

STEREOSPECIFIC RETURN IN THE METHANOLYSIS OF PROPARGYLIC HALIDES.

REMOTE PHENYL DIRECTIVE EFFECT ON THE STEREOSELECTION OF CARBONIUM ION CAPTURE

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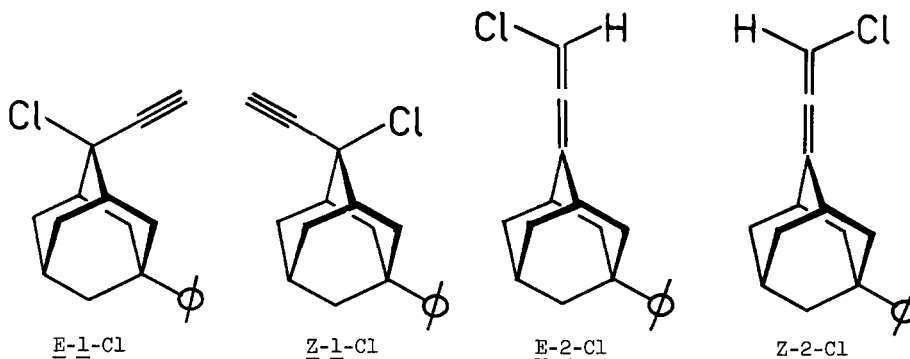
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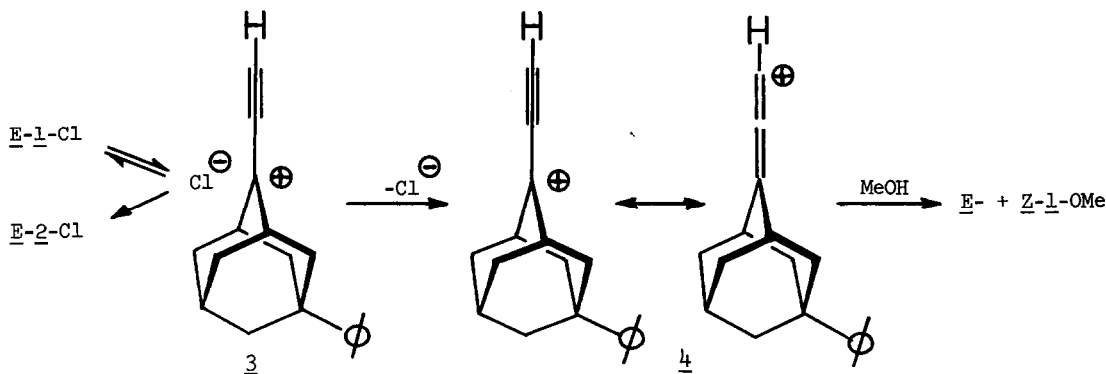
Summary: Product analysis in the methanolysis of an epimeric pair of propargyl chlorides shows that the solvolysis products arise from a common intermediate. The carbonium ion preferentially captures methanol on the Z-side by a 3:1 margin. The return products (the allenic isomers) are formed with complete retention.

Recent work by Schiavelli¹ concerning the solvolytic behavior of chiral haloallenes prompts us to report our related observations of the methanolysis of the geometrically isomeric propargylic chlorides 1. These compounds - as well as the allenic isomers 2 - have known configurations,² and mixtures are readily analyzed by means of HPLC.³



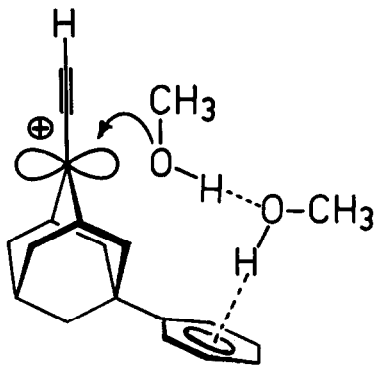
When a 0.003 M solution of E-1-Cl in 80% aqueous methanol is warmed in a sealed tube to $50.4 \pm 0.2^\circ$ for 120 hours, 40% of the solute has reacted; the product (>75% recovery) consists of a mixture of 15% E-1-OMe, 45% Z-1-OMe, and 40% E-2-Cl; no Z-2-Cl can be detected. Similarly, a solution of Z-1-Cl solvolyzes to the extent of 53% and gives a mixture of 16% E-1-OMe,

46% Z-1-OMe, and 38% Z-2-Cl. Shorter exposure times with these conditions leads to less solvolysis, but the product composition is the same. It was ascertained that neither the starting materials nor the product ethers interconvert under our conditions. The results can thus most economically be summarized by the statement that the solvolytic products obtain from a common intermediate, whereas the return products are formed completely stereospecifically, without any cross-over. The stereospecificity implicates an ion pair such as 3; the common intermediate is most probably the free carbonium ion 4.



A second point of interest emerging from our study is the very high ratio of the Z- to E- products. Evidently the phenyl group has a large effect. Conceivably, it may be able to orient surrounding solvent molecules by means of H-bonds in such a way as to favor Z- collapse.

A similar observation has been made with a 1-carboxyl group.⁴ Whatever the origin of this directive effect, however, it raises once again questions⁵ about the validity of the assumption that large groups in the 4- position of a cyclohexyl ring have no direct bearing on the axial to equatorial ratio of 1-substituents when they are used as a means to "lock" such rings against reversal.



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References and Footnotes

- (1) D. Scheffel, P. J. Abbott, G. J. Fitzpatrick, and M. D. Schiavelli, *J. Amer. Chem. Soc.*, **99**, 3769 (1977).
- (2) W. J. le Noble, D. M. Chiou, H. Małuszyńska, and Y. Okaya, *Tetrahedron Lett.*, 3865 (1977).
- (3) Base line separation of all four compounds was achieved, and calibration factors were determined; the details will be submitted in the full publication.
- (4) V. I. Lantvoev, *J. Org. Chem. USSR, Engl. Transl.*, **12**, 2292 (1976).
- (5) See e.g. J. L. Mateos, C. Perez, and H. Kwart, *Chem. Commun.*, 125 (1967).