New formal [3+2] photoaddition of vinyl ethers to *o*-benzoquinones

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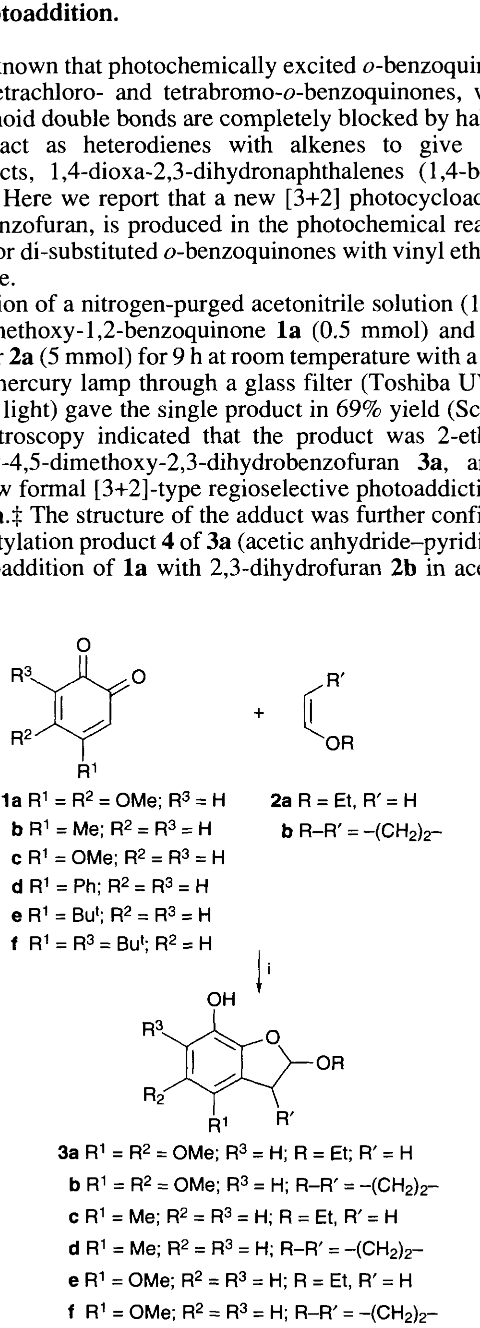
Irradiation of *o*-benzoquinones with vinyl ethers in acetonitrile gives 2-alkoxy-7-hydroxy-2,3-dihydrobenzofurans in 28–74% yields *via* regioselective [3+2] photoaddition.

It is well known that photochemically excited *o*-benzoquinones such as tetrachloro- and tetrabromo-*o*-benzoquinones, where the quinonoid double bonds are completely blocked by halogen atoms, react as heterodienes with alkenes to give [4+2] cycloadducts, 1,4-dioxa-2,3-dihydronaphthalenes (1,4-benzodioxins).[1] Here we report that a new [3+2] photocycloadduct, dihydrobenzofuran, is produced in the photochemical reaction of mono- or di-substituted *o*-benzoquinones with vinyl ethers in acetonitrile.

Irradiation of a nitrogen-purged acetonitrile solution (15 ml) of 4,5-dimethoxy-1,2-benzoquinone **1a** (0.5 mmol) and ethyl vinyl ether **2a** (5 mmol) for 9 h at room temperature with a high-pressure mercury lamp through a glass filter (Toshiba UV-39; >370 nm light) gave the single product in 69% yield (Scheme 1).† Spectroscopy indicated that the product was 2-ethoxy-7-hydroxy-4,5-dimethoxy-2,3-dihydrobenzofuran **3a**, arising from a new formal [3+2]-type regioselective photoaddiction of **1a** with **2a**.‡ The structure of the adduct was further confirmed by the acetylation product **4** of **3a** (acetic anhydride–pyridine).‡ The photoaddition of **1a** with 2,3-dihydrofuran **2b** in acetonitrile similarly afforded regioselective [3+2] adduct **3b** in 74% yield.



