.75 (CH_3, s) and 1.60 (CH_3, s); δ_H(22.5 MHz), 198.69 (C-1), 196.19 (C-4), 135.04 (C-4a), 134.28 (C-8a), 133.91 (C-5), 128.06 (C-8), 126.85 (C-7), 126.32 (C-6), 123.36 (C-2′ and C-3′), 46.51 (C-2), 42.26 (C-3), 35.51 (C-1′), 20.79 (C-4′), 20.56 (CH_3 on C-4′) and 18.21 CH_3 on C-2′); ν_{max}(KBr disc)/cm^{-1} 1689s and 1593m (Found: M$^+$, 242.1307. Calc. for $C_{16}H_{18}O_2$: *M*, 242.1302).

1,4-*Naphthoquinone–Vinyl Acetate*.—Compound **21**, m.p. 142–142 °C, *m*/*z* 244 (M$^+$), δ_H 8.2–7.45 (6-H, 7-H, 8-H, 9-H, d's and overlapping d's, *J* 4.5, 3 and 1.5), 7.52 (2-H, d, $J_{2,3}$ 9), 6.8 (4′-H, dd, $J_{4',3a(trans)}$ 6, $J_{4',3b',(cis)}$ 3.6), 6.4 (3-H, d), 3.3 (3′-Ha, dd, J_{gem} 12.8), 2.95 (3′-Hb, dd) and 2.24 (CH_3, s); ν_{max}(KBr disc)/cm^{-1} 1760s, 1660s and 940s (Found: C, 68.9; H, 4.95. $C_{14}H_{12}O_4$ requires C, 68.84; H, 4.95%). Mixture of three unresolved regio- and stereo-isomers of the spirooxetane **21**, *m*/*z* 244 (M$^+$), 8.18–7.32 (15 H, m), 6.9–6.68 (1 H, m), 6.54–6.23 (3 H, m), 4.1–2.38 (4 H, m), 2.24 (3 H, s), 2.1 (3 H, s) and 2.05 (3 H, s); ν_{max}/cm^{-1} 1760s, 1660s and 940s. Compound **22**, m.p. 134.5–135 °C, δ_H 8.2–8.1 (4-H, 7-H, m), 7.84–7.75 (5 H, 6-H, m), 5.5 (11-H, br dd, *J* 14 and 7), 4.02–3.90 (10-H, overlapping dd's, *J* 8 and 4), 3.47 (1-H, dd, *J* 14 and 7), 3.15–2.95 (12-Ha, m), 2.58–2.42 (12-Hb, m) and 1.98 (3 H, s); ν_{max}(KBr disc)/cm^{-1} 1720s, 1675s and 1595m (Found: M$^+$, 244.0737. Calc. for $C_{14}H_{12}O_4$: *M*, 244.0732).

1,4-*Naphthoquinone–Methyl Acrylate*.—1-*Methoxycarbonyl*-1,2-*dihydrocyclobuta*[b]*naphthalene*-3,8(2aH,8aH)-*dione* **23**, *endo*-isomer m.p. 98.5–100 °C, δ_H 8.24 (4-H, 7-H, dd, $J_{4,5}$,

$J_{7,6}$, 5.3, $J_{4,6}$, $J_{7,5}$ 3.9), 7.8 (5-H, 6-H, dd), 4.0–3.9 (1-H, overlapping d's), 3.78 (3 H, s), 3.75–3.60 (8a-H, overlapping d's), 3.43–3.30 (2a-H, br overlapping d's), 3.0–2.85 (2-Ha, overlapping d's) and 2.65–2.48 (2-Hb, overlapping d's); ν_{max}(KBr disc)/cm^{-1} 1717s and 1674s (Found: C, 68.7; H, 4.95. $C_{14}H_{12}O_4$ requires C, 68.84; H, 4.95%). *exo* **23**, m.p. 123–124 °C; *m/z* 244 (M^+); δ_H 8.14 (4-H, 7-H, m) 7.80 (5-H, 6-H, m), 3.95 (11-H, m), 3.8–3.65 (1-H, 10-H, m), 3.62 (3 H, s) and 2.9–2.7 (2-Ha, 2-Hb, m); ν_{max}(KBr disc)/cm^{-1} 1720s and 1676s (Found: C, 68.85; H, 5.0. $C_{14}H_{12}O_4$ requires C, 68.84; H, 4.95%).

