

## The Importance for Cage Compound Formation of the Oxidation Potential of the Enedionic System in Benzoquinone–Cyclopentadiene Adducts

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Some substituted benzoquinone–cyclopentadiene Diels–Alder adducts do not undergo photocyclization to give cage compounds. For the adducts a parallel increase of relative quantum yield and half-peak oxidation potential, measured by cyclic voltammetry, is observed. A large difference between the energy levels of the interacting orbitals is assumed to be responsible for this lack of reactivity.

Previous reports from this laboratory<sup>1</sup> showed that the 2,3-dimethylthiobenzoquinone–cyclopentadiene adduct, although of *endo* configuration, failed to undergo cage compound formation on irradiation, in contrast to the corresponding unsubstituted adduct. Steric hindrance to photocyclization or an increase of electronic density in the enedione system have been suggested as possible reasons for this lack of reactivity.

It therefore became of interest to investigate the reactivity/substituent effect relationship in the photocyclization. A study of the photocyclization of a series of monosubstituted benzoquinone–cyclopentadiene adducts by oxygen, sulfur and nitrogen-containing groups, synthesized in this laboratory,<sup>2,3</sup> was therefore undertaken.

### Results and Discussion

The Diels–Alder adducts of *endo* configuration (**1a–i**) were irradiated under experimental conditions similar to those reported for the unsubstituted benzoquinone–cyclopentadiene adducts,<sup>4</sup> to give the corresponding cage compounds **2a–i** (Fig. 1). The yields of the new isolated products (**2b, c, f, g**) and their physical data are shown in Table 1. Microanalytical results and IR (Table 2), <sup>1</sup>H NMR (Table 3) and <sup>13</sup>C NMR data (Table 4) are also included.

Results in Table 1 show that, surprisingly, the adducts **2h** and **2i** did not photocyclize. Thus the failure in photocyclization is not limited to the 2,3-dimethylthiobenzoquinone–cyclopentadiene adduct, but may also occur with some monosubstituted derivatives. It thus became clear that the *endo* configuration, though essential, is not a unique condition for photocyclization.

Table 5 shows the quantum yields ( $\phi_{rel}$ ) for photocyclization of the monosubstituted adducts **1a–i**, relative to that of the unsubstituted adduct **1j** for which  $\phi$  was assumed to be 1.00.<sup>5</sup> The value for the 2,3-dimethylthio-substituted adduct **1k** is also included. These data show that not only do the adducts **1h, i, k** not photocyclize but also that adduct **1g** ( $\phi_{rel} = 0.06$ ) photocyclizes slowly.

In seeking a factor responsible for the occurrence of photocyclization we conducted cyclic voltammetry measurements, since the oxidation and reduction half-peak potentials are supposed to give valuable data, for, respectively, the HOMO and LUMO energies of the enedionic double bond.<sup>6</sup> Table 5 shows the  $E_{p/2}^{ox}$  and  $E_{p/2}^{red}$  values for the adducts **1a–k**. The  $\Delta E$  values are the difference between  $E_{p/2}^{ox}$  of the unsubstituted adduct, considered as that of the olefinic double bond, and the substituted adducts. The  $\Delta E$  values<sup>7</sup> are the difference between the corresponding energy levels (Fig. 2).

Although  $\phi_{rel}$  does not correlate at all with the  $E_{p/2}^{red}$  values, a parallel increase of  $\phi_{rel}$  and  $E_{p/2}^{ox}$  values may be observed.

The comparison of  $\Delta E$  with the corresponding  $\phi_{rel}$  values

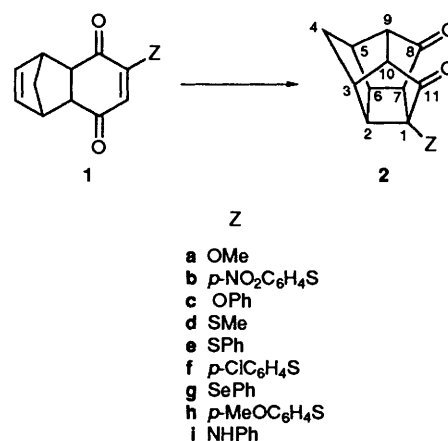


Fig. 1 The nature of compounds 1 and 2

Table 1 Physical data and yields of the new cage compounds

Compound	M.p./°C	Yields <sup>a</sup> (%)
<b>2b</b>	132–134	48
<b>2c</b>	136–138	85
<b>2f</b>	oily	63
<b>2g</b>	106–108	60
<b>2h</b>	—	—
<b>2i</b>	—	—

<sup>a</sup> Isolated pure products.

