HETEROCYCLES, Vol 20, No 6, 1983

REACTIONS OF O-QUINOID COMPOUNDS WITH QUADRICYCLANES IV[1]. CYCLOADDITIONS OF TETRACHLORO-O-BENZOQUINONE WITH QUADRICYCLANONE[2].

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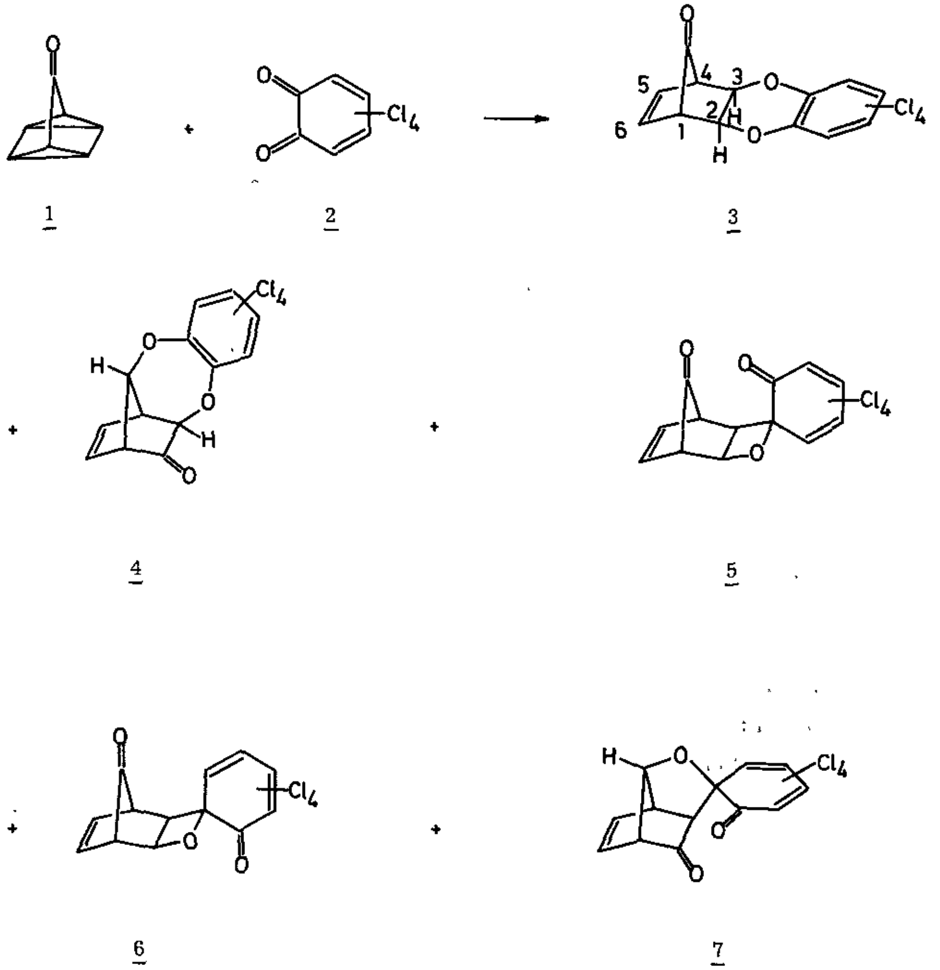
ABSTRACT - Quadricyclanone (1) reacts with tetrachloro-o-benzoquinone (2) to give both $[\sigma 2+\sigma 2+\pi 4]$ (3, 4) and $[\sigma 2+\sigma 2+\pi 2]$ (5, 6, 7) cycloadducts.

