Photoreactions of Duroquinone with Cyclic Polyenes. Entry into New Cage Compounds

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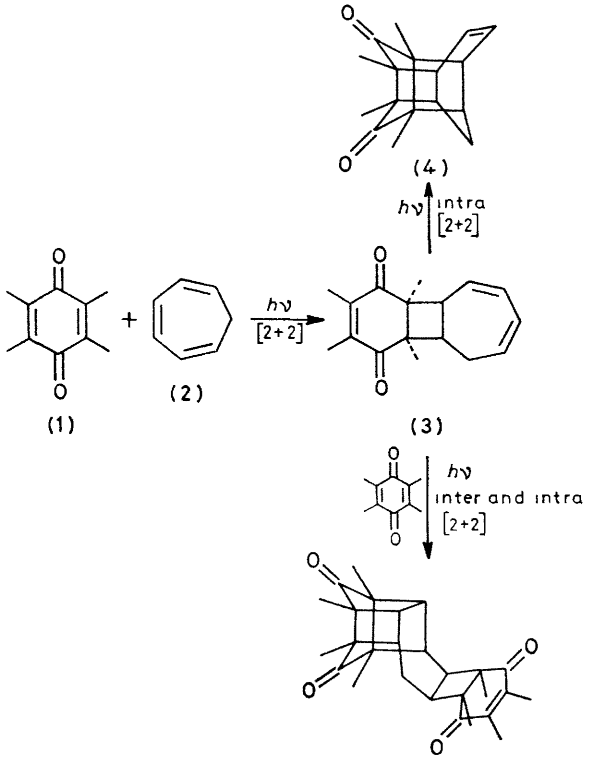
Summary. The photo-induced reactions of duroquinone with cycloheptatriene and cyclo-octatetraene (through its 76 °C melting dimer) afford new cage compounds.

p-QUINONES with unsaturated C–C bonds afford photocycloadducts, and such photocyclizations are one of the most convenient methods for syntheses of cage compounds. The photodimerization of certain *p*-quinones occurs either in solution or in the solid phase,[1] and irradiations of duroquinone–diene systems[2] and Diels–Alder adducts of quinone-1,3-dienes[3] also afford several types of cage products. The photochemical additions of *p*-benzoquinone to cycloheptatriene and cyclo-octatetraene are known to yield [2 + 6]- and [2 + 4]-carbocycloadducts, respectively.[4,5] We report successful syntheses of new cage compounds by the reactions of duroquinone with cyclic polyenes.

On irradiation of a benzene solution of duroquinone (**1**) and cycloheptatriene (**2**) (air or N_2, Pyrex filter) with a 150 W high-pressure mercury lamp, two products, a 1:1 adduct (**4**) (colourless needles, m.p. 155—158 °C, $\nu_{C=O}$ 1690 cm^{-1}, $C_{17}H_{20}O_2$, satisfactory C and H analyses, M^+ 256) and a 2:1 adduct (**5**) (colourless cubes, m.p. 288–291 °C, $\nu_{C=O}$ 1735, 1690, and 1660 cm^{-1}, $C_{27}H_{32}O_4$, satisfactory C and H analyses, M^+ 420) could be isolated by silica gel chromatography.

After irradiation of (**1**) and (**2**) for a short time, the intermediate [2 + 2]cycloadduct (**3**) (unstable pale yellow oil; $\nu_{C=O}$ 1660 cm^{-1}) could be isolated. The formation of (**4**) could be detected by t.l.c. and ^{1}H n.m.r. measurements after irradiation of the isolated cycloadduct (**3**).