Table 2 Microanalytical and IR data for new cage compounds

Compound	Formula ( $M_r$ )	Analytical data Found (Required)	$\nu_{C=O}(KBr)/cm^{-1}$
<b>2b</b>	C <sub>17</sub> H <sub>13</sub> NO <sub>4</sub> S (327.354)	C, 62.4; H, 4.45; N, 3.9 (C, 62.37; H, 4.00; N, 4.28%)	1755, 1741
<b>2c</b>	C <sub>17</sub> H <sub>14</sub> O <sub>3</sub> (266.296)	C, 76.6; H, 5.6 (C, 76.7; H, 5.30%)	1757, 1736
<b>2f</b>	C <sub>17</sub> H <sub>13</sub> ClO <sub>2</sub> S (316.798)	C, 64.8; H, 4.4; Cl, 11.3 (C, 64.45; H, 4.14; Cl, 11.19%)	1758, 1741
<b>2g</b>	C <sub>17</sub> H <sub>14</sub> SeO <sub>2</sub> (329.256)	C, 62.2; H, 4.60 (C, 62.01; H, 4.29%)	1755, 1745

indicates clearly that above 0.67 eV no photocyclization takes place. The viability of cage compound formation may therefore be predicted from cyclic voltammetry data.

**Table 3**  $^1\text{H}$  NMR data of new cage compounds (200 MHz,  $\text{CDCl}_3$  solutions, standard  $\text{Me}_4\text{Si}$ )<sup>a</sup>

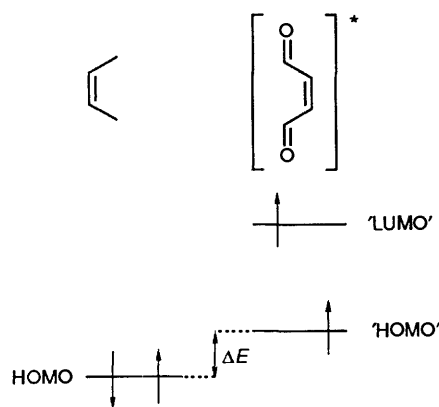
Compound	4-H/4-H'	9-H/10-H	3-H/5-H/7-H	2-H	6-H	Aromatic protons
<b>2b</b>	1.99 (1 H, d, $J = 11.7$ ) 2.14 (1 H, d, $J = 11.7$ )		3.00 (6 H, br m)		3.41 (1 H, m)	7.25 (2 H, d, $J = 8.9$ ) 8.12 (2 H, d, $J = 8.9$ )
<b>2c</b>	2.00 (1 H, d, $J = 11.5$ ) 2.08 (1 H, d, $J = 11.5$ )	2.80 (2 H, br s)	3.04 (3 H, m)	3.31 (2 H, m)		6.70 (2 H, d, $J = 7.8$ ) 6.97 (1 H, t, $J' = 7.4$ ) 7.25 (2 H, dd, $J = 7.8$ , $J' = 7.4$ )
<b>2f</b>	1.90 (1 H, d, $J = 11.4$ ) 2.05 (1 H, d, $J = 11.4$ )		2.87 (6 H, br m)		3.22 (1 H, m)	7.26 (2 H, d, $J = 8.5$ ) 7.31 (2 H, d, $J = 8.5$ )
<b>2g</b>	1.86 (1 H, d, $J = 11.5$ ) 2.03 (1 H, d, $J = 11.5$ )	2.75 (2 H, m)	2.88 (3 H, m)	3.09 (2 H, m)		7.30 (3 H, m) 7.58 (2 H, d, $J = 9.3$ )

<sup>a</sup>  $\delta$  Values in ppm, coupling constant values  $J/\text{Hz}$ .**Table 4**  $^{13}\text{C}$  NMR<sup>a</sup> of new cage compounds (20 MHz,  $\text{CDCl}_3$ , standard  $\text{CDCl}_3$ ,  $\delta = 77.7$  ppm)