1,4-*Naphthoquinone–Acrylonitrile*.—Compound **24** isolated as a yellow oil from flash chromatography, *m/z* 211 (M^+); δ_H(60 MHz) 8.2–7.6 (4 aromatic H overlapping m's), 4.0–3.4 (1-H, 2a-H, 8a-H, overlapping m's) and 3.4–2.4 (2-Ha, 2-Hb, m's); ν_{max}/cm^{-1} 2240m, 1670s and 1585m.

1,4-*Naphthoquinone–Ethyl Vinyl Ether*.—4′-*Ethoxyspiro*-[*naphthalene*-1,2′-*oxetan*]-4(1H)-*one* **25**, δ_H 8.05–7.40 (4 aromatic, H, m's), 7.4 (2-H, d, $J_{2,3}$ 11) 6.2 (3-H, d), 5.7 (4′-H, dd, $J_{4',3a'(trans)}$ 6.0, $J_{4',3b'(cis)}$ 3.6), 3.95–3.40 (Me, m), 3.04 (4′-Ha, dd, J_{gem} 13.7) 2.68 (4′-Hb, dd) and 1.3 (Me, t, *J* 6); ν_{max}/cm^{-1} 1680s and 953m (Found: M^+, 230.0946. Calc. for $C_{14}H_{14}O_3$: *M*, 230.0939).

1-*Ethoxy*-1,2-*dihydrocyclobuta*[b]*naphthalene*-3,8(2aH,8aH)-*dione* **26** m.p. 138–138.5 °C, δ_H 8.14 (4-H, 7-H, dd, $J_{4,5}$, $J_{7,6}$ 5.7, $J_{4,6}$ $J_{7,5}$ 3.3), 7.8 (5-H, 6-H, dd), 4.2 (1-H, 8 lines, $J_{1,8a}$ 8.4), 3.7 (8a-H, m), 3.64 (2a-H, m) and 2.68 (2-Ha, 2-Hb, overlapping dd, $J_{12,11}$ 6.6); ν_{max}(KBr disc)/cm^{-1} 1679s and 1593m (Found: M^+, 230.0943. Calc. for $C_{14}H_{14}O_3$: *M*, 230.0939).

1,4-*Naphthoquinone–4-Methoxystyrene*.—1-(p-*Methoxyphenyl*)-1,2-*dihydrocyclobuta*[b]*naphthalene*-3,8(2aH,8aH)-*dione* **27**, m.p. 136–136.5 °C, δ_H 8.25–8.15 (4-H, 7-H, m), 7.84 (5-H, 6-H, $J_{5,4}$ $J_{6,7}$ 5.4, $J_{5,7}$ $J_{6,4}$ 3.2), 7.28 (2 aromatic H, d, *J* 8), 6.9 (2 aromatic H, d), 3.87–3.75 (8a-H, 1-H, m), 3.82 (OMe, s), 3.60–3.50 (1-H, m) and 2.90–2.70 (2-Ha, 2-Hb, m); ν_{max}(KBr disc)/cm^{-1} 1670s, 1615m and 1520m (Found: M^+, 292.1089. Calc. for $C_{19}H_{16}O_3$: *M*, 292.1095).

