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SILVER ION ASSISTED SOLVOLYSIS OF METHYLENECHLOROCYCLOPROPANES

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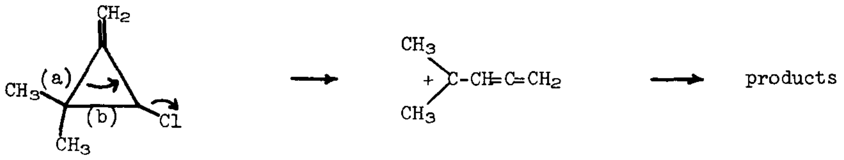
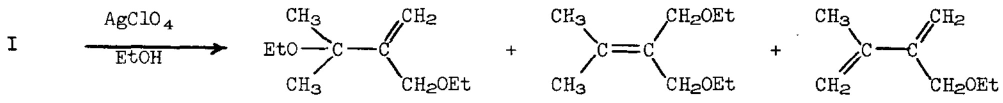
The commonly observed products of solvolysis of methylenehalocyclopropanes (e.g., I) (1) are those predicted on the basis of extensive studies of the reactions of the more readily available gem-dihalocyclopropanes (2). They are derived from the allenic cation by either loss of proton and double bond rearrangement to give the enyne or by attack of nucleophile to give the expected substitution product(s) and, in every case, the product has the carbon skeleton of the intermediate cation.



I

We now report a new and novel mode of solvolysis of I which occurs in the presence of silver ion. The reaction of I (3) with ethanolic silver perchlorate (30°, 34 hr) gave a 30% yield (4) of a mixture of II, III and IV (41, 37 and 22%, respectively) which was separated by preparative glpc on a 20 ft diethylene glycol succinate column.



II III IV

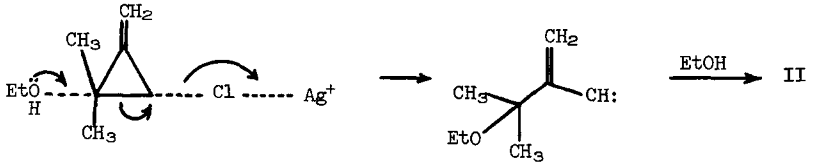
The nmr spectrum of II exhibits signals at τ 8.75 (singlet, 6H), τ 6.13 (doublet of doublets, 2H), τ 4.83 (doublet of doublets, 1H), τ 4.98 (doublet of doublets, 1H), τ 6.4-7.0

(two overlayed quartets, 4H) and τ 8.7-9.1 (two overlayed triplets, 6H). The nmr spectrum of III has signals at τ 8.25 (singlet, 6H), τ 6.08 (singlet, 4H), τ 6.63 (quartet, 4H) and τ 8.87 (triplet, 6H). That of IV shows signals at τ 8.10 (broad singlet, 3H), τ 5.94 (mult, 2H), τ 4.85 (mult, 2H), τ 4.97 (mult, 1H), τ 5.09 (mult, 1H), τ 6.59 (quartet, 2H) and τ 8.83 (triplet, 2H). Other analytical data are consistent with the assigned structures.

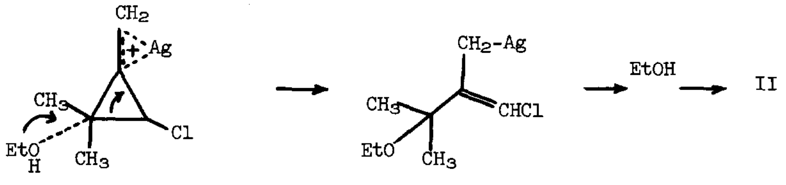
The ratio II:III:IV was observed to vary with time such that after 72 hr the three were present in approximately equivalent amounts. This suggested that their formation might be sequential and catalyzed by acid generated in the initial step. This was confirmed by repeating the reaction in the presence of excess silver carbonate. There was obtained a 34% yield of II along with a trace of 4-ethoxy-4-methyl-1,2-pentadiene. Moreover, treatment of II with ethanolic perchloric acid in an nmr probe demonstrated that II is transformed to III, IV and polymeric material quite rapidly. Equally important is the observation that the substrate (I) is inert to ethanolic perchloric acid. It is thus clear that II is the primary product from the silver ion-ethanol reaction and that its formation represents a mode of cleavage other than that observed under normal solvolytic conditions - breakage of bond (b) rather than (a).

The more obvious mechanisms for the reaction are described in the following approximations of their transition states (A and B). The two differ primarily in that A would appear to be dependent on the presence of a chlorine atom while B would not. This dependence was checked in an experiment using the halogen-free parent hydrocarbon, 2,2-dimethylmethylenecyclopropane. This substance did not react with ethanolic silver perchlorate under a variety of conditions and was recovered essentially quantitatively. The chlorine atom would thus appear to be an essential structural feature for this reaction. The similar reaction of the fluorine analog of I (5) provided no useful information as it gave only polymeric material.

(A)



(B)



While these observations appear to support mechanism A, we favor B because of its formalistic analogy to the rather well understood oxymercuration of I (7). Its reaction with mercuric chloride in ethanol afforded an organomercurial analogous to the organosilver intermediate proposed in mechanism B. Further experiments (which are necessarily rather elaborate) are expected to permit a choice between the two mechanisms.

REFERENCES

1. J. Meinwald, J. W. Wheeler, A. A. Nimetz and J. S. Liu, J. Org. Chem., 30, 1038 (1965). R. M. Babb, Doctoral Dissertation, University of Utah, 1968.
2. For leading references see S. J. Cristol, R. M. Sequeira and C. H. DePuy, J. Am. Chem. Soc., 87, 4007 (1965).
3. T. C. Shields and W. E. Billups, Chem. and Ind., 1999 (1967).
4. This yield is not necessarily a measure of the efficiency of the process as the products slowly polymerize under reaction conditions. No "normal" products, i.e., those derived from breaking bond (a), were observed.
5. This substance, 3-fluoro-2,2-dimethylmethylenecyclopropane, was prepared by the base-catalyzed reaction of dichlorofluoromethane with 2-methyl-2-butene (50%) followed by the general (6) elimination-isomerization reaction.
6. T. C. Shields and P. D. Gardner, J. Am. Chem. Soc., 89, 5425 (1967).
7. R. M. Babb and P. D. Gardner, manuscript submitted.