REACTIONS OF O-QUINOID COMPOUNDS WITH QUADRICYCLANES III\(^1\).

COMPETITIVE \([v_2 + v_2 + \tau_4]\) AND \([v_2 + v_2 + \tau_2]\) CYCLOADDITIONS OF TETRACHLORO-O-BENZOQUINONE WITH QUADRICYCLANOL\(^2\)

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Abstract - Quadricyclanol (1) reacts with tetrachloro-o-benzoquinone (2) to give both \([v_2 + v_2 + \tau_4]\) (3, 4, 5, 6) and \([v_2 + v_2 + \tau_2]\) (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-dilimines\(^5\) yield compounds which may originate from so-called forbidden \([v_2s + v_2s + \tau_4s]\) cycloadditions\(^1,6\). In order to get an understanding of this peculiar behavior the influence of substituents has been studied. Whereas quadricyclane yields \([v_2s + v_2s + \tau_4s]\) cycloadducts exclusively\(^6\) we now have found that quadricyclanol (1) reacts with 2 giving products which are the result of competitive \([v_2s + v_2s + \tau_4s]\) (3, 4, 5, 6) and \([v_2s + v_2s + \tau_2s]\) (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), 3505 cm\(^{-1}\). - UV(CHCl\(_3\)): \(\lambda(\text{lg} \varepsilon) = 293 (3.12), 299 \text{ nm} (3.17)\). - \(^1\)H-NMR(CDC\(_3\)): \(\delta = 2.40-2.63 \text{ (m, OH)}, 3.40 \text{ (m, H-1, H-4)}, 4.21 \text{ (m, H-7)}, 4.46 \text{ (d, H-2, H-3), J}_{27} = J_{37} = 1.2 \text{ Hz}, 6.10 \text{ ppm ("t", H-5, H-6)}.\)

4\(^12\): 15% yield, colorless needles, mp 205°C. - IR(KBr): 1428 (C=O), 3505 cm\(^{-1}\). - UV(CHCl\(_3\)): \(\lambda(\text{lg} \varepsilon) = 292 \text{ (sh, 3.22)}, 299 \text{ nm} (3.31)\). - \(^1\)H-NMR(CDC\(_3\)): \(\delta = 2.13 \text{ (d, OH, J}_{10}, 3 = 8 \text{ Hz}), 3.35 \text{ (m, H-1, H-4)}, 4.15 \text{ (m, H-2, H-3)}, 4.88 \text{ (d, H-7, J}_{7,1,0} = 8 \text{ Hz}), 6.23 \text{ ppm (m, H-5, H-6)}.\)

5\(^12\): 19% yield, colorless prisms, mp 183°C. - IR(KBr): 1420 (C=O), 3325 cm\(^{-1}\). - UV(CHCl\(_3\)): \(\lambda(\text{lg} \varepsilon) = 292 \text{ (sh, 3.22)}, 299 \text{ nm} (3.31)\). - \(^1\)H-NMR(CDC\(_3\)): \(\delta = 2.11 \text{ (d, OH, J}_{10}, 2 = 6.2 \text{ Hz), 3.15 \text{ (m, H-1 or H-4), 3.40 \text{ (m, H-1 or H-4), 4.45 \text{ (m, H-7), 4.60 \text{ (dd, H-3, J}_{32} = 2 \text{ Hz, J}_{37} = 1.6 \text{ Hz), 5.03 \text{ (dd, H-2, J}_{21} = 4 \text{ Hz), 6.03 - 6.41 \text{ ppm (m, H-5, H-6, J}_{56} = 6.5 \text{ Hz).\)}}}\)

6: 8% yield, colorless crystals, mp 178°C. - IR(KBr): 1418 (C=O), 3578 cm\(^{-1}\). - UV(CHCl\(_3\)): \(\lambda(\text{lg} \varepsilon) = 293 \text{ (sh, 2.94)}, 299 \text{ nm (2.98)\). - \(^1\)H-NMR(CDC\(_3\)): \(\delta = 2.90 \text{ (d, OH, J}_{10}, 2 = 10.8 \text{ Hz), 3.05 - 3.38 \text{ (m, H-1, H-4), 4.15 \text{ (ddd, H-2, J}_{2,10}, 3 = 10.8 \text{ Hz), J}_{23} = 6.5 \text{ Hz, J}_{27} = 1.5 \text{ Hz), 4.68 \text{ (m, H-7), 4.73 \text{ (d, H-3, J}_{32} = 6.5 \text{ Hz), 5.88 \text{ (ddd, H-6, J}_{65} = 6.5 \text{ Hz, J}_{61} = 3.5 \text{ Hz, J}_{64} = 6.5 \text{ Hz).}}\)
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_{3}CN): \lambda(\varepsilon) = 218 (4.22), 355 nm (3.51). - ^1H-NMR(CDC{l}_3)^11: \delta = 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 (ddd, 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 2 and 4 on oxidation with pyridinium chlorochromate (CH_{2}Cl_{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(CDC{l}_3)^11: \delta = 3.48 (m, H-1, H-4), 4.33 (s, H-2, H-3), 6.58 ppm (^1H, 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. -

\[ \text{IR(KBr): } 1419 \text{ (C=O), } 1755 \text{ cm}^{-1}. \]

\[ \text{H-NMR(CDC}_{3}\text{)}: 3.45 \text{ (m, H-1, H-4), } 4.45 \text{ (d, H-3, J}_{37} = 1.9 \text{ Hz), } 5.05 \text{ (dd, H-7, J}_{73} = 1.9 \text{ Hz, J}_{74} = 2 \text{ 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. 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) 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 carhinols 5 and 6.

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. 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 H-NMR data of the photochemically generated 9,10-phenanthrene-quinone - quadricyclane adduct are in accord with this assignment. Expectedly 2 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°C). The same adduct has already been obtained in the 7-acetoxyquadricyclane series.

It is of interest to note that both 7-acetoxyquadricyclane 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
outcome of the \([v2 + v2 + v4]\) addition. Whereas \(\frac{1}{4}\) yields all possible stereo-isomers \((3, 4, 5, 6)\), 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 \(\frac{1}{2}\) (e.g. formation of \(\frac{5}{2}\)). 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

7. It is well known that both quadricyclanes \(1^1, 8\) and \(2^9\) form CT complexes.
11. Numbering as in 3.
12. The acetate of this adduct has also been obtained from 7-acetoxyquadricyclane and \(2^1\).

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