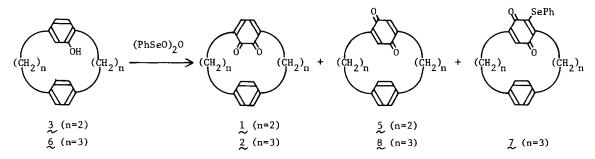
SYNTHESIS OF O-BENZOQUINONES DERIVED FROM [2.2]- AND [3.3]PARACYCLOPHANES

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Summary Oxidation of [2.2]- and [3 3]paracyclophanols with benzeneseleninic anhydride readily afforded the corresponding cyclophane-o-quinones which showed the intramolecular charge-transfer interactions

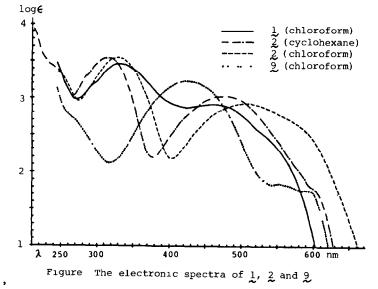
A number of cyclophanes containing a p-benzoquinone moiety (cyclophane-p-quinones) have been synthesized and their intramolecular charge-transfer (CT) interactions have been studied¹⁾ On the other hand, no cyclophane-o-quinone has appeared in the literature except 12-(t-butylamino)[2 2]paracyclophane-4,5-quinone²⁾ [n.n]Paracyclophane-o-quinones were of particular interest since the normally unstable o-benzoquinone group was expected to be stabilized by strong intramolecular CT interactions with the benzene rings, especially when n=3³⁾ We now wish to report a facile synthesis of two new cyclophane-o-quinones, [2 2]paracyclophane-4,5-quinone 1 and [3 3]paracyclophane-5,6-quinone 2

Oxidation of [2.2]paracyclophan-4-ol 3^{77} with benzeneseleninic anhydride 4^{47} was, probably as a result of strain, very sluggish and required refluxing for 5 h in benzene Separation by column chromatography (silica gel, benzene) afforded [2 2]paracyclophane-4,7-quinone 5 [yellow plates, dec.>226°C]⁷⁷ and 1 [deep red prisms (chloroform), dec >213°C]⁶⁰ in 39 4% and 37.2% yield, respectively In contrast, the oxidation of [3 3]paracyclophan-5-ol 6^{87} was much faster and was complete after heating at 60°C for 1 h in benzene The reaction mixture was separated by column chromatography to give 6-phenylseleno[3 3]paracyclophane-5,8-quinone 7 (23 7%, orangered needles, mp 116.5-117 5°C)⁶⁰, [3 3]paracyclophane-5,8-quinone 8 [13 3%, yellow plates, mp 166 5-168°C (11t³⁾166-167.5°C)], and 2 (40 7%, black-red prisms, mp 150-151°C)⁶⁰



Both 1 and 2 are remarkably stable in the crystalline state compared to 3,6-dimethyl-obenzoquinone 9^{5} However, 2 slowly decomposed in solution to a complex mixture of products. In contrast, 1 in chloroform changed very gradually into a dimer [yellow fine needles, dec. >308°C, MS(m/e): 104 (100%), 238 (17%) and 476 (0 6%, M⁺), IR (KBr) $\gamma_{C=0}$ 1702 (m), 1662 (s) and $\vec{\gamma}_{C=C}$ 1616 (m) cm⁻¹] at room temperature in the dark; heating accelerated the conversion. The dimer was probably formed by the Diels-Alder reaction Further elucidation of its structure was not possible because it was practically insoluble in all the solvents tested.

The color of the solution of 2 was markedly solvent dependent (brown and violet in nonpolar and polar solvents, respectively). As shown in Figure, the shoulders at the longest wavelength region are subject to hypsochromic shifts in polar solvents (n-7t). The absorption maxima of 1 and 2 around 500 nm are assigned as the intramolecular CT bands due to the transannular interaction between the o-benzoguinone and benzene rings on the basis of the solvent effect $[\lambda_{max}, nm (\epsilon,$ solvent), 1 439 (996, cyclohexane),



459 (833, CH₃CN) and 461 (843, CHCl₃), 2: 476 (1070, cyclohexane), 503 (865, CH₃CN) and 507 $(858, CHCl_3)$] and the considerable shift to the longer wavelength in going from the [2 2]- to the more favorable [3.3]phane system The behavior of these bands is similar to that of the CT bands of the corresponding cyclophane-p-quinones^{3,7)}. The assignment is also supported by the marked red shift of the band upon introduction of an electron-rich t-butylamino group into the benzene ring of $\frac{1}{2} (\lambda_{max} 605 \text{ nm})^{2}$.

REFERENCES AND NOTES

1) Y. Hienuki, T Tsuji, and S. Nishıda, Tetrahedron Lett, 22, 863 (1981) and references cited therein.

2) A. R. Forrester and R. Ramasseul, J. Chem Soc. (B), <u>1971</u>, 1638.

 T. Shinmyozu, T. Inazu, and T. Yoshino, Chem Lett., 1977, 1347
 D. H. R. Barton, A G. Brewster, S V Ley, and M. N Rosenfeld, J Chem. Soc Chem. Comm., 1976, 985.

5) Because of instability 9 could not be obtained pure by oxidation of 2,5-dimethylphenol with 4. The oxidation of 3,6-dimethylcatechol with $AgCO_3/Cellite$ gave analytically pure 9 in 96% \tilde{y} ield, red prisms, mp 81 5-83°C, decomposed on standing at room temperature

6) Satisfactory elemental analyses were obtained for all the new compounds. Spectral data are as follows [IR (CH_2Cl_2 , $\gamma_{C=0}$, cm⁻¹), ¹H-NMR ($CDCl_3$, 60 MHz, δ , ppm)]

1: IR, 1667; ¹H-NMR, 6 92, 6 50 (m, ArH), 5 90 (s, quinone), and 2.0-3.3 (m)

- 2: IR, 1676 (w), 1659 (s), ¹H-NMR, 7 12, 6 93 (m, ArH), 6.10 (s, quinone), and 1.6-3.2 (m)
- 7. IR, 1655 (s), 1650 (s), ¹H-NMR, 7.1-7.6 (m, PhSe), 6.88 (AA'BB'm, ArH), 6.00 (s, quinone) and 1.7-3.1 (m), MS, M⁺ 422.

9: IR, 1681 (w), 1659 (s), ¹H-NMR, 6 70 (s, quinone) and 1.96 (br. s, CH₃).

7) D. J. Cram and A. C. Day, J. Org. Chem <u>31</u>, 1227 (1966).
8) M. Sheehan and D J. Cram, J. Am. Chem Soc , <u>91</u>, 3544 (1969).

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