REACTIONS OF O-QUINOID COMPOUNDS WITH QUADRICYCLANES III[1]. COMPETITIVE $[\sigma 2+\sigma 2+\pi 4]$ AND $[\sigma 2+\sigma 2+\pi 2]$ CYCLOADDITIONS OF TETRACHLORO-O-BENZOQUINONE WITH QUADRICYCLANOL[2]

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Abstract - Quadricyclanol (1) reacts with tetrachloro-o-benzoquinone (2) to give both $[\sigma 2+\sigma 2+\pi 4]$ (3, 4, 5, 6) and $[\sigma 2+\sigma 2+\pi 2]$ (7) cycloadducts.

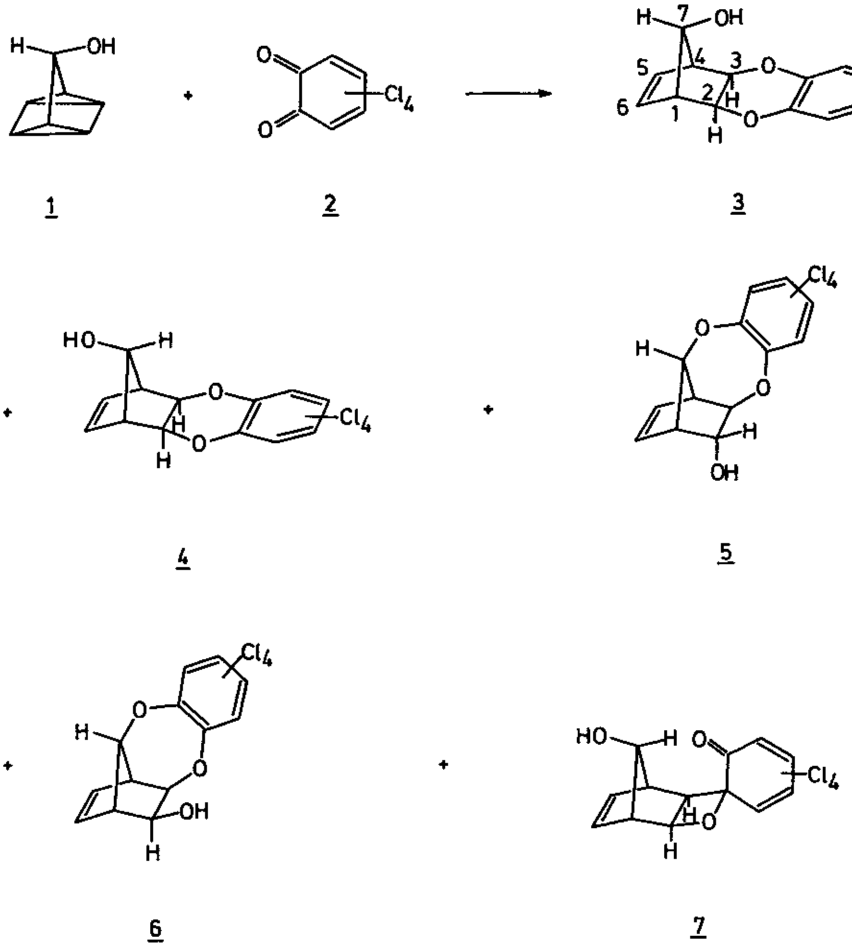
It is well known that tetracyclo$[3.2.0.0^{2,7}.0^{4,6}]$heptanes (quadricyclanes) may react with electron deficient unsaturated compounds to give adducts which can be considered as resulting from allowed pericyclic reactions[3,4]. In contrast with these observations both tetrachloro-o-benzoquinone (2) and o-benzoquinone-diimines[5] yield compounds which may originate from so-called forbidden $[\sigma 2s+\sigma 2s+\pi 4s]$ cycloadditions[1,6]. In order to get an understanding of this peculiar behavior the influence of substituents has been studied. Whereas quadricyclane yields $[\sigma 2s+\sigma 2s+\pi 4s]$ cycloadducts exclusively[6] we now have found that quadricyclanol (1) reacts with 2 giving products which are the result of competitive $[\sigma 2s+\sigma 2s+\pi 4s]$ (3, 4, 5, 6) and $[\sigma 2s+\sigma 2s+\pi 2s]$ (7) reaction ways. A mixture of 1 and 2 forms a deeply colored benzene solution which obviously contains a charge-transfer complex[7]. After being allowed to stand for 2 h at room temperature the following 1:1 adducts could be isolated.