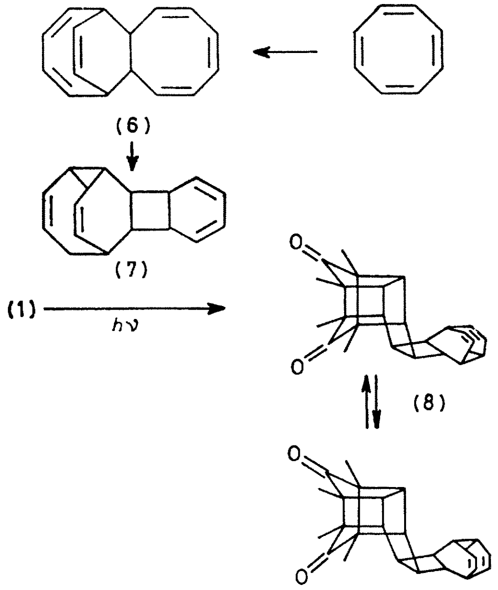


SCHEME 1

The product ratio (**4**) : (**5**) depended on the initial molar ratio of (**1**) : (**2**), but did not vary with irradiation time. For the synthesis of the cage compound (**4**), use of large molar excess of (**2**) was needed because of the competitive intra- and inter-molecular photocyclizations of (**3**).

A solution of duroquinone (**1**) and cyclo-octatetraene (COT) in benzene was irradiated under similar conditions for 72 h. Chromatography on a short silica gel column yielded a single product (**8**); m.p. 193—195 °C; $\nu_{C=O}$ 1730 and 1695 cm^{-1}, in low yield (3—5%) Elemental analysis and mass spectroscopy, *m/e* 372 (M^+), indicate that the material is a 1 : 2 adduct between (**1**) and COT. A quite low conversion suggested that the photoreaction of duroquinone with COT was different from that of *p*-benzoquinone with COT[5] or (**1**) with cycloheptatriene.

Photochemical isomerizations of COT[6] could be ruled out because of the low triplet level of duroquinone.[7] COT is known to be thermally dimerized to afford the tricyclohexadecahexaene (**6**) and/or the pentacyclohexadecatetraene (**7**),[8] and COT dimers react readily with some unsaturated compounds.[9] Indeed duroquinone reacted photochemically with the pentacyclohexadecatetraene (**7**) to give (**8**) in 63% yield, but not with (**6**).



SCHEME 2

Spectral data suggest that (**8**) has carbonyl groups in a five-membered ring and a greater than six-membered ring, and indicate the presence of a cage structure. Cope rearrangements of dihydrobullvalenes are not very rapid.[8,10] Measurements of the ^{1}H n.m.r. spectra of this adduct (**8**) at low temperatures confirmed the caged dihydrobullvalene structure (Figure).

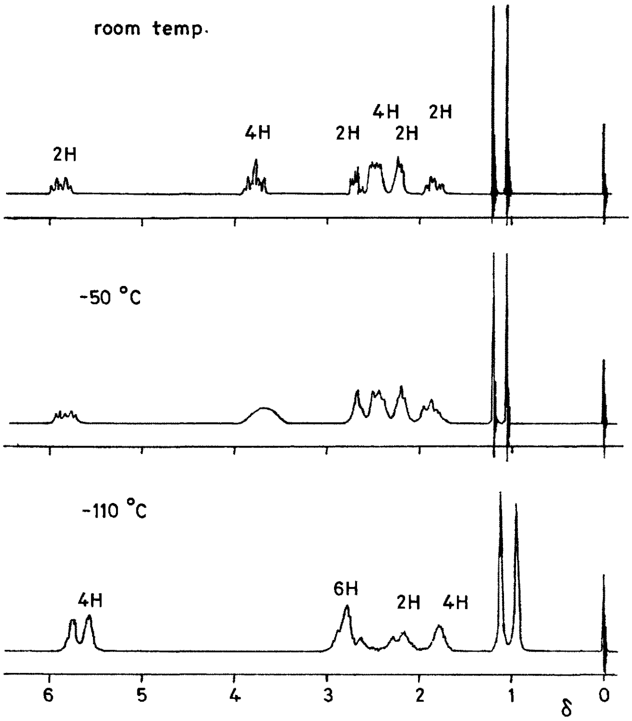


FIGURE ^{1}H N.m.r. spectra of the adduct (**8**).

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