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The Stereochemistry of Fragmentation Reactions of Small Ring Heterocycles

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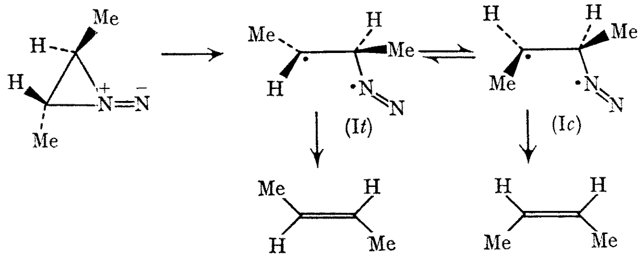
SINCE the Woodward and Hoffmann[1] selection rules predict a nonconcerted reaction for the decomposition of episulphones and the diazenes derived from aziridines whilst these processes occur stereospecifically,[2,3] Freeman and Graham[5] have suggested that the rules are inapplicable.[4] To equate stereospecificity with concertedness is not necessarily valid. Decomposition of an intermediate such as diradical (I*t*) (Scheme 1) could be faster than bond rotation.

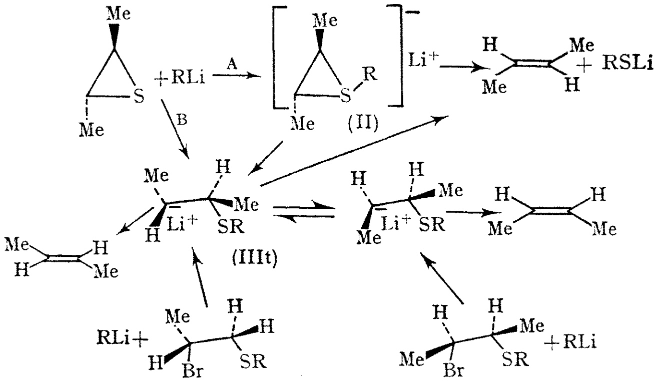


SCHEME 1.

For convenience only the effective geometry of the radical at carbon is pictured as planar.

One pathway for decomposition of a compound in which sulphur has expanded its valence shell to 10 electrons is extrusion of two ligands with concomitant bond formation between the ligands.[5] Desulphurization of episulphides by organolithium compounds is not completely stereoselective.[6] Orbital symmetry concepts predict that an intermediate such as (II) (Scheme 2) should decompose in a *concerted* disrotatory mode (mechanism A). The change in the correlation diagram arises from *d*-orbital participation in the episulphide decomposition. Alternatively, the lithium carbanion (III) could be formed and decompose to products at a rate competitive with bond rotation to account for the small loss of stereochemistry (mechanism B). We have reinvestigated the stereochemistry of this process and that of the decomposition of (III) generated independently but under conditions closely parallelling the episulphide decomposition.

cis- and *trans*-But-2-ene episulphide were generated by the method of Bordwell.[7] V.p.c. analysis† indicated the *trans*-episulphide to be free of any *cis*-compound; whereas, 0·6% *trans*-compound accompanied the *cis*-isomer. We were unable to detect any *cis*-but-2-ene from the *trans*-episulphide and obtained only 0·6% (after correction for isomeric impurity) *trans*-but-2-ene from the *cis*-episulphide (Table).



SCHEME 2.

Butene isomer distributions in n-butyl-lithium-induced decompositions.

Starting compound	*cis*- But-2-ene	*trans*- But-2-ene
cis-But-2-ene episulphide	98·8	1·2
trans-But-2-ene episulphide	—	100·0
threo-2-Bromo-3-ethylthiobutane . .	56·0	44·0
erythro-2-Bromo-3-ethylthiobutane	20·5	79·5

The *erythro* and *threo*-carbanions (III; R = Et) were generated from the corresponding bromides. *threo*-2-Bromo-3-ethylthiobutane was generated from *cis*-but-2-ene

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† A 20% silicone oil (low Corning 710) on chromosorb P column was employed. All analysis are ±0·1%.

and the *erythro*-isomer from *trans*-but-2-ene.[8] No intercontamination of these isomers could be detected by n.m.r. (*ca.* 1% would be detected). Initial metal halogen exchange, which proceeds with retention of configuration, produces the *erythro*- and *threo*-lithium salts from the corresponding bromides. Inversion of the carbanion and bond rotation competes with elimination, with considerable crossover in the products.[9] The intermediate carbanion can be trapped by methanol giving 2-butylthiobutane.

Since carbanions like (III) lose their stereochemical identity mechanism B for the organolithium-induced episulphide decomposition is eliminated. The trigonal bipyramid intermediate (II) appears to be formed and decomposes almost exclusively in a concerted fashion. The small amount of crossover in the *cis*-case presumably arises *via* a nonconcerted pathway. If the initial intermediate in this latter pathway is the *erythro*-carbanion (III*t*), the butene isomer ratio derived from this carbanion, implies a difference in transition-state energies of the concerted and nonconcerted process of only 2·0 kcal./mole. This assumption is based on edge co-ordination of the lithium cation with the carbon–sulphur bond to facilitate bond cleavage. Alternatively, co-ordination of the lithium with inversion of configuration at carbon produces the *threo*-carbanion: the butene isomer ratio then gives a transition-state energy difference of 4·0 kcal./mole.

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