The Stereochemistry of Homo-allenyl Participation

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IT has been established from kinetic evidence that the solvolysis of homo-allenyl arenesulphonates occurs through the double bond.[1] Also, the composition of the products resulting from such solvolyses varies markedly with substitution. Acyclic, cyclobutyl, and cyclopropyl derivatives can result simply by changing the position of substitution of a methyl group.[2] To account for these products, schemes involving both classical and non-classical ions have been suggested.[3] However, nothing has been reported concerning the stereochemistry of the participation process in the solvolysis step. We now report our preliminary findings.

Optically active, 4,5-hexadienyl toluene-*p*-sulphonate (I) mainly of the *S*-configuration was prepared,† and gently hydrolysed. Three products were obtained, racemic hexa-4,5-dien-2-ol (II) (28%), and *cis*- and *trans*-2-acetylmethylcyclopropane (III and IV) (70%). The cyclopropanes (III) and (IV) were formed in nearly equal amounts (33% and 37%). The *trans*-derivative (IV) was found to have retained more than 95% of the optical activity of the starting product during cyclisation. This ratio was found as follows. Compound (II) was hydrogenated to the corresponding optically active hexan-2-ol of known rotation,[4] and hence the optical purity of compound (I) was deduced. Similarly compound (IV) was oxidised to the corresponding *trans*-2-methylcyclopropane carboxylic acid.[5] Since the optical purity of (I) and (IV) was known, the retention of optical activity after reaction could be deduced. The absolute configuration of the *trans*-compound (IV) was established by conversion to the corresponding carboxylic acid which was then compared

† The corresponding alcohols have been separated by fractional recrystallisation, in acetone, of the brucine salts of the monophthalic ester.

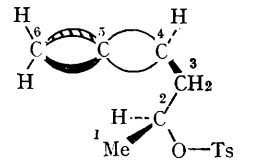
with the known (—)-*trans*-2-methylcyclopropanecarboxylic acid.[5] The carbon bearing the methyl group was found to have the *R*-configuration. Thus, it can be concluded that, for the *trans*-cyclized product, not only inversion of configuration occurs at the solvolysis carbon atom, but that the resulting configuration is retained in the cyclized product.‡

These results suggest that the hydrolysis of the homo-allenyl toluene-*p*-sulphonate (formation of *cis*- and *trans*-substituted cyclopropanes) takes place mainly through a pair of diastereoisomeric transition states. Clearly, one such state will involve internal nucleophilic attack by the C(4)–C(5) double bond at C(2) with inversion of configuration (I). Annihilation of the developing positive charge could either occur at C(5) during the participation process, or could take place later on the bicyclic non-classical ion (V) or the vinyl cation (VI).

The racemic non-cyclic product (II) does not require any special process for its formation as it involves a classical carbonium ion formation at C(2) in which the asymmetry is lost.

Finally, it should be emphasized that the distribution of charge in the bicyclic ion (V) and the subsequent reactivity of the latter may change on substitution. This fact is confirmed by experiment.

We thank Professor C. W. Jefford for useful discussions.

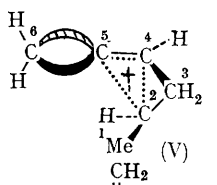


(I) (—)-(2*S*)

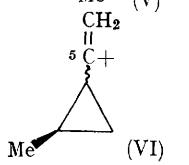
Ts= Toluene-*p*-sulphonyl

$CH_2{:}C{:}CH{\cdot}CH_2{\cdot}CHMe{\cdot}OH$

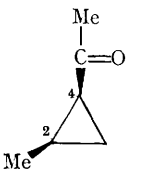
(II)



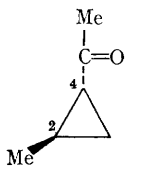
(V)



(VI)



(III) (+)-(4*S*:2*R*)



(IV) (—)-(4*R*:2*R*)

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‡ The absolute configuration of the *cis*-cyclized compound has not yet been determined, but is under investigation,

[1] R. S. Bly, A. R. Ballentine, and S. U. Koock, *J. Amer. Chem. Soc.*, **1967**, **89**, 6993; T. L. Jacobs and R. Macomber, *Tetrahedron Letters*, 1967, 4877.

[2] M. Bertrand and M. Santelli, *Compt. rend.*, 1964, **259**, 2251; *ibid.*, 1968, **266**, 231; M. Hanack and J. Haeffner, *Tetrahedron Letters*, 1964, 2191; *Chem. Ber.*, 1966, **99**, 1077.

[3] Cf. ref. 1 and footnote 17 therein.

[4] W. M. Foley, F. J. Welch, E. M. La Combe, and H. S. Mosher, *J. Amer. Chem. Soc.*, 1959, **81**, 2779.

[5] T. Sugita and Y. Inouye, *Bull. Chem. Soc. Japan*, 1966, **39**, 1075.