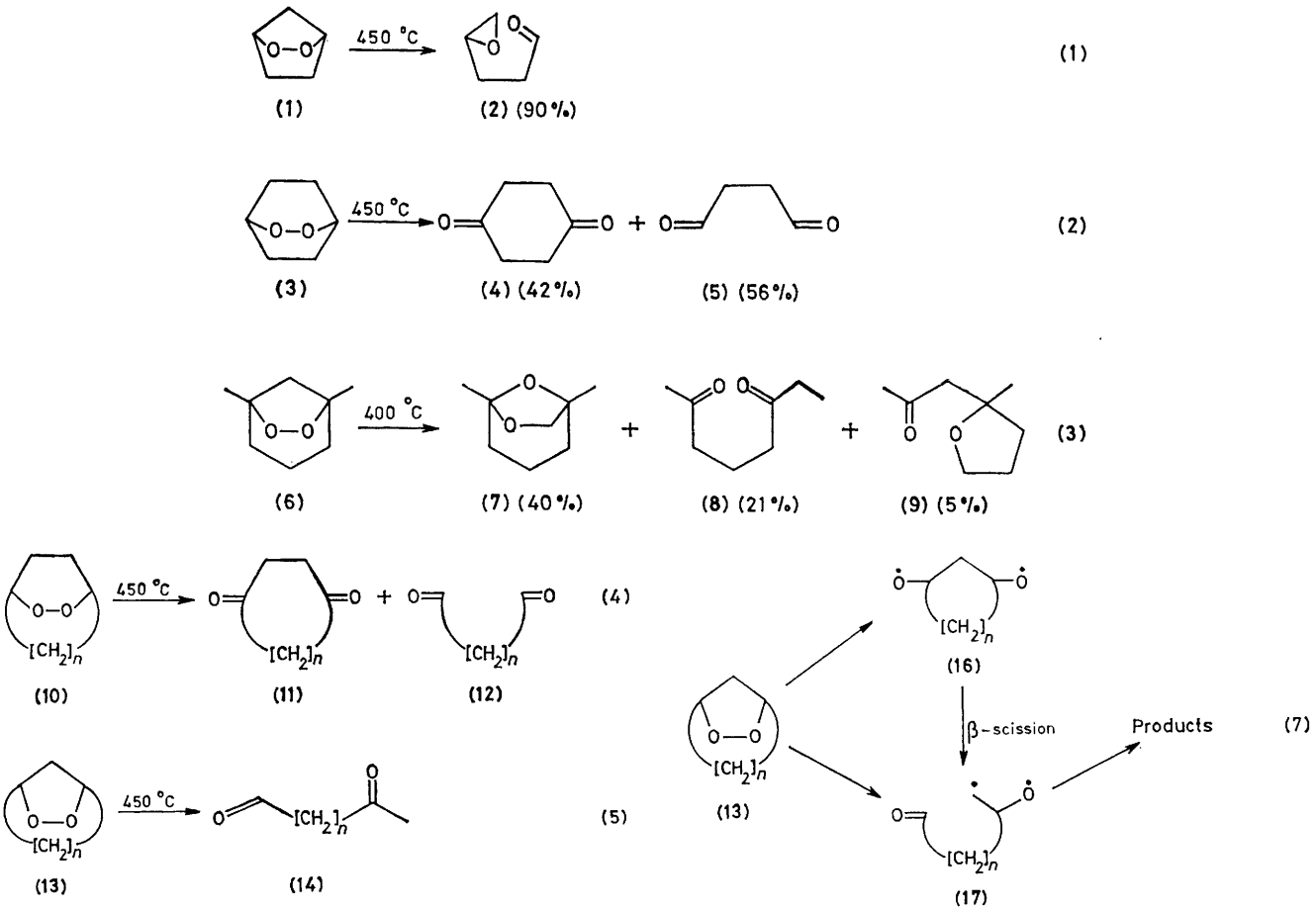
Formation of Dicarbonyl Compounds in the Flash Vacuum Pyrolysis of Saturated Bicyclic Peroxides

A. J. Bloodworth,* David S. Baker, and Henny J. Eggelte

Christopher Ingold Laboratories, Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

Under flash vacuum pyrolysis, dioxabicyclo[*n*.2.1]alkanes (*n* = 3,4, and 5) isomerise to keto-aldehydes, $MeCO[CH_2]_nCHO$, whereas dioxabicyclo[*n*.2.2]alkanes (*n* = 2,3, and 4) fragment to give, by loss of hydrogen and ethylene, mixtures of cycloalkane-1,4-diones and dialdehydes, $OHC[CH_2]_nCHO$.

