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MECHANISM OF THE THERMAL RING-CLEAVAGE OF OXETANS

By Howard A.J. Carless

(Dept. of Chemistry, Birkbeck College, Malet St, London WC1E 7HX)

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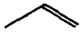
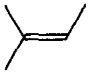
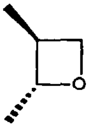
Despite the considerable evidence that has been acquired for cyclobutane[1] and 1,2-dioxetan[2] pyrolysis, less is known about oxetan pyrolysis. Ring cleavage reactions have been observed to give alkene and carbonyl compound,[3] and the cleavage has been interpreted on a biradical mechanism.[4] Until very recently, no experimental evidence had been produced to show whether oxetan ring-cleavage occurred through a biradical or a concerted process. However, accurate thermochemical data for the pyrolysis of cis and trans-2,3-dimethyl oxetan have now been published, and provide evidence for a biradical mechanism.[5] This prompts me to report the results of pyrolyses of a variety of methyl-substituted oxetans; the present experiments show the generality of biradical intermediates in such ring-cleavage reactions, and suggest that both C-C and C-O bond breakings can be involved in the initial reaction step.

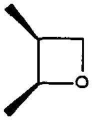
The isomeric trans and cis-2,3-dimethyloxetans (1) and (2) were prepared.[6] The 2,3,4-trimethyloxetans (3)-(5) were prepared by a photocycloaddition reaction,[7] as were the 2,2,3,4-tetramethyloxetans (6) and (7).[8] The major detected products of pyrolysis of oxetans (1-7) under nitrogen at 430-450° were the ring-cleavage products of alkene and carbonyl compound, and the alkene mole ratios are summarised in the Table.

Table. Mole Ratios of Alkene Products.

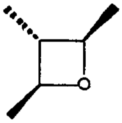
Oxetan				
(1)	4.55	2.85	1.00	-
(2)	3.25	0.55	1.00	-
(3)	-	3.05	1.00	-
(4)	-	1.30	1.00	-
(5)	-	0.36	1.00	-
(6)	-	2.30	1.00	60
(7)	-	0.62	1.00	22



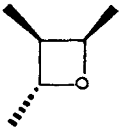
(1)



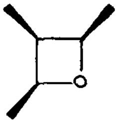
(2)



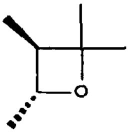
(3)



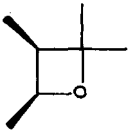
(4)



(5)

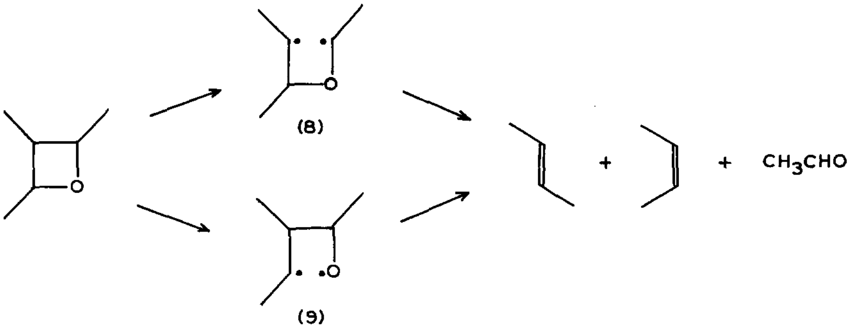


(6)



(7)

It is significant that a mixture of *trans*- and *cis*-but-2-ene was formed in all cases, although the isomeric oxetans were not appreciably interconverted, nor was but-2-ene significantly isomerised, under the reaction conditions. The results support the involvement of 1,4-biradicals such as (8-9) arising from oxetans (3-5) in the production of but-2-ene.



Biradicals (8) and (9) must have sufficient lifetime for bond rotations to compete with fission of the second bond. There is considerable, though not complete, loss of stereochemical configuration in going from oxetan to alkene product. The present conclusions contrast with the just-published data for pyrolyses of 2-methyl-3-phenyloxetans, where the high stereoselectivity observed may reflect restricted rotation at the benzylic radical centre involved.[9]

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