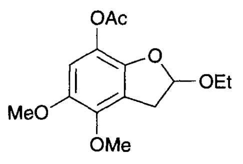
Scheme 1 *Reagents and conditions:* i, *hν*, acetonitrile

Mono-substituted *o*-benzoquinones, such as 4-methyl-**1b**, 4-methoxy-**1c** and 4-phenyl-1,2-benzoquinone **1d**, also reacted with **2a** under irradiation (> 450 nm light) in acetonitrile to give a single-regioselective [3+2] adduct, **3c**, **e** and **g** in 28, 68 and 44% yields, respectively. Similarly, the corresponding photocycloadducts, **3d**, **f** and **h** were obtained from the photoreaction of these quinones with 2,3-dihydrofuran **2b** in 66, 62 and 62% yields respectively. Another possible regioisomeric [3+2] adduct, **5**, was not formed in these photoreactions. Thus the site-selective addition of vinyl ethers occurred exclusively to the quinonoid double bond substituted by methyl, methoxy or phenyl, as judged by the coupling constants of benzene ring protons between R^{2}(H) and R^{3}(H) in **3c–h** (J 8.1–8.5 Hz).

However, 4-*tert*-butyl-1,2-benzoquinone **1e** afforded two inseparable regioisomeric [3+2] adducts, **3i** and **5i**, in 51% yield after irradiation (>450 nm light) of an acetonitrile solution containing ethyl vinyl ether. Some characteristic ^{1}H NMR signals are clearly assignable to **3i** and **5i**: For **3i** a singlet (9 H) at δ 1.32, a broad singlet (1 H, OH) at δ 4.79, a doublet (1 H, J_{ortho} 8.8 Hz) at δ 6.60, and a doublet (1 H, J_{ortho} 8.8 Hz) at δ 6.78; For **5i** a singlet (9 H) at δ 1.27, a broad singlet (1 H, OH) at δ 4.83, a doublet (1 H, J_{meta} 1.50 Hz) at δ 6.76 and a doublet (1 H, J_{meta} 1.50 Hz) at δ 6.81. The regioisomeric ratio was estimated to be **3i**/**5i** = 1.5 : 1 by ^{1}H NMR integration of the separated signals.

The photoaddition of 3,5-di-*tert*-butyl-1,2-benzoquinone **1f** with ethyl vinyl ether under the same conditions as the photoreaction of **1e** gave the [3+2] adduct **3j** and the decarbonylation product 2,4-di-*tert*-butylcyclopentadienone **6**,[2] in 44 and 36% yields respectively.

When benzene was employed as the solvent in the place of acetonitrile in the above photoreactions, another type of [4+2] photocycloadduct was produced. For example, with **1a** in benzene containing **2a**, the [3+2] adduct **3a** was obtained along with the byproduct **7a** in 45 and 13% yields respectively. The structure of byproduct **7a** was confirmed by spectroscopy‡ as being a [4+2] adduct, 2-ethoxy-6,7-dimethoxy-1,4-dioxa-2,3-dihydronaphthalene. In contrast, the reaction of **1e** with **2a** in benzene gave **7b** (35%) as a major product along with **3i** (27%). Thus, the distribution of the adducts depended on solvent polarity and on the *o*-benzoquinone substituents.



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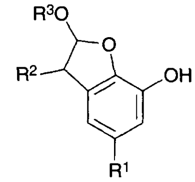
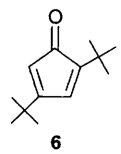


5a R^{1} = Bu^{t}; R^{2} = H; R^{3} = OEt



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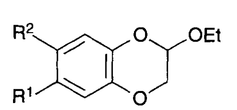