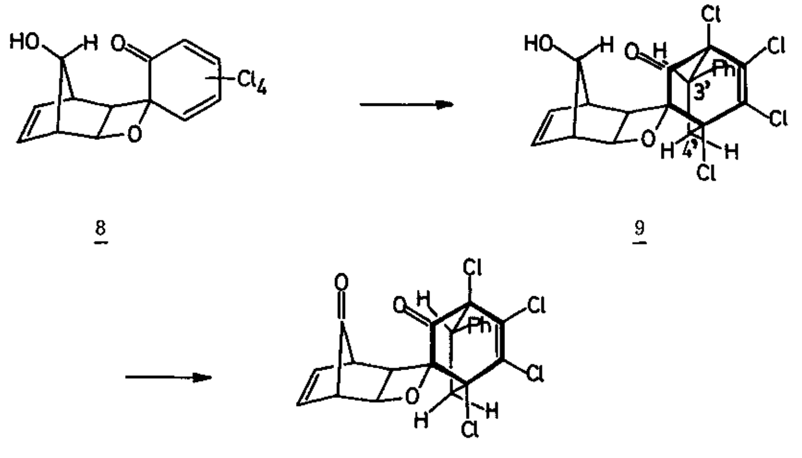
Recent investigations have shown that isobenzofurans (benzo[c]furans)[3], fulvenes[4], and five-membered mesoionic heterocycles of type A[5] may react with o-quinoid compounds (o-quinones, o-benzoquinone-diimines) to give $[\pi 4+\pi 4]$ cycloadducts. In an extension of this work we have found that quadricyclanes exhibit a similar, but more complicated behavior: both $[\sigma 2+\sigma 2+\pi 2]$[6] and $[\sigma 2+\sigma 2+\pi 4]$ adducts have been isolated[1]. As double bonded atoms or groups (O, CH_2) in position 7 of the quadricyclane nucleus alter the electronic structure of this molecule considerably[8], it was expected that in these cases a significant change in the product distribution should take place. The reaction of quadricyclanone (1) with tetrachloro-o-benzoquinone (2), which is reported in this paper, confirms this presumption.

Compared with quadricyclane the reaction of 1 with 2 is slow[10]. After being allowed to stand at room temperature in dichloromethane for 14 days the following five 1:1-adducts could be isolated: 3: 1-2% yield, colorless needles, mp 173°C (ether)[11]; 4: 20%yield, colorless prisms, mp 175°C (ether)[11]; 5: 0.5% yield, yellow prisms, mp 156°C (benzene). - IR(KBr): 1692, 1775 cm^{-1}. - UV(CH_3CN): $\lambda(\lg\varepsilon)$ = 210 (4.19), 245 (3.77), 335 (3.41), 380 nm (sh, 3.18). - ^1H-NMR($CDCl_3$)[12]: δ = 2.86 (dd, H(3), J_{32} = 4.4 Hz, J_{34} = 1 Hz), 3.03 (m, H(4), J_{45} = 4.1 Hz, J_{43} = 1.0 Hz, J_{46} = 0.8 Hz), 3.60 (m, H(1)), 5.01 (dd, H(2), J_{23} = 4.4 Hz, J_{21} = 1.8 Hz), 6.41 (ddd, H(6), J_{65} = 6.7 Hz, J_{61} = 4.1 Hz, J_{64} = 0.8 Hz), 6.68 ppm (ddd, H(5), J_{56} = 6.7 Hz, J_{54} = 4.1 Hz, J_{51} = 0.8 Hz); 6: 40% yield, yellow prisms, mp 181°C (benzene). - IR(KBr): 1708, 1782 cm^{-1}. - UV(CH_3CN): $\lambda(\lg\varepsilon)$ = 201 (4.09), 221 (4.01), 243 (sh, 3.78), 330 (3.49), 390 nm (3.24). - ^1H-NMR($CDCl_3$): δ = 2.82 (dd, H(3), J_{32} = 5.9 Hz, J_{34} = 0.8 Hz), 3.28 (m, H(4), J_{45} = 3.8 Hz, J_{43} = 0.8 Hz, J_{46} = 0.7 Hz), 3.62 (m, H(1)), 5.09 (dd, H(2), J_{23} = 5.9 Hz, J_{21} = 2 Hz), 6.39 (ddd, H(6), J_{65} = 7 Hz, J_{61} = 4.1 Hz, J_{64} = 0.7 Hz), 6.74 ppm (ddd, H(5), J_{56} = 7 Hz, J_{54} = 3.8 Hz, J_{51} = 0.5 Hz); 7: 0.5% yield, yellow prisms, mp 212°C (benzene). - IR(KBr): 1702, 1758 cm^{-1}. - UV(CH_3CN): $\lambda(\lg\varepsilon)$ = 217 (4.07), 246 (3.86), 314 (3.45), 348 (3.34), 380 nm (3.24). - ^1H-NMR($CDCl_3$): δ = 2.82 (dd, H(3), J_{34} = 1.8 Hz, J_{37} = 1.8 Hz), 3.33 - 3.62 (m, H(1), H(4)), 5.30 (m, H(7), J_{73} = 1.8 Hz), 6.0 ppm (m, H(5), H(6)).