3: 5% yield, colorless crystals, mp 238°C. - IR(KBr): 1430 (C-O)[1,10], 3505 cm^{-1}. - UV($CHCl_3$): $\lambda(\lg\varepsilon)$ = 293 (3.12), 299 nm (3.17). - ^1H-NMR($CDCl_3$): δ = 2.40-2.63 (m, OH), 3.40 (m, H-1, H-4), 4.21 (m, H-7), 4.46 (d, H-2, H-3, $J_{27}=J_{37}=1.2$ Hz), 6.10 ppm ("t", H-5, H-6).

4[12]: 15% yield, colorless needles, mp 205°C. - IR(KBr): 1428 (C-O), 3505 cm^{-1}. - UV($CHCl_3$): $\lambda(\lg\varepsilon)$ = 292 (sh, 3.22), 299 nm (3.31). - ^1H-NMR($CDCl_3$)[11]: δ = 2.13 (d, OH, $J_{OH,7}=8$ Hz), 3.35 (m, H-1, H-4), 4.15 (m, H-2, H-3), 4.88 (d, H-7, $J_{7,OH}=8$ Hz), 6.23 ppm (m, H-5, H-6).

5[12]: 19% yield, colorless prisms, mp 183°C. - IR(KBr): 1420 (C-O), 3325 cm^{-1}. - UV($CHCl_3$): $\lambda(\lg\varepsilon)$ = 293 (sh, 3.13), 298 nm (3.20). - ^1H-NMR($CDCl_3$)[11]: δ = 2.11 (d, OH, $J_{OH,2}=6.2$ Hz), 3.15 (m, H-1 or H-4), 3.40 (m, H-1 or H-4), 4.45 (m, H-7), 4.60 (dd, H-3, $J_{32}=2$ Hz, $J_{37}=1.6$ Hz), 5.03 (dd, H-2, $J_{2,OH}=6.2$ Hz, $J_{21}=4$ Hz), 6.03 - 6.41 ppm (m, H-5, H-6, $J_{56}=6.5$ Hz).

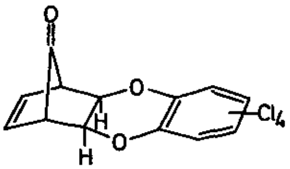
6: 8% yield, colorless crystals, mp 178°C. - IR(KBr): 1418 (C-O), 3578 cm^{-1}. - UV($CHCl_3$): $\lambda(\lg\varepsilon)$ = 293 (sh, 2.94), 299 nm (2.98). - ^1H-NMR($CDCl_3$)[11]: δ = 2.90 (d, OH, $J_{OH,2}=10.8$ Hz), 3.05 - 3.38 (m, H-1, H-4), 4.15 (ddd, H-2, $J_{2,OH}=10.8$ Hz, $J_{23}=6.5$ Hz, $J_{27}=1.5$ Hz), 4.68 (m, H-7), 4.73 (d, H-3, $J_{32}=6.5$ Hz), 5.88 (ddd, H-6, $J_{65}=6.5$ Hz, $J_{61}=3.5$ Hz, $J_{64}=$



