Tetrahedron Letters No. 23, pp. 2075-2076, 1971. Pergamon Press. Printed in Great Britain.

ON THE STEREOCHEMISTRY AND THE MECHANISM OF SODIUM-AMMONIA REDUCTION OF CYCLIC ALLENES

R. Vaidyanathaswamy, G.C. Joshi and D. Devaprabhakara
Department of Chemistry, Indian Institute of Technology, Kanpur-16, India

(Received in UK 29 March 1971; accepted in UK for publication 5 May 1971)

Although Birch's reagent is known to reduce cyclic allenes to olefins,[1,2] the mechanism of this reduction is not well understood. The present study of sodium-ammonia reduction of C-9 to C-14 cyclic allenes deals with the stereospecificity of the reduction and also the potential path(s) through which the olefins arise. Our results are summarised in the TABLE.

TABLE

Cyclic allene	$Na-NH_3$ Product composition* (%)		$Na-NH_3-C_2H_5OH$ Product composition* (%)	
	cis	trans	cis	trans
1,2-Cyclononadiene	100	-	100	-
1,2-Cyclodecadiene	100	-	66	34
1,2-Cycloundecadiene	73	27	45	55
1,2-Cyclododecadiene	75	25	46	54
1,2-Cyclotridecadiene	50	50	17	83
1,2-Cyclotetradecadiene	27	73	14	86

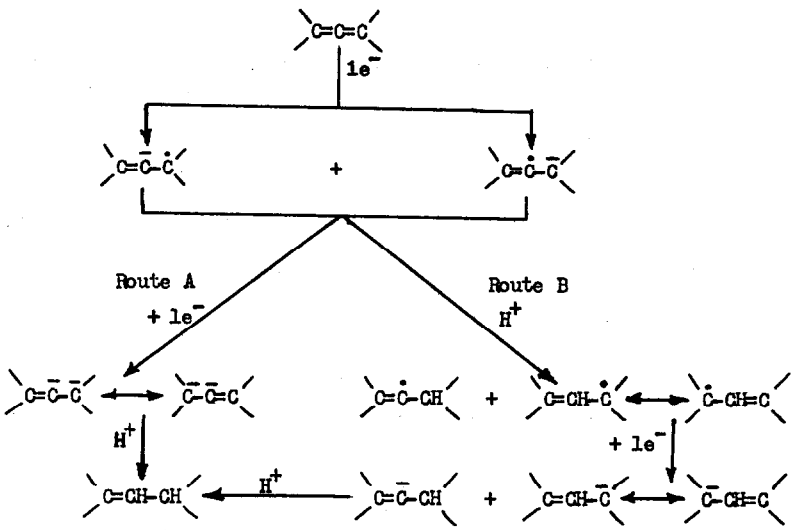
* Yields of the products were of the order 80-90%. GLC analysis was used to find the percentage of geometrical isomers formed, and the IR spectra of the GLC separated samples were compared with authentic samples. In the case of unknown products, elemental analyses and spectral properties were used for identification.

Analysis of the products after partial reduction, use of lithium instead of sodium and the relative rates of reduction of cyclic allenes and acetylenes rule out the possibility of the rearrangement of cyclic allene to acetylene before reduction.[3]

The SCHEME shows the possible routes (A and B) for the formation of olefins from allenes.

In the absence of a proton donor we favour route A and in its presence route B. The balance between the stability of the intermediates and the products determines the stereospecificity of the reduction. By experimental results[4,5] and theoretical calculations,[6] it has been

SCHEME



shown that cis-allylic anion is more stable than the trans-isomer, but the reverse is true with allylic radicals. This explains why there is more of trans-olefin in the presence of a proton donor as compared to its absence. The steady increase in the amount of trans-olefin from C-10 to C-14 alleneS can be explained on the basis of relative stabilities of isomeric olefins.[7]

Further work in this direction and the utility of this reduction in the stereoselective synthesis of cyclic trisubstituted olefins will be published later.

REFERENCES

1. P.D. Gardner and M. Narayana, J. Org. Chem., 26, 3518 (1961).
2. D. Devaprabhakara and P.D. Gardner, J. Am. Chem. Soc., 85, 648 (1963).
3. G. Nagendrappa, R.K. Srivastava and D. Devaprabhakara, J. Org. Chem., 35, 347 (1970).
4. S. Bank, J. Am. Chem. Soc., 87, 3245 (1965).
5. S. Bank, A. Schriesheim and C.A. Rowe, Jr., J. Am. Chem. Soc., 87, 3244 (1965).
6. R. Hoffmann and R.A. Olofson, J. Am. Chem. Soc., 88, 943 (1966).
7. A.C. Cope, P.T. Moore and W.R. Moore, J. Am. Chem. Soc., 82, 1744 (1960).