Protonated Cyclopropane Intermediates in the Addition of Chlorine to Methyl- and Ethyl-cyclopropane

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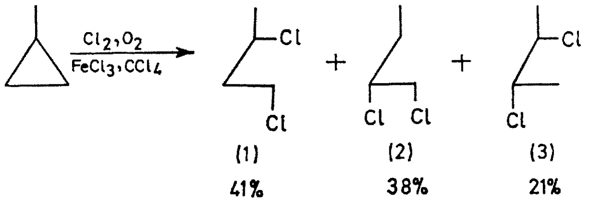
Summary The dichlorides produced from the ionic addition of chlorine to alkylcyclopropanes partially arise *via* protonated cyclopropane intermediates.

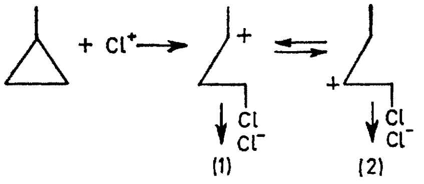
THE radical addition[1] of chlorine to a variety of cyclopropanes has been reported. The ionic addition has received much less attention. We now describe the ionic addition of chlorine to methylcyclopropane and ethylcyclopropane.

Treatment of a CCl_4 solution of methylcyclopropane with Cl_2 and a catalytic amount of $FeCl_3$ gave the dichlorides shown in equation 1. The reaction system was kept in the dark and under an oxygen atmosphere to prevent any radical contribution. Although (**1**) and (**2**) can form *via* classical carbonium ions, equation 2, for (**3**) to do so is unlikely since it would require an intermediate primary carbonium ion (followed by a 1,2 hydride shift).

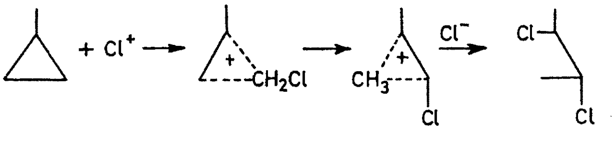


(1)

It is suggested that (**3**) (and possibly all or part of **1** and **2**) arises *via* protonated cyclopropanes as illustrated in equation 3. Such intermediate ions have already been demonstrated in the addition of Br_2,[2] CH_3COCl,[3] and HA[4] to cyclopropane. Corner-protonated structures have been used in equation 3, but a similar, though more complex, interpretation can be made using edge protonated structures. It was independently shown that $FeCl_3$ did not equilibrate the dichlorides.



(2)



(3)

Similar results were found with ethylcyclopropane. The following dichloropentanes arose from the ionic addition of Cl_2 to ethylcyclopropane in an oxygen atmosphere: 49% *erythro*-2,3-, 30% *threo*-2,3-, 11% 1,4-, 7% 1,3-, and 3% 1,2-dichloropentane. The 1,2-, 1,3-, and 1,4-dichloropentanes can be accommodated by a classical cation path involving secondary carbonium ions. A classical cation path for the dominant 2,3-products requires an intermediate primary carbonium ion. Again, it is more likely that the 2,3-dichloropentanes arise *via* protonated cyclopropane intermediates, whose exact structures are in doubt.

The g.l.c. analysis of the products has been published.[5]

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