1 Hz), 6.23 ppm (ddd, H-5, J_{56} = 6.5 Hz, J_{54} = 3.5 Hz, J_{51} = 0.8 Hz).

7: 32% yield, yellow crystals, mp 109°C. - IR(KBr): 1697, 3370 cm^{-1}. - UV(CH_3CN): λ(lg ε) = 218 (4.22), 355 nm (3.51). - ^1H-NMR($CDCl_3$)[11] : δ= 1.83 (m, OH), 2.58 (dd, H-3, J_{32} = 5.5 Hz, J_{34} = 1 Hz), 2.88 (m, H-4), 3.38 (m, H-1, J_{12} = 1.5 Hz), 4.78 (dd, H-2, J_{23} = 5.5 Hz, J_{21} = 1.5 Hz), 5.43 (m, H-7), 5.98 (dddd, H-6, J_{65} = 5.6 Hz, J_{61} = 2.7 Hz, J_{64} = 1 Hz, J_{67} = 1 Hz), 6.27 ppm (dddd, H-5, J_{56} = 5.6 Hz, J_{54} = 2.9 Hz, J_{51} = 1 Hz, J_{57} = 1 Hz).

Both 3 and 4 on oxidation with pyridinium chlorochromate (CH_2Cl_2, RT, 24 h) yield the same norbornenone derivative 8 (colorless crystals, mp 173°C. - IR(KBr) : 1429 (C-O), 1780 cm^{-1} . - ^1H-NMR($CDCl_3$)[11] : δ= 3.48 (m, H-1, H-4), 4.33 (s, H-2, H-3), 6.58 ppm ("t", H-5, H-6)) as do 5 and 6 which yield 9 (colorless crystals, mp 175°C. - IR(KBr): 1419 (C-O), 1755 cm^{-1}. - ^{1}H-NMR(CDCl$_3$)^{11} : δ= 3.45 (m, H-1, H-4), 4.45 (d, H-3, J_{37} = 1.9 Hz), 5.05 (dd, H-7, J_{73} = 1.9 Hz, J_{74} ≈ 2 Hz), 6.25 ppm (m, H-5, H-6). Lack of coupling between H-2 (H-3) and H-1 (H-4) in 8 shows that 3 and 4 are exo adducts[13]. A typical W-coupling between H-7 and H-2 (H-3) in 3 with J = 1.7 Hz and a characteristic small long range coupling between H-7 and H-5 (H-6)[14] in 4 with J = 0.8 Hz determines the position of the OH group in these compounds. An analogous reasoning together with the observed positions of the endo and exo hydrogens clarifies the structure of the epimeric carbinols 5 and 6.



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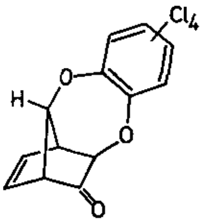

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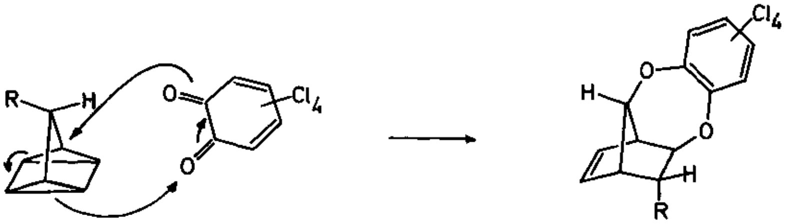
The structure of compound 7 has also been determined by spectroscopic and chemical investigations. Both the IR and UV spectrum of 7 exhibit absorptions which have also been found in spirodihydropyrans formed from 2 and dienes[15]. As it is well known that quadricyclane adds electron deficient alkenes, alkynes, and carbonyl compounds exclusively in an exo manner, the same stereochemical outcome is postulated in the present case. Both the large downfield shift of H-7 and other very similar ^{1}H-NMR data of the photochemically generated 9,10-phenanthrenquinone - quadricyclane adduct[16] are in accord with this assignment. Expectedly 7 adds styrene in a Diels-Alder reaction in a completely stereo- and regiospecific manner yielding a compound (93% yield, colorless crystals, mp 231°C), which on treatment with acetic anhydride in pyridine gives a monoacetate (colorless crystals, mp 198°). The same adduct has already been obtained in the 7-acetoxyquadricyclane series[1].

