

REACTIONS OF O-QUINOID COMPOUNDS WITH QUADRICYCLANES IV¹.
 CYCLOADDITIONS OF TETRACHLORO-O-BENZOQUINONE WITH
 QUADRICYCLANONE².

Willy Friedrichsen⁺ and Eggert Büldt

Institut für Organische Chemie der Universität Kiel

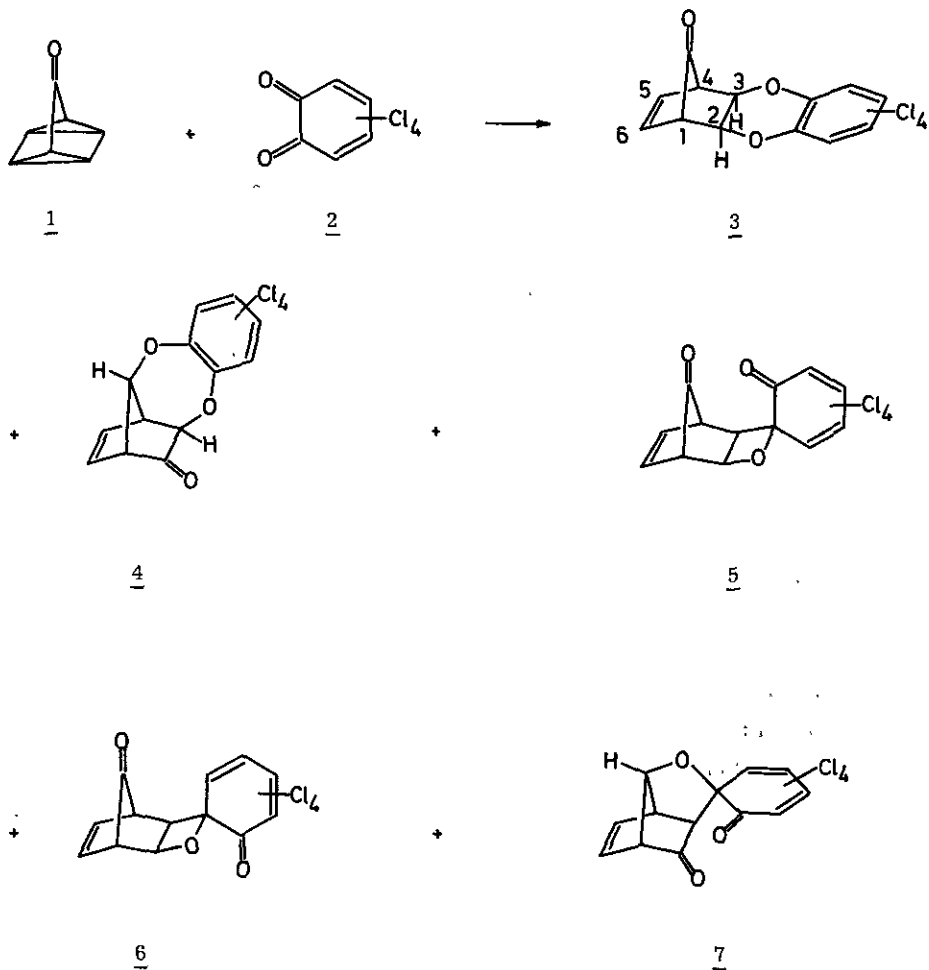
Olshausenstraße 40 - 60, D-2300 Kiel, FRG

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.