Compound	C-8/ C-11	C-1	C-9	C-10	C-7	C-5	C-3	C-2	C-4	C-6	Aromatic carbons
<b>2b</b>	209.2 206.1	55.2	54.7	50.6	53.8	45.6	44.4	43.5	40.5	37.8	128.8, 142.8 124.1, 146.0
<b>2c</b>	209.4 208.3	80.5	54.6	50.9	49.2	43.9	43.6	44.4	41.6	36.9	154.5, 121.9 129.8, 129.1
<b>2f</b>	209.4 207.3	56.7	53.0	50.3	48.1	45.8	44.1	43.4	40.5	37.1	130.0, 129.2 129.1, 134.0
<b>2g</b>	209.9 208.2	52.5	54.7	51.5	53.6	47.2	44.1	44.0	40.5	37.4	126.4, 128.6 129.1, 135.8

<sup>a</sup> Assignments based on results of 2D HETCOR (Bruker AC-200) and DEPT experiments.  $\delta$  Values in ppm.**Table 5** Relative quantum yields, oxidation and reduction half-peak potentials of the substituted adducts and energy level differences between the interacting double bonds

Compound	$\phi_{\text{rel}}^c$	$E_{\text{P}/2}^{\text{oxd}}/\text{V}$	$E_{\text{P}/2}^{\text{red d}}/\text{V}$	$\Delta E^e/\text{eV}$
<b>1a</b>	0.71	1.97	-1.60	0.06
<b>1b</b>	0.51	1.71	-1.23	0.32
<b>1c</b>	0.39	1.61	-1.49	0.42
<b>1d</b>	0.45	1.60	-1.51	0.43
<b>1e</b>	0.44	1.55	-1.34	0.48
<b>1f</b>	0.35	1.54	-1.36	0.49
<b>1g</b>	0.06	1.36	-1.32	0.67
<b>1h</b>	0.00	1.25	-1.48	0.78
<b>1i</b>	0.00	1.07	-1.60	0.96
<b>1j</b> <sup>a</sup>	1.00	2.03	-1.43	0.00
<b>1k</b> <sup>b</sup>	0.00	1.13	-1.45	0.90

<sup>a</sup> Unsubstituted adduct. <sup>b</sup> 2,3-Dimethylthiobenzoquinone-cyclopentadiene adduct. <sup>c</sup> Quantum yields, relative to the unsubstituted adduct **1j**. <sup>d</sup> In V vs.  $\text{Ag}/\text{Ag}^+$ . <sup>e</sup>  $E_{\text{P}/2}^{\text{oxd}}$  of **1j** -  $E_{\text{P}/2}^{\text{oxd}}$  of **1a-i**, **1k**.**Fig. 2**  $\Delta E$  in the excited Diels-Alder adducts **1a-i**, **1k**;  $\Delta E = 0$  for **1j**

It may be concluded that the factor which determines the photocyclization is the difference between the energy levels of the two interacting orbitals. The results also suggest that the [2 + 2] photocyclization of the Diels-Alder adducts occurs through the HOMO/HOMO' interaction,<sup>8</sup> most probably initiated by a photochemical electron transfer (PET).<sup>9</sup>

It seems reasonable to assume that the increase in  $\Delta E$  values for adducts **1h**, **i**, **k**, responsible for the lack of reactivity, is most probably due to the predominance of the mesomeric over the inductive effect of the substituents. This is confirmed by inspection of the literature  $\sigma^+$  values,<sup>10</sup> which shows that an increase in the  $E_{\text{P}/2}^{\text{oxd}}$  values corresponds to a decrease in the  $\sigma^+$  absolute values. This trend does not hold for the methoxy derivative **1a**, most probably due to the non-coplanarity of the methoxy group with the enedionic system,<sup>11</sup> leading to a decrease of the mesomeric and predominance of the inductive effect.

## Experimental

**Photochemical and Analytical Methods.**—A solution in acetonitrile of compounds **1a-i**<sup>1-3</sup> ( $4.0 \times 10^{-2}$  mol  $\text{dm}^{-3}$ ) was irradiated in a  $15 \times 3.5$  cm Pyrex tube, using a Hanovia Hg lamp (679A36, 450 W), until total conversion of the starting material (2–21 h) had occurred. The reactions were monitored by GC using a Hewlett-Packard 5790A instrument fitted with a flame ionization detector and a HP-1 ( $5 \text{ m} \times 0.53 \text{ mm} \times 2.65 \mu\text{m}$  film thickness) capillary column, or by  $^1\text{H}$  NMR spectroscopy, using a Varian T-60 spectrometer. Purification of the photoproducts **2a-g** was achieved by filtration through a  $3.0 \times 0.5$  cm silica gel column (Merck 230–400 mesh), using benzene as eluent ( $1.3 \times 10^{-3}$   $\text{dm}^3 \text{ s}^{-1}$ ). The benzene solution was rapidly dried over  $\text{P}_2\text{O}_5$ , filtered and the solvent removed under reduced pressure. The resulting yellow oils were dissolved in an equal volume of chloroform yielding, after 1–12 days, microcrystalline solids (except for compound **1f** which did not crystallize), fully characterized as the cage compounds **2a-g**. Physical data, yields and spectroscopic data for the new

