REACTION OF QUADRICYCLANE WITH ELECTRON DEFICIENT *p*-BENZOQUINONES

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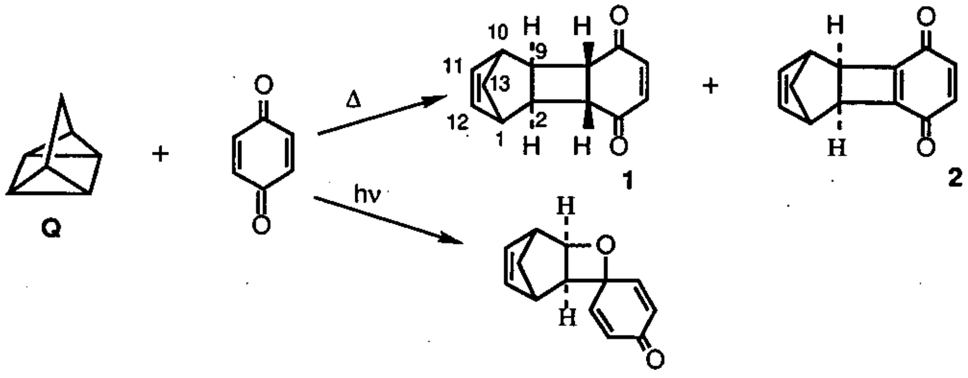
Abstract------Quadricyclane reacted thermally in a $[\pi 2+\sigma 2+\sigma 2]$ manner with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and chloranil to give cyclobutanes and a spiro oxetane, respectively.

Quadricyclane (**Q**) has long been recognized as being unique in cycloaddition because of its ability to cycloadd in a $[\pi 2+\sigma 2+\sigma 2]$ manner. Since this process was first interpreted by Tabushi in 1972,[1] analogous examples of cycloadditions of C=C, C=O, C=N, and N=N groups to **Q** have been extensively investigated.[2] It is known that the ene moiety of *p*-benzoquinones cycloadds toward **Q** in this manner. Thus, *p*-benzoquinone itself was reported to thermally react with **Q** to give exclusively the exo-trans adducts (**1**) and (**2**) in 75 and 6% yield, respectively.[3] To our knowledge, however, the reactions of **Q** with the electron deficient quinones, which are utilized in a wide variety of synthetic processes as oxidising agents, such as 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and chloranil, have not been described in the literature.[4]

DDQ reacted smoothly with **Q** in benzene at room temperature to yield the exo-trans (**3**, 92%)[5] and exo-cis (**4**, 4%) products.[5] The structure of **3** was easily determined to have the exo-trans stereochemistry by comparison of its ^{1}H-nmr spectrum with that of **1**.[3] In addition, the cyano groups deshield strongly one of the methylene protons (13-H, δ_H 2.48). In sharp contrast, the signals of one of methylene protons (13-H) of **4** are substantially shifted to upfield (δ_H 0.64). And this can be attributed to the shielding effect of the approximate ene dione moiety. Furthermore, the signals of 2-H and 9-H are considerably shifted to low field (δ_H 3.25) due to the magnetic anisotropy of the adjecent cyano groups. Thus the exo-cis configuration of **4**, the formation of which does not obey the secondary orbital interaction in the endo-transition state,[4,6] was definitely confirmed.

Chrolanil was reacted with **Q** in benzene at 100 °C for 3.5 h to give an unexpected adduct (**5**)[5] in 42% yield. The exo-spiro oxetane structure of **5** was easily determined by the following spectroscopic data. Namely, the predominant absorption band at 1670 cm^{-1} in its ir spectrum shows the presence of the cyclohexadienone moiety. Also, one of the methylene protons (9-H) is observed to be strongly deshielded (δ_H 3.15) indicating that the hydrogen is almost located on the same plane with that of the cyclohexadienone ring.

This type of oxetane was expected to be formed under the given photochemical conditions. In fact, Fehnel and Brokaw[7] found that the *photolysis* of **Q** and *p*-benzoquinone in benzene led to the formation of the same type of exo-spiro oxetane (**6**) in a 56% yield. On the other hand, it was reported that chloranil reacted with **Q** under the conditioins of uv irradiation to give norbornadiene by way of radical cations.[8] According to the MO calculations[9] on energy levels and coefficients of



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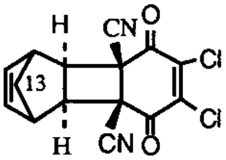

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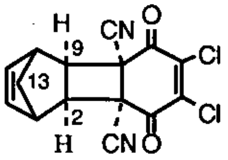