1,4-*Naphthoquinone–(Z)-Stilbene*.—3′,4′-*Diphenylspiro*-[*naphthalene*-1,2′-*oxetan*]-4(1H)-*one* **28**, m.p. 138–139 °C, *m/z* 338 (M^+), δ_H 8.2–7.0 (14 aromatic H, m's), 7.37 (2-H, d, $J_{2',3}$ 10.2), 6.48 (4′-H, d, $J_{4',3'}$ 8), 6.28 (3-H, d) and 4.65 (3′-H, d); ν_{max}(KBr disc)/cm^{-1} 1667s and 967s (Found: C, 85.25; H, 5.4. $C_{24}H_{18}O_2$ requires C, 85.18; H, 5.36%).

1,2-*Diphenyl*-1,2-*dihydrocyclobuta*[b]*naphthalene*-3,8(2aH,-8aH)-*dione* **29**, m.p. 146–146.5 °C, *m/z* 338 (M^+); δ_H 8.2 (4-H, 7-H, dd, $J_{4,5}$ $J_{7,6}$ 5.8, $J_{4,6}$ $J_{7,5}$ 3.2), 7.81 (5-H, 6-H, dd), 7.2–7.0 (10 aromatic H, m), 4.31 (2a-H, 8a-H, br d, $J_{2a,2}$ $J_{8a,1}$ 5.2) and 4.1 (1-H, 2-H, br d); ν_{max}(KBr disc)/cm^{-1} 1678s, 1642s and 1595s (Found: C, 85.15; H, 5.3. $C_{24}H_{18}O_2$ requires C, 85.18; H, 5.36%).

1,4-*Naphthoquinone–(E)-3-Ethoxyacrylonitrile*.—3′-*Cyano*-4′-*ethoxyspiro*[*naphthalene*-1,2′-*oxetan*]-4(1H)-*one* **30**, δ_H 8.2–7.55 (4 aromatic H, m's), 7.36 (2-H, d, $J_{2,3}$ 10), 6.6 (3-H, d), 5.8 (4′-H, d, $J_{4',3'}$ 4.8), 3.93 (3′-H, d), 4.05–3.75 [CH_2, q's, (prochiral geminal anisochronicity)] and 1.38 (Me, t, *J* 6.6); ν_{max}/cm^{-1} 2217w, 1669s and 918s (Found: M^+, 255.0897. Calc. for $C_{15}H_{13}NO_3$: *M*, 255.0891).

Compound **31**, m.p. 102–103.5 °C, *m/z* 255 (M^+); δ_H 8.2–7.5 (4 aromatic H, m's), 7.34 (2 H, d, $J_{2,3}$ 10), 6.42 (3-H, d), 5.85 (4′-H, d, $J_{4',3'}$ 4.2), 3.98 (CH_2, 1 H equivalent, dq, *J* 6), 3.87 (3′-H, d), 3.78 (CH_2, 1 H equivalent, dq, *J* 6) and 1.36 (Me, t, *J* 6); ν_{max}(KBr disc)/cm^{-1} 2251m, 1672s and 960s (Found: C, 70.75; H, 5.1; N, 5.5. $C_{15}H_{13}NO_3$ requires C, 70.58; H, 5.13; N, 5.49%).

Compound **32**, m.p. 142.5–144 °C, *m/z* 255 (M^+); δ_H 8.12 (aromatic H, d, *J* 6.6), 7.84 (aromatic H, d, *J* 6.6), 7.73 (aromatic H, d, *J* 8.8), 7.62 (2-H, d, $J_{2,3}$ 8.5), 7.6 (aromatic H, d, *J* 8.8), 6.57 (3-H, d), 5.72 (4′-H, d, $J_{4',3'}$ 5.2), 4.25 (3′-H, d), 4.02 (CH_2, 1 H equivalent, dq, *J* 6.6), 3.80 (CH_2, 1 H equivalent, dq, *J* 6.6) and 1.42 (CH_3, t, *J* 6.6); ν_{max}(KBr disc)/cm^{-1} 2251m, 1672s and 960s (Found: C, 70.5; H, 5.1; N, 5.5. $C_{15}H_{13}NO_3$ requires C, 70.58; H, 5.13; N, 5.49%).

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