AN EXAMPLE OF A CONCERTED TRANS-ADDITION OF Br_2 TO A DOUBLE BOND

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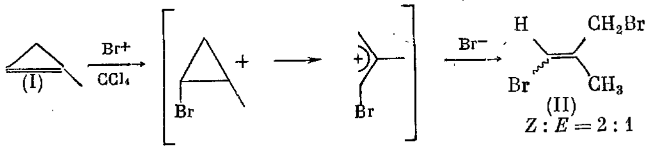
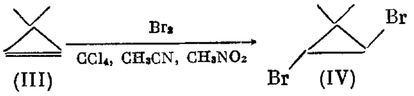
The ease of opening of the cyclopropyl cation to the allyl cation [1] makes cyclopropenes unique model compounds for distinguishing electrophilic addition to the double bond by a concerted mechanism and by a two-step mechanism involving a cationic intermediate [2].

We have shown that the addition of Br_2 to 1-methylcyclopropene (I) at −15°C in CCl_4 proceeds with opening of the three-membered ring leading exclusively to the dibromide (II) whose structure indicates two-step bromine addition:



The bromination of 3,3-dimethylcyclopropene (III) at −15°C in CCl_4, CH_3CN, and CH_3NO_2 led to trans-1,2-dibromo-3,3-dimethylcyclopropane (IV) in 80% yield:



Since the position of the methyl substituents in (I) and (III) should give (III) an advantage relative to opening of the three-membered ring upon the intermediate formation of the corresponding cyclopropyl cations [3], our results indicate that the trans-addition of Br_2 to the unsubstituted double bond in (III) is a concerted electrocyclic process [2]. Support for this hypothesis is also found in the independence of the yield of (IV) of the nature of the solvent, while, in the case of the bromination of (I), replacing CCl_4 with CH_3CN or CH_3NO_2 significantly lowered the yield of (II) due to the formation of unidentified products. The difference in the mechanisms for bromine addition to (I) and (III) is apparently the result of the effect of the methyl group at the double bond which creates steric hindrance for synchronous trans-addition and facilitates the two-step process by polarization of the double bond.

These results account for the difference in behavior for bromination of cyclopropene and 1,3,3-trimethylcyclopropene which had not previously found a satisfactory explanation in the literature [4].

LITERATURE CITED

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