7a R^{1} = R^{2} = OMe
b R^{1} = H, R^{2} = Bu^{t}

The probable reaction paths for the formation of the regioselective [3+2] adducts are as follows. Ikegami and his coworkers[3] reported that the energy separation of the excited triplet states of *o*-quinones between $n\pi^*$ and $\pi\pi^*$ is small and the T_1 state has dominantly $\pi\pi^*$ character in polar solvents while it is $n\pi^*$ in nonpolar ones. Irradiation of **1** in acetonitrile probably generates the excited $\pi\pi^*$ triplet state, which reacts at the 3-position with the terminal alkenic carbon of vinyl ethers through a triplet exciplex to give a biradical intermediate or a more ionic intermediate formed by electron transfer. The regioselectivity found in the present addition is a clear indication of the involvement of a more stabilized biradical or ionic intermediate in the formation of 2-alkoxy-2,3-dihydrofurans **3**. The intermediate enolizes followed by hydrogen or proton transfer from the O-2 to the O-1 atom, and cyclizes intramolecularly to give **3**. When, on the other hand, benzene is used as a solvent, the T_1 state of **1** exhibits some $n\pi^*$ character and the initial addition also occurred at quinone-carbonyl group yielding the 1,4-dioxa-2,3-dihydronaphthalenes **7**.

It is interesting that in the case of 4-substituted *o*-benzoquinones such as **1b–d** the C-3–C-4 double bond selectively reacted with alkenes to give **3** but in 4-*tert*-butyl-*o*-benzoquinone the other quinonoid C-5–C-6 double bond also reacted with alkenes to give **5i** and **3i**.

Footnotes

† All products were isolated by TLC (silica gel) from the irradiated mixture. Yields were isolated and based on quinone used.

‡ Satisfactory spectroscopic and analytical data were obtained for all new compounds. *Selected physical and spectroscopic data* for **3a**: oil; ν_{max}/cm^{-1} 3580 (OH); *m*/*z* 240 (M^+, 100); ^{1}H NMR δ (270 MHz, $CDCl_3$) 1.24 (3 H, t, *J* 7.1 Hz, $OCH_2C\mathit{H}_3$), 3.13 (1 H, dd, *J* 2.3 and 16.7 Hz, 3-H), 3.39 (1 H, dd, *J* 6.4 and 16.7 Hz, 3-H), 3.62 (1 H, dq, *J* 7.1 and 9.5 Hz, $OC\mathit{H}HCH_3$), 3.76 (3 H, s, OCH_3), 3.80 (3 H, s, OCH_3), 3.91 (1 H, dq, *J* 7.1 and 9.5 Hz, $OCH\mathit{H}CH_3$), 4.95 (1 H, s, OH), 5.76 (1 H, dd, *J* 2.3 and 6.4 Hz, 2-H) and 6.41 (1 H, s, 6-H). For **4**: oil; ν_{max}/cm^{-1} 1765 (C=O); *m*/*z* 282 (M^+, 31), 240 [$(M - CH_2{=}C{=}O)^+$, 100)]; ^{1}H NMR δ 1.21 (3 H, t, *J* 7.1 Hz), 2.29 (3 H, s, $OCOCH_3$), 3.13 (1 H, dd, *J* 2.2 and 16.6 Hz), 3.39 (1 H, dd, *J* 6.4 and 16.6 Hz), 3.60 (1 H, dq, *J* 7.1 and 9.5 Hz), 3.77 (3 H, s), 3.86 (3 H, s), 3.88 (1 H, dq, *J* 7.1 and 9.5 Hz), 5.75 (1 H, dd, *J* 2.2 and 6.4 Hz) and 6.49 (1 H, s). For **7a**: oil; *m*/*z* 240 (M^+, 100); ^{1}H NMR δ 1.25 (3 H, t, *J* 7.1 Hz, $OCH_2C\mathit{H}_3$), 3.70 (1 H, dq, *J* 7.1 and 9.8 Hz, $OC\mathit{H}HCH_3$), 3.80 (3 H, s, OCH_3), 3.82 (3 H, s, OCH_3), 3.95 (1 H, dq, *J* 7.1 and 9.8 Hz, $OCH\mathit{H}CH_3$), 4.03 (1 H, dd, *J* 1.7 and 10.9 Hz, 3-H), 4.11 (1 H, dd, *J* 2.7 and 10.9 Hz, 3-H), 5.19 (1 H, dd, *J* 1.7 and 2.7 Hz, 2-H), 6.48 (1 H, s, 5- or 8-H) and 6.50 (1 H, s, 8- or 5-H).

References

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