The structures of 3 and 4 have been determined by correlating them with adducts obtained in the 7-quadricyclanol series[1]. The tetrachloro-2,4-cyclohexadienone moieties in 5, 6, and 7 are



easily detectable by their UV spectra. Additionally 5 reacts with styrene (dichloromethane, 24 h, RT) forming a single (TLC) Diels-Alder adduct[13] (10[14] .: 79% yield, colorless crystals, mp 196 °C (ether). - IR(KBr): 1750, 1780 cm^{-1}. - UV(CHCl$_3$): λ(lg ε) = 249 (3.43), 288 (sh, 2.36), 297 (2.39), 327 (sh, 2.21), 338 nm (2.03). - ^{1}H-NMR (CDCl$_3$): δ = 2.50 (m, 1 H, H(4$'_{en}$) or H(4$'_{ex}$)), 2.73 (dd, H(3), J_{32} = 6.2 Hz, J_{34} = 1 Hz), 3.06 (m, H(4)), 3.16 - 3.36 (m, 2 H, H(3$'$), H(4$'_{en}$) orH(4$'_{ex}$)), 3.52 (m, H(1)), 4.98 (dd, H(2), J_{23} = 6.2 Hz, J_{21} = 1.9 Hz), 6.37 (dd, H(6), J_{65} = 7 Hz, J_{61} = 4 Hz), 6.73 (dd, H(5), J_{56} = 7 Hz, J_{54} = 4 Hz), 6.33 - 7.43 ppm (m, 5 H, ar-H)), which has also been obtained by reaction of 8[1] with styrene (dichloromethane, 24 h, RT) via 9 (93% yield, colorless crystals, mp 231 °C (ether). - IR(KBr): 1739, 3570 cm^{-1}. - UV(CHCl$_3$): λ(lg ε) = 248 (3.44), 263 (sh, 2.93), 271 (2.63), 325 nm (2.28). - ^{1}H-NMR(CDCl$_3$): δ = 1.93 (d, OH, $J_{OH,7}$ = 10 Hz), 2.48 (dd, H(3), J_{32} = 5.3 Hz, J_{34} = 0.9 Hz), 2.55 (m, H(4$'_{ex}$) or H(4$'_{en}$)),



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2.85 (m, H(4)), 3.18 - 3.33 (m, H(3'), H($4'_{ex}$) or H($4'_{en}$)), 3.25 - 3.38 (m, H(1)), 4.76 (dd, H(2), J_{23} = 5.3 Hz, J_{21} = 2 Hz), 6.00 (d, H(7), $J_{7,OH}$ = 10 Hz), 5.83 - 6.16 (m, H(6)), 6.30 (ddd, H(5), J_{56} = 5.3 Hz, J_{54} = 2.8 Hz, J_{51} = 1 Hz), 6.97 - 7.45 ppm (m, 5 H)) and subsequent oxidation with pyridinium chlorochromate (dichloromethane, 24 h, RT; 80% yield).

The structure of 7 has also been clarified by chemical and spectroscopic methods. The presence of a 2,4-cyclohexadienone moiety has again been confirmed by the preparation of a styrene adduct (83% yield, colorless crystals, mp 206°C (ether). - IR(KBr): 1755 cm^{-1}); a carbonyl group at 1758 cm^{-1} is in accordance with spectra of other 2-norbornenones. Both the value of δH(7) (5.30 ppm) and a longe-range coupling between H(7) and H(3) (J_{73} = 1.8 Hz) are only compatible with a regioisomer of type 7. Compounds of this type have hitherto been described only as results of photochemical reactions of quadricyclanes[15].

Again it has been substantiated that almost all cycloadducts of quadricyclanes result from an exo-attack[16]. The same holds for the formally symmetry forbidden $[\sigma 2+\sigma 2+\pi 4]$ adducts (e.g. 3). Perhaps the most noticable result of the aforementioned reactions is a remarkable shift in the product distribution on going from 7-quadricyclanol to 1[1] (Table) with a strong stereochemical preference of the $[\sigma 2+\sigma 2+\pi 2]$ adduct 6. A definitive explanation of this phenomenon must await further investigations with other o-quinoid compounds.

Table: Product distribution

Product / Starting material	Type 3	Type 4	Type 5	Type 6	Type 7
7-Quadricyclanol[1]	20%	27%	32%	-	-
1	1-2%	20%	0.5%	40%	0.5%

ACKNOWLEDGEMENT : The generous support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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Received, 22nd February, 1983