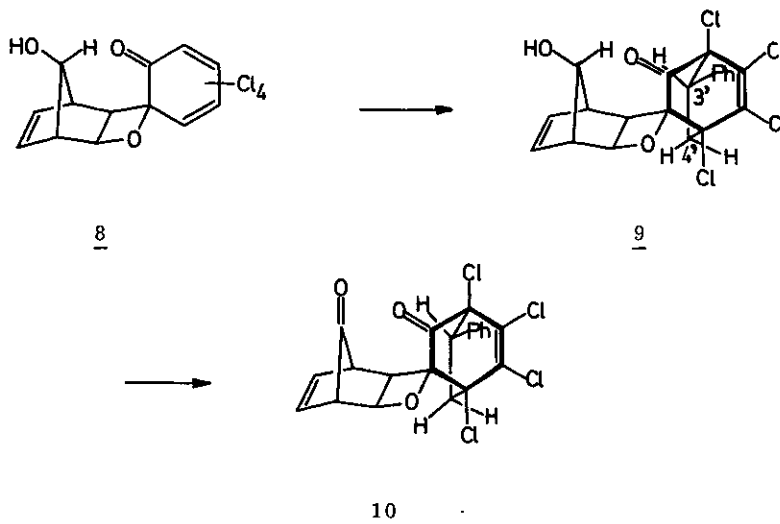
Recent investigations have shown that isobenzofurans (benzo[c]furans)³, fulvenes⁴, and five-membered mesoionic heterocycles of type A⁵ may react with o-quinoid compounds (o-quinones, o-benzoquinone-dilimines) to give [$\pi 4 + \pi 4$] cycloadducts. In an extension of this work we have found that quadricyclanes 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 isolated¹. As double bonded atoms or groups (O, CH₂) in position 7 of the quadricyclane nucleus alter the electronic structure of this molecule considerably⁸, 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 slow¹⁰. 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(CH₃CN): λ (lg ϵ) = 210 (4.19), 245 (3.77), 335 (3.41), 380 nm (sh, 3.18). - ¹H-NMR(CDCl₃)¹²: δ = 2.86 (dd, H(3), J₃₂ = 4.4 Hz, J₃₄ = 1 Hz), 3.03 (m, H(4), J₄₅ = 4.1 Hz, J₄₃ = 1.0 Hz, J₄₆ = 0.8 Hz), 3.60 (m, H(1)), 5.01 (dd, H(2), J₂₃ = 4.4 Hz, J₂₁ = 1.8 Hz), 6.41 (ddd, H(6), J₆₅ = 6.7 Hz, J₆₁ = 4.1 Hz, J₆₄ = 0.8 Hz), 6.68 ppm (ddd, H(5), J₅₆ = 6.7 Hz, J₅₄ = 4.1 Hz, J₅₁ = 0.8 Hz); 6: 40% yield, yellow prisms, mp 181°C (benzene). - IR(KBr): 1708, 1782 cm⁻¹. - UV(CH₃CN): λ (lg ϵ) = 201 (4.09), 221 (4.01), 243 (sh, 3.78), 330 (3.49), 390 nm (3.24). - ¹H-NMR(CDCl₃): δ = 2.82 (dd, H(3), J₃₂ = 5.9 Hz, J₃₄ = 0.8 Hz), 3.28 (m, H(4), J₄₅ = 3.8 Hz, J₄₃ = 0.8 Hz, J₄₆ = 0.7 Hz), 3.62 (m, H(1)), 5.09 (dd, H(2), J₂₃ = 5.9 Hz, J₂₁ = 2 Hz), 6.39 (ddd, H(6), J₆₅ = 7 Hz, J₆₁ = 4.1 Hz, J₆₄ = 0.7 Hz), 6.74 ppm (ddd, H(5), J₅₆ = 7 Hz, J₅₄ = 3.8 Hz, J₅₁ = 0.5 Hz); 7: 0.5% yield, yellow prisms, mp 212°C (benzene). - IR(KBr): 1702, 1758 cm⁻¹. - UV(CH₃CN): λ (lg ϵ) = 217 (4.07), 246 (3.86), 314 (3.45), 348 (3.34), 380 nm (3.24). - ¹H-NMR(CDCl₃): δ = 2.82 (dd, H(3), J₃₄ = 1.8 Hz, J₃₇ = 1.8 Hz), 3.33 - 3.62 (m, H(1), H(4)), 5.30 (m, H(7), J₇₃ = 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 series¹. 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 adduct¹³ (10^{14} : 79% yield, colorless crystals, mp 196° C (ether). - IR(KBr): 1750, 1780 cm^{-1} . - UV(CHCl_3): $\lambda(\lg \epsilon) = 249$ (3.43), 288 (sh, 2.36), 297 (2.39), 327 (sh, 2.21), 338 nm (2.03). - $^1\text{H-NMR}$ (CDCl_3): $\delta = 2.50$ (m, 1 H, $\text{H}(4'_{\text{en}})$ or $\text{H}(4'_{\text{ex}})$), 2.73 (dd, $\text{H}(3)$, $J_{32} = 6.2$ Hz, $J_{34} = 1$ Hz), 3.06 (m, $\text{H}(4)$), 3.16 - 3.36 (m, 2 H, $\text{H}(3')$, $\text{H}(4'_{\text{en}})$ or $\text{H}(4'_{\text{ex}})$), 3.52 (m, $\text{H}(1)$), 4.98 (dd, $\text{H}(2)$, $J_{23} = 6.2$ Hz, $J_{21} = 1.9$ Hz), 6.37 (dd, $\text{H}(6)$, $J_{65} = 7$ Hz, $J_{61} = 4$ Hz), 6.73 (dd, $\text{H}(5)$, $J_{56} = 7$ Hz, $J_{54} = 4$ Hz), 6.33 - 7.43 ppm (m, 5 H, ar-H), which has also been obtained by reaction of 8¹ 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): $\lambda(\lg \epsilon) = 248$ (3.44), 263 (sh, 2.93), 271 (2.63), 325 nm (2.28). - $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.93$ (d, OH, $J_{\text{OH},7} = 10$ Hz), 2.48 (dd, $\text{H}(3)$, $J_{32} = 5.3$ Hz, $J_{34} = 0.9$ Hz), 2.55 (m, $\text{H}(4'_{\text{ex}})$ or $\text{H}(4'_{\text{en}})$),



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 δ H(7) (5.30 ppm) and a long-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 quadricyclanes¹⁵.

Again it has been substantiated that almost all cycloadducts of quadricyclanes result from an *exo*-attack¹⁶. The same holds for the formally symmetry forbidden [$\sigma 2 + \sigma 2 + \pi 4$] adducts (e.g. 3). Perhaps the most noticeable result of the aforementioned reactions is a remarkable shift in the product distribution on going from 7-quadricyclanol to 1¹ (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	Type <u>3</u>	Type <u>4</u>	Type <u>5</u>	Type <u>6</u>	Type <u>7</u>
Starting material					
7-Quadricyclanol ¹	20%	27%	32%	-	-
<u>1</u>	1-2%	20%	0.5%	40%	0.5%

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