Thermolysis of cyclic peroxides has proved to be a process of both synthetic value,[1] and theoretical interest as a source of oxygen-centred diradicals.[2] Interest in the peroxide chemistry associated with prostaglandin biosynthesis has recently stimulated the synthesis of several new saturated bicyclic peroxides,[3] and although studies of the thermolysis of these compounds are only in their infancy, a variety of novel transformations has already been reported. Thus whereas the flash vacuum pyrolysis (f.v.p.) of 2,3-dioxabicyclo[2.2.1]-heptane (**1**) afforded 4,5-epoxypentanal (**2**) [equation (1)], that of its [2.2.2] homologue (**3**) resulted in fragmentation by the competing processes of dehydrogenation and loss of



ethylene [equation (2)].[4] Other decomposition modes were observed when 1,5-dimethyl-6,7-dioxabicyclo[3.2.1]octane (**6**) was heated at 400 °C in the vapour phase, the pheromone frontalin (**7**) being the major product [equation (3)].[5] All the observed products [equations (1)—(3)] can be accounted for in terms of *differing behaviour* in the various cycloalkanedioxyl radicals produced by homolysis of the peroxide bonds. In an attempt to clarify how the fate of such diradicals depends upon their structure, we have undertaken a systematic study in which the [*n*.2.2] homologues (**10**; $n = 2$—**4**)[6] and the [*n*.2.1] homologues (**13**; $n = 3$—5)[7] of compound (**1**) have been thermolysed, again using f.v.p. conditions[4] to minimise the risk of induced and secondary decompositions.

Clear patterns of behaviour have emerged from our results. Thus the [3.2.2] and [4.2.2] peroxides underwent fragmentations parallel to those [equation (2)] of the [2.2.2] compound, giving mixtures of cycloalkane-1,4-diones (**11**) and α,ω-dialdehydes (**12**) [equation (4)], the yields being 85% of (**11**) and 10% of (**12**) when $n = 3$, and 61% of (**11**) and 6% of (**12**) when $n = 4$.† The [*n*.2.1] peroxides, on the other hand, were converted in high yields (>90%) into the keto-aldehydes (**14**) [equation (5)]. The products from both series of reactions were identified by the usual spectroscopic techniques and by comparison with authentic samples or literature data.

The absence of any appreciable amount of cleavage of the *n*-carbon bridge in [*n*.2.2] peroxides where $n > 2$, suggests that synchronous double β-scission occurs in the dioxyl radicals (**15**) and partitions between formation of hydrogen and ethylene [equation (6)]. The direct formation of ethylene from peroxides (**10**) by a concerted process cannot be ruled out but seems unlikely since it does not occur in the related monocyclic compound, 3,3,6,6-tetramethyl-1,2-dioxacyclohexane.[8] The smaller proportion of dehydrogenation for the [2.2.2] compound compared with the higher homologues may simply arise from the statistical factor of having *two* incipient ethylene units. The concept of elimination of a hydrogen molecule from a conformationally suitable cycloalkanedioxyl species is further supported by the fact that the f.v.p. of 9,10-dioxabicyclo[3.3.2]decane[9] afforded cyclo-octane-1,5-dione as the major product.

The absence of any appreciable amount of cleavage of the *n*-carbon bridge in [*n*.2.1] peroxides is probably best explained in terms of a concerted two-bond fission occurring to render the 1,3-diradical (**17**) rather than the cycloalkanedioxyl radical (**16**) [equation (7)].

Similar behaviour has been found previously for monocyclic 1,2-dioxacyclopentanes,[10] and in the bicyclo-com-

† 7-Ethenyloxepan-2-ol (25%) was also obtained.

pounds (**13**) the required orbital overlap is favourable. The puzzling aspect of the [*n*.2.1] series is the fact that the [2.2.1] peroxide gives mainly epoxy-aldehyde, whereas the higher homologues afford predominantly keto-aldehydes. It is difficult to see why the value of *n* should influence the extent of rearrangement in the diradical (**17**). For the [4.2.1] system we confirmed that 6,7-epoxyheptanal does not isomerise to 6-oxoheptanal (**14**) under f.v.p. conditions.

Our results indicate that thermolyses of dioxabicycloalkanes that contain a 5- or a 6-membered peroxide ring resemble those of the corresponding monocyclic peroxides.[4,8,9] If a one-carbon bridge is present, it is broken with formation of a carbonyl group, and isomerisation takes place. If a two-carbon bridge is present (and a one-carbon bridge is absent), fragmentation occurs with the elimination of ethylene. The main difference between dioxabicyclo[*n*.2.2]alkanes and 1,2-dioxacyclohexanes is that conformational constraints imposed upon the derived 1,6-dioxygen radicals by the presence of the cycloalkane rings render elimination of a hydrogen molecule a highly favourable process which competes with the loss of ethylene.

We thank the S.E.R.C. for financial support.

Received, 7th June 1982; Com. 648

References

1 W. Adam, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 619.
2 W. Adam, *Acc. Chem. Res.*, 1979, **12**, 390.
3 W. Adam and A. J. Bloodworth, *Top. Curr. Chem.*, 1981, **97**, 121.
4 A. J. Bloodworth and D. S. Baker, *J. Chem. Soc., Chem. Commun.*, 1981, 547..
5 R. M. Wilson and J. W. Rekers, *J. Am. Chem. Soc.*, 1981, **103**, 206.
6 D. J. Coughlin, R. S. Brown, and R. G. Salomon, *J. Am. Chem. Soc.*, 1979, **101**, 1533, and references therein.
7 A. J. Bloodworth and H. J. Eggelte, *J. Chem. Soc., Chem. Commun.*, 1982, 865.
8 W. Adam and J. Sanabia, *J. Am. Chem. Soc.*, 1977, **99**, 2735.
9 A. J. Bloodworth, J. A. Khan, and M. E. Loveitt, *J. Chem. Soc., Perkin Trans.* 1, 1981, 621.
10 W. Adam and N. Duran, *J. Am. Chem. Soc.*, 1977, **99**, 2729.