Tetrahedron Letters No. 16, pp 1411 - 1412, 1978. Pergamon Press. Printed in Great Britain.

AN UNUSUAL LITHIUM ALUMINUM HYDRIDE REDUCTION OF AN ISOLATED OLEFIN IN A 1,2-DIAMINE SYSTEM

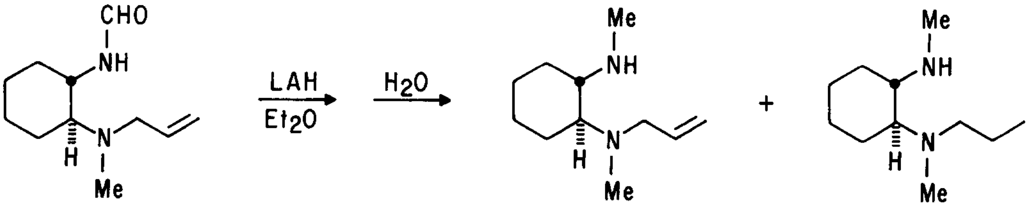
Jacob Szmuszkovicz*, John H. Musser,[1] and L. G. Laurian
Research Laboratories of The Upjohn Company, Kalamazoo, Michigan 49001

(Received in USA 12 December 1977; received in UK for publication 6 March 1978)

Neighboring group participation of oxygen in the mechanism of lithium aluminum hydride (LAH) reductions of carbon-carbon multiple bonds is well documented.[2-8] On the other hand, examples of nitrogen participation in these reductions are rare.[9,10]

We report here on the LAH reduction of an isolated olefin in a 1,2-diamine system.

The preparation of <u>trans</u>-N-allyl-N'-formyl-N-methyl-1,2-cyclohexanediamine (1, bp 116-118°, 0.3 mm) was accomplished by the reaction of 7-azabicyclo[4.1.0]heptane with N-allylmethylamine followed by treatment of ethyl formate. LAH reduction of 1 in diethyl ether at reflux temperature gave the mixture of 2 and 3 in 79% yield (bp 104-105°, 13mm). A 100 MHz spectrum in $CDCl_3$ showed a ratio of 62:38 (allyl to propyl). Further evidence for 2 and 3 was detected in the mass spectrum which showed ions [P^+: 184; P^+: 182] corresponding to both parents.



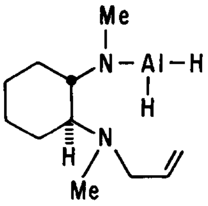
1 2 3

Two attempts were made to understand the mechanism of the transformation 1 ⟶ 3.

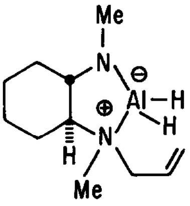
First, we prepared compound 2 by an independent route and subjected it to identical conditions used for the reduction of 1 in order to determine if the presence of oxygen covalently bonded to substrate is required for the formation of 3. Compound 2 was prepared in 51% yield by the reaction of 7-methyl-7-azabicyclo [4.1.0] heptane with N-allylmethylamine. LAH reduction of 2 gave 74% yield of a mixture of the starting material and compound 3 in a ratio of 83:17 as indicated by NMR integration.

Second, we have shown that N-allyl-N,N-dimethylamine was not reduced by LAH-Et$_2$O under the same conditions used for the reduction of 1.

Based on the foregoing information we suggest that the transformation 2 ⟶ 3 proceeds either through a covalent intermediate A in which only the secondary amine is involved, or through a charged intermediate B involving both nitrogens.



A



B

In conclusion, the transformation 2 ⟶ 3 represents an unusual example of a LAH reduction of an isolated double bond in a 1,2-diamine system.

References

1. Post-doctoral Research Associate, The Upjohn Company, 1976-1977.
2. B. Franzus and E. I. Snyder, J. Am. Chem. Soc., 87, 3423 (1965).
3. E. I. Snyder, J. Org. Chem., 32, 3531 (1967).
4. M. J. Jorgenson and A. F. Thacher, Chem. Commun., 973 (1968).
5. M. J. Jorgenson and A. F. Thacher, Chem. Commun., 1290 (1969).
6. W. T. Borden, J. Am. Chem. Soc., 92, 4898 (1970).
7. R. Baudouy and J. Gore, Tetrehedron, 31, 383 (1975).
8. B. Chantegrel and S. Gelin, Bull. Soc. Chim. France, 2639 (1975).
9. A. P. Marchand and R. W. Allen, Tetrahedron Lett., 67 (1975).
10. S. Jolidon and H. J. Hansen, Helv. Chim. Acta, 60, 978 (1977).