It is of interest to note that both 7-acetoxyquadricyclane[1] and 1 give exactly the same ratio of $[\sigma 2 + \sigma 2 + \pi 4]$ to $[\sigma 2 + \sigma 2 + \pi 2]$ adducts (1.47), but that there is a difference in the stereochemical



(1)

outcome of the $[\sigma 2 + \sigma 2 + \pi 4]$ addition. Whereas 1 yields all possible stereoisomers (3, 4, 5, 6) 7-acetoxyquadricyclane only gives compounds of type 4 and 5. This result may be rationalized on reasons of steric hindrance. Both 4 and 5 are formed by an attack at the less hindered side of 1 (e.g. formation of 5 (1)). It is expected that an entirely different electronic structure of the quadricyclane changes the product distribution in an even more significant way. Reactions with quadricyclanone have confirmed this assumption.

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REFERENCES

1. H. E. Büldt, T. Debaerdemaeker, and W. Friedrichsen, Tetrahedron 36, 267 (1980).
2. Presented in part at the 8th Int. Congr. Heterocycl. Chem., Graz, Austria 1981.
3. 3a. C. D. Smith, J. Am. Chem. Soc. 88, 4273 (1966). - 3b. N. Rieber, J. Alberts, J. A. Lipsky, and D. M. Lemal, J. Am. Chem. Soc. 91, 5668 (1969). - 3c. G. Kaupp and H. Prinzbach, Chem. Ber. 104, 182 (1971). - 3d. W. Eberbach, M. Perrould-Aruelles, H. Achenbach, E. Druckrey, and H. Prinzbach, Helv. Chim. Acta 54, 2579 (1971). - 3e. I. Tabushi, K. Yamamura, and Z. Yoshida, J. Am. Chem. Soc. 94, 787 (1972). - 3f. H. Tanida and T. Tsushima, Tetrahedron Lett. 1972, 395. - 3g. R. W. Hoffmann and J. Becherer, Tetrahedron 34, 1187 (1978). - 3h. J. Becherer, N. Hauel, and R. W. Hoffmann, Liebigs Ann. Chem. 1978, 312. - 3i. O. De Lucchi and V. Lucchini, J. Chem. Soc. Chem. Comm. 1982, 464.
4. C. W. Jefford, J.-C. E. Gehrêt, and V. de los Heros, Bull. Soc. Chim. Belg. 88, 973 (1979).
5. Review : W. Friedrichsen and A. Böttcher, Heterocycles 16, 1009 (1981).
6. W. Friedrichsen, E. Büldt, and R. Schmidt, Tetrahedron Lett. 1975, 1137.
7. It is well known that both quadricyclanes[1,8] and 2[9] form CT complexes.
8. I. Tabushi and K. Yamamura, Tetrahedron 31, 1827 (1975).
9. 9a. I. Prins, J. W. Verhoeven, and Th. J. de Boer, Org. Magn. Res. 9, 543 (1977). - 9b. W. Friedrichsen, I. Kallweit, and R. Schmidt, Liebigs Ann. Chem. 1977, 116.
10. E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe, J. Chem. Soc. [London] 1960, 3123.
11. Numbering as in 3.
12. The acetate of this adduct has also been obtained from 7-acetoxyquadricyclane and 2[1].
13. L. M. Jackman and S. Sternhell, "Applications of NMR Spectroscopy in Organic Chemistry". Pergamon Press, New York 1969.
14. 14a. A. P. Marchand and J. E. Rose, J. Am. Chem. Soc. 92, 3724 (1968). - 14b. K. Browne and R. I. Kagi, Austr. J. Chem. 26, 1831 (1973).
15. M. F. Ansell and V. J. Leslie, J. Chem. Soc. (C) 1971, 1423.
16. T. Sasaki, K. Kanematsu, I. Ando, and O. Yamashita, J. Am. Chem. Soc. 99, 871 (1977).

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