

## Six-centred Transition States in Reactions Involving Halogen Compounds

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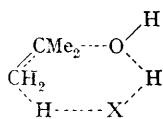
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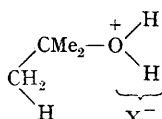
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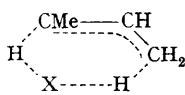
WHEREAS the unimolecular decomposition of organic halides has normally been regarded as proceeding through four-centred (homolytic)<sup>1</sup> or two-centred (quasi-heterolytic)<sup>2</sup> transition states, those of esters and related compounds proceed through a six-centred transition state.<sup>3</sup> We report some reactions involving halogens which can best be interpreted as proceeding through six-centred transition states. Thus to explain the hydrogen halide catalysis of the dehydration of *t*-butyl alcohol, the transition states (I) or (II) were



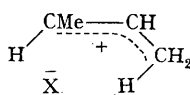
(I)



(II)



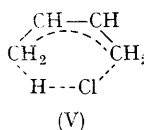
(III)



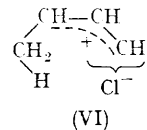
(IV)

suggested.<sup>4</sup> Again, the hydrogen-halide catalysed isomerisation of olefins<sup>5</sup> was interpreted as involving (III) or (IV).

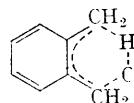
Three new examples of this type of mechanism are now reported. In the area of unimolecular dehydrohalogenation, it is now apparent that the fast-starts observed in the pyrolysis of  $\gamma$ -methylallyl chloride<sup>6</sup> are due to the presence in the substrate (predominantly *trans*) of a small amount of the *cis*-compound. The greatly enhanced rate of elimination of the latter compound is consistent with the transition states (V) or (VI). Again the



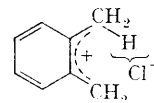
(V)



(VI)



(VII)

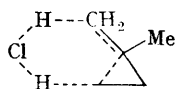


(VIII)

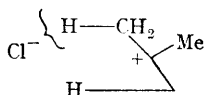
ready production of benzylcyclobutane on pyrolysis of  $\alpha$ -chloro-*o*-xylene<sup>7</sup> suggests (VII) or (VIII). The last and most definitive example<sup>8</sup> comes from the study of the HCl-catalysed conversion of 1,1-dimethylcyclopropane which yields uniquely

2-methylbut-2-ene. In this case the transition state can be represented by (IX) or (X).

Further work on these systems is in progress, both in Britain and in Australia.



(IX)



(X)

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- <sup>1</sup> A. Sherman, O. T. Quimby, and R. O. Sutherland, *J. Chem. Phys.*, 1936, **4**, 732.
- <sup>2</sup> A. Maccoll in "The Transition State", *Chem. Soc. Special Publ.*, No. 16, London, 1962, p. 158.
- <sup>3</sup> C. D. Hurd and F. H. Blunk, *J. Amer. Chem. Soc.*, 1938, **60**, 2419.
- <sup>4</sup> A. Maccoll and V. R. Stimson, *J. Chem. Soc.*, 1960, 2836.
- <sup>5</sup> A. Maccoll and R. A. Ross, *J. Amer. Chem. Soc.*, 1965, **87**, 4997.
- <sup>6</sup> P. G. Rodgers, Ph.D. Thesis, University of London, 1966.
- <sup>7</sup> S. K. Wong, unpublished results.
- <sup>8</sup> J. Shapiro and E. S. Swinbourne, *Canad. J. Chem.*, in the press; *Chem. Comm.*, 1967, 465.