Hetero Diels–Alder Reactions of 3,5-Di-*tert*-Butyl-*o*-Benzoquinone with Acyclic Dienes: Novel Synthesis of 1,4-Benzodioxines

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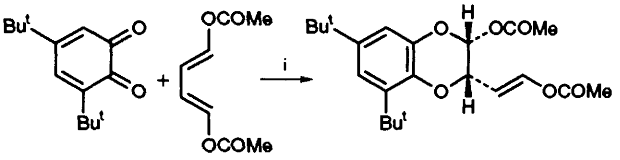
3,5-Di-*tert*-butyl-*o*-benzoquinone acts as a 1,4-dioxabutadiene in its reaction with acyclic dienes leading to 1,4-benzodioxines in very high yields.

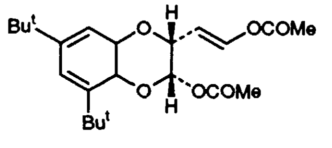
o-Benzoquinones have attracted considerable attention since they can function as carbodienes, heterodienes or dienophiles in cycloaddition reactions.[1] Although a number of Diels–Alder reactions in which the quinone reacts in one of these ways have been reported,[2–8] the reasons why they should do so are not clear, especially for the reaction of *o*-quinones with acyclic dienes. Buta-1,3-diene, 1-methoxybuta-1,3-diene and 2,3-dimethylbuta-1,3-diene react with various substituted *o*-benzoquinones,[9–12] in all cases serving as the 4 π component.

As a part of an investigation on the cycloaddition of *o*-quinones we studied the reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone **1** with acyclic dienes. The quinone acts as a heterodiene leading to the formation of 1,4-benzodioxines in high yields. Although *o*-quinones are known to give benzodioxines with heterocyclic dienes,[13–14] this pathway is unprecedented in their reactions with acyclic dienes[15]† (Scheme 1).



1 **2** **3**

Scheme 1 *Reagents and conditions*: i, toluene, sealed tube, 120 °C, 30 h, 90%



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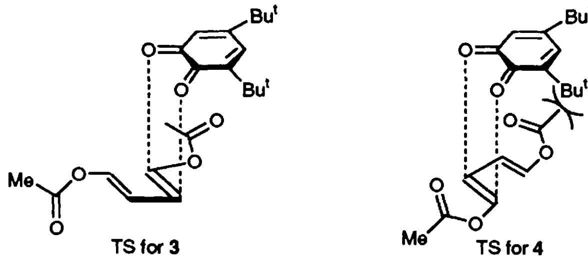

Fig. 1 Transition states (TS) for **3** and **4**

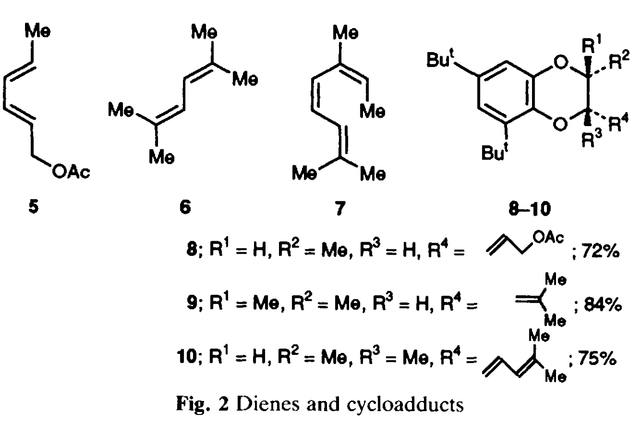

Fig. 2 Dienes and cycloadducts

The product was characterised by spectral analysis.‡ Although it is not possible to rule out the alternative structure **4** on the basis of spectral data, the transition state leading to **3** has no unfavourable steric interactions (Fig. 1).

Similar results were obtained with the acetate **5** and the dimethyl compound **6** leading to **8** and **9** in 72 and 84% yields respectively. Interestingly the triene, alloocimene **7**, also gave the benzodioxine **10** in 75% yield (Fig. 2).

Although the participation of the *o*-quinone as a 1,4-dioxabutadiene may be explained by steric hinderance of the carbodiene by the *tert*-butyl groups, the influence of electronic factors cannot be excluded. Preliminary MNDO and MMX level calculations are also in accordance with the observed results.[16] S. K. thanks DST and RRL for research fellowships. Thanks are due to Dr Jay B. Nair of Bristol–Myers Squibb, USA for the high resolution NMR spectra.