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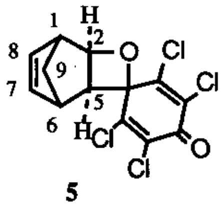

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Frontier MOs of *p*-benzoquinone, DDQ, and chloranil, the differences among these values may be too small to account for the distinct reactivities of chloranil to **Q** and those of *p*-benzoquinone and of DDQ. In addition, the polarographic half-wave potential of chloranil is intermediate between those of *p*-benzoquinone and DDQ.[10] Therefore, it may be rationalized by reasons of steric hindrance of the chlorine atoms that chloranil behaves preferentially as a hetero ene, i.e. C=O, toward **Q** giving the oxetane (**5**).[11] The exo stereochemistry of **5** can be interpreted again in terms of secondary orbital interactions between reactants as in the way of the reaction of *p*-benzoquinone and DDQ to **Q**.[6]

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4. Cf. K. Kanematsu, S. Morita, S. Fukushima, and E. Osawa, J. Am. Chem. Soc., 1981, **103**, 5211.
5. All new compounds are characterised by the following data. **3**, mp 278 °C (decomp.) (from AcOEt-Hexane) (Found: C, 56.5; H, 2.5; N, 8.7; Cl, 22.3. $C_{15}H_8N_2O_2Cl_2$ requires C, 56.45; H, 2.5; N, 8.8; Cl, 22.2); ν_{max} (Nujol) /cm^{-1} 2255 (CN) and 1710 (unsaturated ketone); δ_H(270 MHz; $CDCl_3$) 1.88 (1 H, ddd, *J* 1.3, 1.3, and 11.7 Hz, 13-H), 2.41 (2 H, d, *J* 0.8 Hz, 2- and 9-H), 2.48 (1 H, d, *J* 11.7 Hz, 13-H), 3.38 (2 H, ddd, *J* 0.8, 1.3, and 1.5 Hz, 1- and 10-H), and 6.18 (2 H, dd, *J* 1.3 and 1.5 Hz, 11- and 12-H); m/z 318 (M^+, 12%), 283 (5), 91 (39), 66 (100). **4**, mp ⟩ 310 °C (from AcOEt-Hexane) (Found: C, 56.4; H, 2.5; N, 8.7; Cl, 22.05. $C_{15}H_8N_2O_2Cl_2$ requires C, 56.45; H, 2.5; N, 8.8; Cl, 22.2); ν_{max} (Nujol)/cm^{-1} 2250 (CN), 1700 (unsaturated ketone); δ_H(270 MHz; $CDCl_3$) 0.64 (1 H, d, *J* 11.5 Hz, 13-H), 1.41 (1 H, ddd, *J* 1.3, 1.5, and 11.5 Hz, 13-H), 3.03 (2H, ddd, *J* 0.7, 1.3, and 1.5 Hz, 1- and 10-H), 3.25 (2 H, d, *J* 0.7 Hz, 2- and 9-H), 6.15 (2 H, dd, *J* 1.3 and 1.5 Hz, 11- and 12-H); m/z 318 (M^+, 8%), 283 (6),

91 (40), 66 (100). **5**, mp 160 °C (decomp.) (from AcOEt) (Found: C, 46.0; H, 2.4; Cl, 42.0. $C_{15}H_8O_2Cl_4$ requires C, 46.2; H, 2.4; Cl, 42.0); ν_{max} (Nujol)/cm^{-1} 1670 (unsaturated ketone); δ_H(270 MHz;$CDCl_3$) 1.56 (1 H, d, *J* 9.9 Hz, 9-H), 2.56 (1 H, d, *J* 5.0 Hz, 5-H), 3.08 (1 H, br s, 6-H), 3.15 (1 H, d, *J* 9.9 Hz, 9-H), 3.34 (1 H, br s, 1-H), 4.98 (1H, d, *J* 5.0 Hz, 2-H), 5.93 (1 H, dd, *J* 3.3 and 5.6 Hz, 8-H), 6.23 (1 H, dd, *J* 3.3 and 5.6 Hz, 7-H); m/z 336 (M$^+$, 13%), 271 (16), 243 (24), 91 (91), 66 (100).

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11. *o*-Chloranil was reported to exclusively cycloadd to **Q** in a forbidden $[\pi4+\sigma2+\sigma2]$ manner,[12] while to a 7-substituted **Q** in both $[\pi4+\sigma2+\sigma2]$ and $[\pi2+\sigma2+\sigma2]$ manners giving a complicated mixture of products including some oxetanes.[13]
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