compounds **2b**, **c**, **f**, **g** are reported in Tables 1–4. M.p.s are uncorrected and were determined using a Dinamic Optics AHT Koffler apparatus. Microanalyses were performed on a Perkin-Elmer 240B elemental analyser.  $^1\text{H}$  NMR spectra were recorded on a Bruker AC-200 spectrometer in 10% (v/v) deuteriochloroform solutions, using  $\text{Me}_4\text{Si}$  as internal standard.  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AC-80 spectrometer in 50% (v/v) deuteriochloroform solutions. IR spectra were obtained with Perkin-Elmer 1750FT or 180 instruments. Relative quantum yields (Table 5) were determined upon irradiation of  $[\text{}^2\text{H}_6]$ benzene solutions of compounds **1a–g**, **j** ( $1.6 \times 10^{-1} \text{ mol dm}^{-3}$ ) in 5 mm NMR Pyrex tubes, using a Hanovia Hg lamp (679A36, 450 W). The photoreaction was monitored by determining the integral intensities of the olefinic proton signals at six different time intervals. The zero-order constants,  $k_{\text{obs}}$ , were evaluated from linear plots of integration values *vs.* time by least-squares methods. The  $\varphi_{\text{rel}}$  values are the quotient of such constants, for each compound, over that for compound **1j** ( $\varphi_{\text{rel}} = 1.00$ ,  $k_{\text{obs}} = 3.75 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ ).

*Cyclic Voltammetry.*—Measurements were performed at ambient temperature at a platinum bead electrode with a platinum counter-electrode and  $\text{Ag}/\text{Ag}^+$  reference electrode in purified acetonitrile,<sup>12</sup> [dried over molecular sieves (4 Å) containing tetraethylammonium perchlorate (TEAP)<sup>13</sup> ( $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ )] using a 'home-built' potentiostat/sweep unit combined with a Houston Instrument RE0074 X–Y recorder. The  $\text{Ag}/\text{Ag}^+$  reference electrode comprised a silver wire in the acetonitrile/TEAP solution containing silver nitrate ( $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ). The substrate concentration was *ca.*  $10^{-3} \text{ mol dm}^{-3}$ .  $E_{\text{p}/2}^{\text{ox}}$  and  $E_{\text{p}/2}^{\text{red}}$  were determined from voltammograms recorded at  $200 \text{ mV s}^{-1}$  over the range 0–2.4 V (oxidation) and 0––2.2 V (reduction) by measuring the potentials at half-

peak current of the first oxidation and reduction peak, respectively.

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### References

- 1 B. Wladislaw, L. Marzorati and C. Di Vitta, *Phosphorus and Sulfur*, 1985, **25**, 147.
- 2 B. Wladislaw, L. Marzorati, C. Di Vitta and I. P. de Arruda Campos, *Phosphorus, Sulfur and Silicon*, 1990, **47**, 153.
- 3 B. Wladislaw, L. Marzorati and I. P. de Arruda Campos, *An. Acad. Brasil. Cienc.*, in the press.
- 4 R. C. Cookson, R. R. Hill and J. Hudec, *J. Chem. Soc.*, 1964, 3043.
- 5 S. Lazare, P. de Mayo and W. R. Ware, *Photochem. Photobiol.*, 1981, **34**, 187.
- 6 M. A. Fox, K. Campbell, G. Maier and L. H. Franz, *J. Org. Chem.*, 1983, **48**, 1762.
- 7 I. R. Gould, D. Ege, J. E. Moser and S. Farid, *J. Am. Chem. Soc.*, 1990, **112**, 4290.
- 8 I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Wiley, Bristol, 1985, p. 208.
- 9 J. Mattay, *Synthesis*, 1989, 233.
- 10 C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
- 11 R. C. Prince, P. L. Dutton and J. M. Bruce, *FEBS Lett.*, 1983, **160**, 155.
- 12 J. F. O'Donnell, J. T. Ayres and C. K. Mann, *Anal. Chem.*, 1965, **37**, 1161.
- 13 H. O. House, E. Feny and N. P. Peet, *J. Org. Chem.*, 1971, **36**, 2371.

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