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Footnotes

† *o*-Chloroanil is known to undergo cycloaddition at the carbonyl group with 2,3-dimethylbutadiene at 0 °C. At higher temperature this spiro compound undergoes Claisen rearrangement to form the benzodioxin (ref. 7). In this case there is no evidence for the formation of the spiro compound.

‡ Typical experimental details are as follows. A solution of 3,5-di-*tert*-butyl-*o*-benzoquinone (0.2 g, 0.9078 mmol) and 1,4-diacetoxybuta-1,3-diene (0.155 g, 0.9078 mmol) in dry toluene (1 ml) was evacuated, sealed under nitrogen and heated at 120 °C for 30 h. The solvent was removed in *vacuo* and chromatographed on silica gel (5% ethyl acetate–light petroleum) to afford **3** (0.32 g, 90% as colourless crystals, mp 113–115 °C.

Spectral data for **3**: IR ν/cm^{-1} (CH_2Cl_2): 1770. UV–VIS λ_{max}/nm (MeOH): 212 (ε 18475), 280 (2200), ^1H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, *J* 12.53 Hz, 1H), 6.94 (d, *J* 2.35 Hz, 1H, Ar H), 6.84 (d, *J* 2.33 Hz, 1H, Ar H), 6.2 (d, *J* 3.29 Hz, 1H), 5.5 (dd, *J* 12.53 Hz, 1H), 4.6 (dd, *J* 3.3, 3.07 Hz, 1H), 2.123 (s, 3H), 2.12 (s, 3H), 1.36 (s, 9H), 1.26 (s, 9H). ^{13}C NMR (22.4 MHz, $CDCl_3$): δ 169.61, 167.5, 144.08, 140.5, 140.0, 138.12, 137.39, 117.03, 112.56, 107.94, 89.32, 70.58, 35.0, 34.46, 31.45, 29.76, 21.08, 20.58. MS: *m/z* 391 (M + 1), 390 (M^+, 100%).

References

1 K. T. Finley, in *The Chemistry of Quinonoid Compounds*, ed. S. Patai and Z. Rappoport, Wiley, New York, 1988, vol. II, pp. 537–717.
2 M. F. Ansell, A. F. Gosden, V. J. Leslie and R. A. Murray, *J. Chem. Soc. C*, 1971, 1401.
3 M. F. Ansell, A. J. Bignold, A. F. Gosden, V. J. Leslie and R. A. Murray, *J. Chem. Soc., C*, 1971, 1414.
4 W. M. Horspool, J. M. Tedder and Z. U. Din, *J. Chem. Soc. C*, 1969, 1692.
5 R. Al-Hamdani and S. Salih, *J. Chem. Soc., Chem. Commun.*, 1978, 397.
6 R. Al-Hamdani and S. Salih, *J. Iraqi Chem. Soc.*, 1981, **6**, 53, 61.

7 M. F. Ansell and V. J. Leslie, *J. Chem. Soc. C*, 1971, 1423.

8 W. Friedrichsen, W. D. Schroer and R. Smidt, *Liebigs Ann. Chem.*, 1976, 793.

9 S. Mazza, S. Danishefsky and P. McCurry, *J. Org. Chem.*, 1974, **39**, 3610.

10 S. Danishefsky, P. F. Schuda, S. Mazza and S. Kato, *J. Org. Chem.*, 1976, **41**, 3468.

11 S. Danishefsky, P. F. Schuda and W. Carruthers, *J. Org. Chem.*, 1977 **42**, 2179.

12 D. D. Weller and E. P. Stirchack, *J. Org. Chem.*, 1983, **48**, 4873.

13 N. Latif, N. Mishriky and N. S. Girgis, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1052.

14 D. L. Boger and S. N. Weinreb, in *Hetero Diels–Alder Methodology in Organic Synthesis*, Academic Press, Inc., 1987, pp. 167–213.

15 There is a report on the reaction of enamines with 1,2-benzoquinones giving rise to 1,4-benzodioxine (Ref. Y. Omote, A. Tomatake, C. Kashima, *J. Chem. Soc., Chem. Commun.*, 1988, 151). The authors thank a referee for bringing it to their attention.

16 E. D. Jemmis, V. Nair, S. Kumar and M. V. B. Reddy, unpublished results.