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SODIUM-AMMONIA REDUCTION OF SOME CYCLIC VINYL BROMIDES

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Although Birch reduction is known to reduce vinyl halides to olefins[2-5], the mechanism of this reduction is not well understood. The present study of C-9 and C-13 cyclic vinyl bromides deals with the stereochemistry of the reduction and the potential pathway(s) through which the olefins arise. Our results are summarised in the TABLE.

TABLE

Cyclic Vinyl Bromide†	Na-NH_3 Product Composition (%)‡
1-Bromo-cis-cyclononene	cis-Cyclononene (100 %)
1-Bromo-trans,cis-1,5-cyclononadiene	cis,cis-1,5-Cyclononadiene (100 %)
1-Bromo-cis,cis-1,5-cyclononadiene	cis,cis-1,5-Cyclononadiene (100 %)
1-Bromo-cis-Cyclotridecene	cis-Cyclotridecene (>98 %)
1-Bromo-trans-Cyclotridecene	trans-Cyclotridecene (>98 %)

† Cyclic vinyl bromides were prepared by known procedures and were characterised thoroughly by elemental analyses and spectroscopic data.

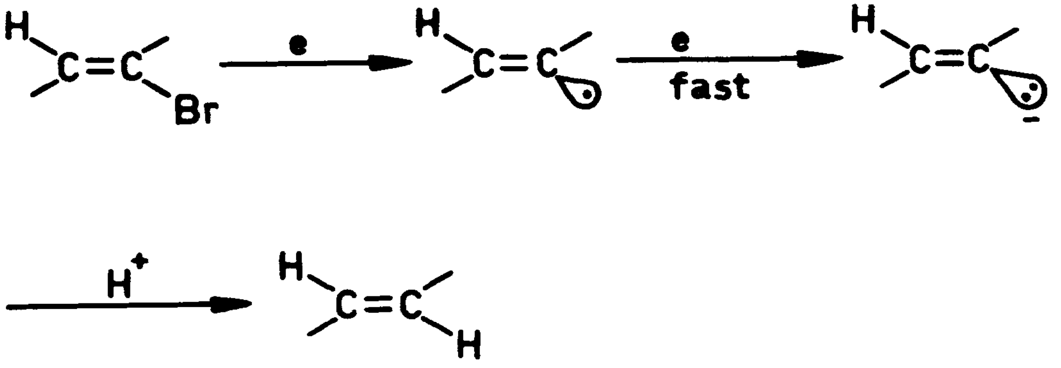
‡ Yields of the products were of the order 80-90 %. GLC analysis was used to find the percentage of geometrical isomers formed, and IR spectra of the GLC separated samples were compared with authentic samples.

All the reductions were performed in diethyl ether solvent using 5-g atom of sodium in liquid ammonia. Our results show that all the vinyl bromides have been reduced to olefins with high degree of retention in configuration except the strained system, 1-bromo-*trans*,*cis*-1,5-cyclononadiene which has undergone reduction with complete inversion. Our examination of reduction of 1-bromo-*trans*,*cis*-1,5-cyclononadiene with tri-n-butyltinhydride[6] gave a mixture of *trans*,*cis*-1,5-cyclononadiene and *cis*,*cis*-1,5-cyclononadiene in the ratio 1:2, while metallation with metal magnesium or n-butyllithium followed by protonation afforded only *cis*,*cis*-1,5-cyclononadiene. Furthermore, 1-bromo-*trans*-cyclotridecene underwent isomerisation to produce *ca*. 4o % of *cis*-cyclotridecene in the olefinic product when reduced with tri-n-butyltinhydride[6] or with a limited amount of sodium (2.2 g-atom) in liquid ammonia following inverse addition procedure.

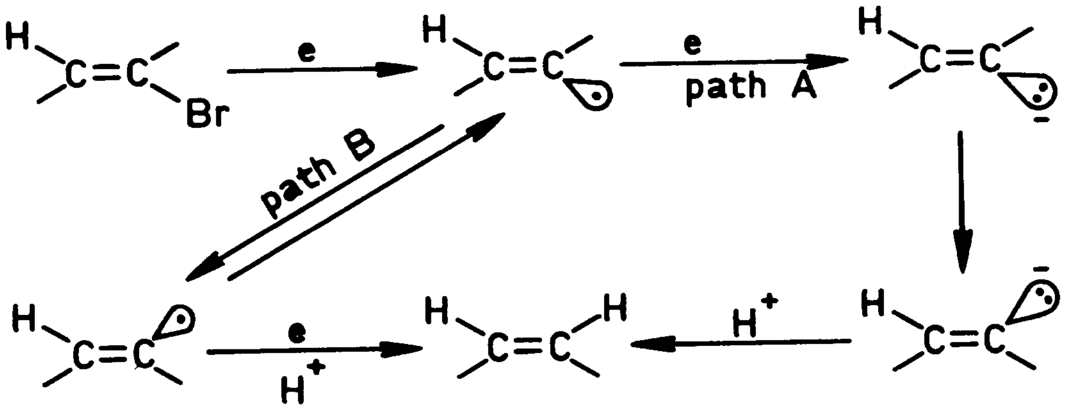
The SCHEME shows the suggested routes for the formation of olefins from strain-free and strained cyclic vinyl bromides.

SCHEME

For a strain-free vinyl bromide in excess of sodium:



For a strained vinyl bromide in excess of sodium:



Our results suggest that a vinyl bromide undergoes sodium-ammonia reduction stepwise to form vinyl radical and vinyl carbanion intermediates. In excess of sodium, the reduction of the vinyl radical from a strain-free vinyl bromide (trans or cis) must be faster than the equilibration with its geometrical isomer. This implies that the vinyl carbanion retains its configuration. In the case of a strained vinyl bromide such as 1-bromo-trans,cis-1,5-cyclononadiene, the trans-vinyl carbanion undergoes fast isomerisation to cis-vinyl carbanion prior to protonation (path A). The fast isomerisation observed could be due to the low activation energy value or high $-\Delta F$ value for the inversion of trans- to cis-isomer. However, the possible isomerisation of the initially formed trans-vinyl radical to cis-vinyl radical which can also give rise to cis-olefin via path B cannot be ruled out completely. Finally, we have excluded the possibility of initial isomerisation of 1-bromo-trans,cis-1,5-cyclononadiene to cis,cis-isomer prior to its reduction as the trans,cis-isomer recovered from incomplete reduction did not contain any significant amount of cis, cis-isomer.

Further work with C-1o and C-12 isomeric cyclic vinyl bromides, and also on the utility of these reactions in the stereospecific synthesis of trisubstituted cyclic olefins by alkylation of the intermediate carbanion species, is in progress.

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