Oxidative Ring Cleavage of *o*-Benzoquinone by Potassium Peroxomonosulphate

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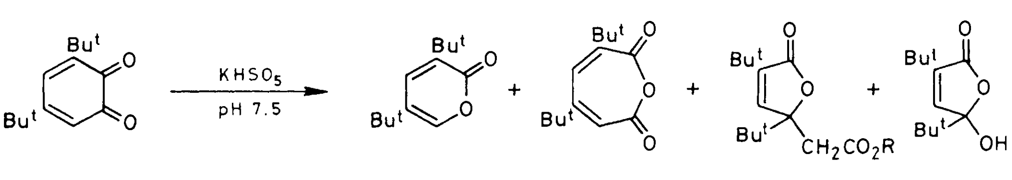
Oxidation of 3,5-di-t-butyl-1,2-benzoquinone by potassium peroxomonosulphate gave both extra- and intra-diol cleavage products.

Oxidative carbon–carbon bond cleavage of aromatic substrates, notably phenols and pyrocatechols, is the most important reaction catalysed by certain extra- and intra-diol dioxygenases.[1] Although both extra- and intra-diol cleavages are known in enzymic oxidation of pyrocatechols, little is known about the extradiol cleavage in nonenzymatic pro-



	(1)	(2)	(3)	(4)	(5)
Dioxane—MeOH—H$_2$O		37%	42%	21% (R=Me)	trace
Dioxane—H$_2$O		80%	3%	trace (R = H)	17%

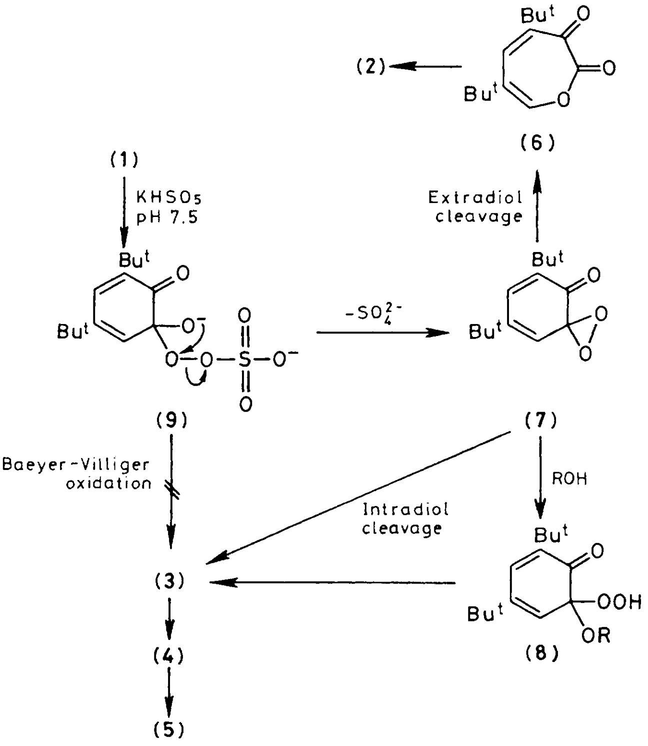
Scheme 1

cesses and the direct evidence of the intermediate is not fully elucidated.

Now, in order to throw light on the enzymic carbon–carbon bond cleavage of aromatic compounds, we studied the oxidation of *o*-benzoquinone by potassium peroxomonosulphate which is known to give dioxirane in the presence of ketones† and isolated both extra- and intra-diol cleavage products in high yields.

3,5-Di-t-butyl-1,2-benzoquinone (**1**) (1 mmol) was treated with potassium peroxomonosulphate (5 mmol) by the modified method of Edwards[2] in dioxane (50 ml), buffered water (pH 7.5, phosphate buffer, 50 ml), and methanol (50 ml) kept at 10 °C.‡ The pyrone (**2**), the oxacycloheptadienedione (**3**), and the furanone (**4**) were obtained in 37, 42, and 21% yields, respectively. Sometimes a trace of the hydroxyfuranone (**5**) was detected. Control experiments showed that methanolysis of the isolated dione (**3**) gave (**4**) quantitatively under the reaction conditions. Further oxidation of (**4**) gave (**5**). In the absence of methanol, however, (**2**) was obtained predominantly in 80% yield, and the yields of (**3**) and (**4**) were reduced (Scheme 1). Oxidation of (**1**) by *m*-chloroperbenzoic acid under the same conditions did not give (**3**). These results suggest that the Baeyer–Villiger oxidation of *o*-benzoquinone (**1**) may not be involved under the reaction conditions, since oxidation of (**1**) by *m*-chloroperbenzoic acid gave the dione (**3**) exclusively.[3] A careful product analysis showed the formation of the dione (**6**),§ but its instability prevented isolation in pure form. The dione (**6**) readily decomposed to (**2**).[4] The time course of the oxidation of (**1**) in dioxane–H$_2$O solution showed that (**6**) and (**3**) appeared in the early stages; (**6**) then gradually disappeared with a concomitant increase in the amount of (**2**). At the end of the reaction (**6**) had disappeared completely, yielding (**2**) and (**3**). This indicates that the primary product is the dione (**6**), which is a precursor of (**2**). We consider that the formation of (**6**) took place *via* extradiol cleavage, which resembles ruthenium-catalysed oxidation.[4] Products (**3**), (**4**), and (**5**) are derived from intradiol cleavage.

These results show that the most appropriate mechanism for the oxidation of *o*-benzoquinone (**1**) by potassium peroxomonosulphate involves the formation of the dioxirane intermediate (**7**) followed by migration of the vinyl group to afford the dione (**6**) (Scheme 2).



Scheme 2

These findings may provide mechanistic insight into the extradiol cleavage reaction in enzymatic oxidation.

Received, 24th January 1983; Com. 111

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† It is known that oxidation of ketones with potassium peroxomonosulphate produces an epoxidizing intermediate for which a dioxirane structure has been suggested.[2]

‡ During the addition of potassium peroxomonosulphate the pH was monitored with a pH-stat and kept at 7.5 by addition of 0.5 M NaOH solution. The mixture was stirred at 10 °C for 3 h and extracted with benzene and the extract dried over MgSO$_4$. After removal of solvent *in vacuo*, the resulting oily residue was analysed by preparative h.p.l.c.

§ Spectral data for (**6**): ^{1}H n.m.r. (CCl$_4$) δ 1.18 (s, 9H), 1.31 (s, 9H), and 7.19 (m, 2H); ^{13}C n.m.r. (CDCl$_3$) δ 181.86, 161.06, 143.89, 136.19, 136.19, 127.36, 34.78, 31.91, 29.47, and 28.33 p.p.m.; ν_{max} (CCl$_4$) 1755 and 1710 cm^{-1}.

References

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2 J. O. Edwards, R. H. Pater, R. Curci, and F. DiFuria, *Photochem. Photobiol.*, 1979, **30**, 63; R. E. Montgomery, *J. Am. Chem. Soc.*, 1974, **96**, 7820; R. Curci, M. Fiorentino, L. Troishi, J. O. Edwards, and R. H. Pater, *J. Org. Chem.*, 1980, **45**, 4758; A. R. Gallopo and J. O. Edwards, *ibid.*, 1981, **46**, 1684.

3 T. R. Demin and M. M. Rogic, *J. Org. Chem.*, 1980, **45**, 1153.

4 M. Matsumoto and K. Kuroda, *J. Am. Chem. Soc.*, 1982, **104**, 1433, reported a similar decomposition of an α-oxo-lactone to a 2-pyrone.