Dehydrogenation of Cyclic and Bicyclic Secondary Alkyl Peroxides during Flash Vacuum Pyrolysis

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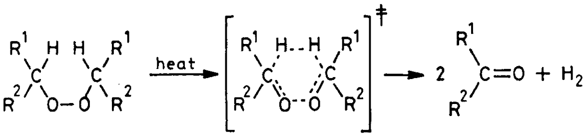
Summary Dehydrogenation to the corresponding diketone occurs to the extent of 16% and 42% respectively in the flash vacuum pyrolysis of 3,6-dimethyl-1,2-dioxacyclohexane and 2,3-dioxabicyclo[2.2.2]octane, but is unimportant in similar pyrolyses of 3,5-dimethyl-1,2-dioxacyclopentane and 2,3-dioxabicyclo[2.2.1]heptane.

Pyrolysis of acyclic secondary alkyl peroxides affords up to 90% of hydrogen in solution but negligible amounts in the vapour phase. Mechanistic studies[1] indicate that the hydrogen is formed by a concerted process (equation 1) in which the transition state has significant polar character. In the gas phase, where solvent stabilization of such a transition state cannot occur, the normal homolytic cleavage of the O–O bond takes precedence and products derived from free secondary alkoxyl radicals are obtained (equation 2). Homolysis in cyclic or bicyclic peroxides produces oxygen diradicals and novel chemical behaviour may ensue.[2] We now report a new example of this, in which dehydrogenation occurs to an appreciable extent when suitable cyclic and bicyclic secondary alkyl peroxides, for which preparative routes have only recently become available, are pyrolysed in the gas phase.

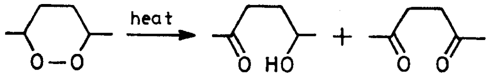


(1)

$$R^1R^2CH{-}O{-}O{-}CHR^1R^2 \xrightarrow{heat} 2R^1R^2CH{-}\dot{O} \longrightarrow \text{Products} \qquad (2)$$

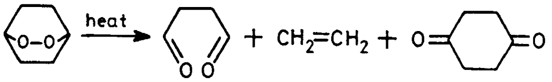
Flash vacuum pyrolysis was carried out by pumping a sample (200 mg) of each peroxide at 10^{-3} mmHg through a Pyrex tube (35 cm × 1·5 cm diam.) at 450 °C and collecting the products in a trap at liquid nitrogen temperature. (*N.B.* This procedure precludes direct observation of hydrogen). The product mixtures, which always accounted for > 95% of the starting material, were analysed by ^{1}H and ^{13}C n.m.r. spectroscopy, g.l.c., and g.c./m.s., and the identity of each major component was confirmed by comparison with an authentic sample.

A 4 : 1 mixture of *trans*- and *cis*-3,6-dimethyl-1,2-dioxacyclohexane (**1**)[3] afforded 5-hydroxyhexan-2-one (**2**) (60%) and hexa-2,5-dione (**3**) (16%) (equation 3) together with several minor products with yields in the range 0·5 to 6·5%, while 2,3-dioxabicyclo[2.2.2]octane (**4**)[4] gave succindialdehyde (**5**) (56%), ethylene (identified by conversion into 1,2-dibromoethane), and cyclohexane-1,4-dione (**6**) (42%) (equation 4).



(3)

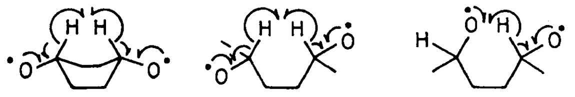
(**1**) (**2**) (**3**)



(4)

(**4**) (**5**) (**6**)

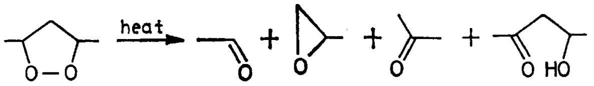
We suggest that the dehydrogenations proceed *via* β-scission in the corresponding oxygen diradicals and possibly involve the boat-like transition state (**7**) for bicyclic compound (**4**) and the cisoid transition state (**8**) for the major (*trans*) isomer of compound (**1**). Unlike peroxides (**4**) and *trans*-(**1**), in the *cis*-isomer of compound (**1**) the disposition of the α-hydrogens is such that a concerted dehydrogenation (*cf.* equation 1) is formally possible. However, the associated chemistry[1] renders this highly improbable in the gas phase and a diradical pathway, with a transition state analogous to (**8**), can again be envisaged. The extents of dehydrogenation in the individual isomers of compound (**1**) are as yet unknown.



(**7**) (**8**) (**9**)

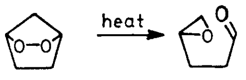
The thermal isomerization of peroxide (**1**) into hydroxy-ketone (**2**) is unique and may be accounted for by a 1,5-hydrogen transfer after homolysis. Thus the formation of both compounds (**2**) and (**3**) can be explained in terms of a common oxygen diradical partitioning between transition states (**9**) and (**8**). Neither of these pathways is available to the oxygen diradical formed by thermolysis of 3,3,6,6-tetramethyl-1,2-dioxacyclohexane, and here β-scission leads to formation of acetone and ethylene.[5] The analogous process in peroxide (**1**) would yield acetaldehyde and about 3% was detected in the thermolysis product. The conversion of peroxide (**4**) into succindialdehyde and ethylene is the pathway previously reported for thermolysis in solution.[6] Although a concerted mechanism is allowed, these products can also be rationalised in terms of alternative β-scissions in the same oxygen diradical that undergoes dehydrogenation.

Indirect support for the mechanistic suggestions made above came from the fact that flash vacuum pyrolysis of a 1 : 1 mixture of *cis*- and *trans*-3,5-dimethyl-1,2-dioxacyclopentane (**10**)[3] (equation 5) and of 2,3-dioxabicyclo[2.2.1]-heptane (**12**)[7] (equation 6) did not yield any appreciable amount of the appropriate 1,3-diketone. Hydrogen formation *via* transition states analogous to (**7**) and (**8**) is rendered more difficult in the oxygen diradicals derived from compounds (**10**) and (**12**) because the α-hydrogens are unable to approach as close to one another.



(5)

(**10**) (**11**)



(6)

(**12**) (**13**)

Compound (**12**) afforded 4,5-epoxypentanal (**13**) (90%) almost exclusively, as found previously[8] for thermolysis in cyclohexane solution. Compound (**10**) appeared to behave like its tertiary analogues[9] much more than did compound (**1**). Thus acetaldehyde (32%), propene oxide (13%), and acetone (20%) were major products and only a trace, if any, of hydroxy-ketone (**11**) was obtained. This may reflect the reduced tendency for a 1,4- compared with a 1,5-hydrogen transfer in the corresponding oxygen diradicals, but may also result from a substantial contribution to the decomposition pathway of compound (**10**) from a concerted two-bond fragmentation of the type found in solution for the tertiary analogues.[9]

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