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MASKED REARRANGEMENTS IN THE TRIETHYLSILANE-BORON TRIFLUORIDE REDUCTION OF TRANS-STILBENE OXIDE TO 1,2-DIPHENYLETHANE

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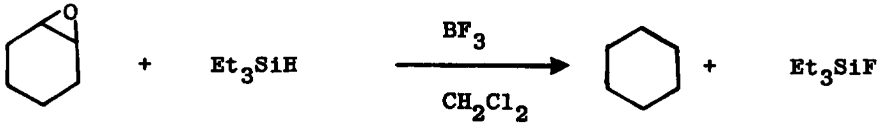
Recent studies have shown that organosilicon hydrides and gaseous boron trifluoride together form a powerful yet selective system for reducing oxygen-containing organic compounds to the corresponding hydrocarbons. Dichloromethane solutions of triethylsilane and many alcohols,[1] aldehydes,[2] and ketones[2] undergo reaction in a short time at room temperature or below upon admission of boron trifluoride. We wish to report here that epoxides are also reduced to hydrocarbons under these conditions, although at a considerably slower rate than exhibited by alcohols or carbonyl compounds under comparable conditions.

In a typical experiment, a dichloromethane (0.50 mL) solution of cyclohexane oxide (0.25 mmol) and triethylsilane (1.00 mmol) was placed in an NMR tube, chilled to 0 °C, and saturated with scrubbed BF_3 gas[3] over a 5-min period. The tube was then stoppered and allowed to stand at 20 °C. After one hour, only a trace of cyclohexane could be observed by NMR; however, periodic observation of the NMR spectrum showed the slow formation of cyclohexane over a period of several weeks. By way of contrast, cyclohexanone similarly treated was completely converted into cyclohexane within one hour.

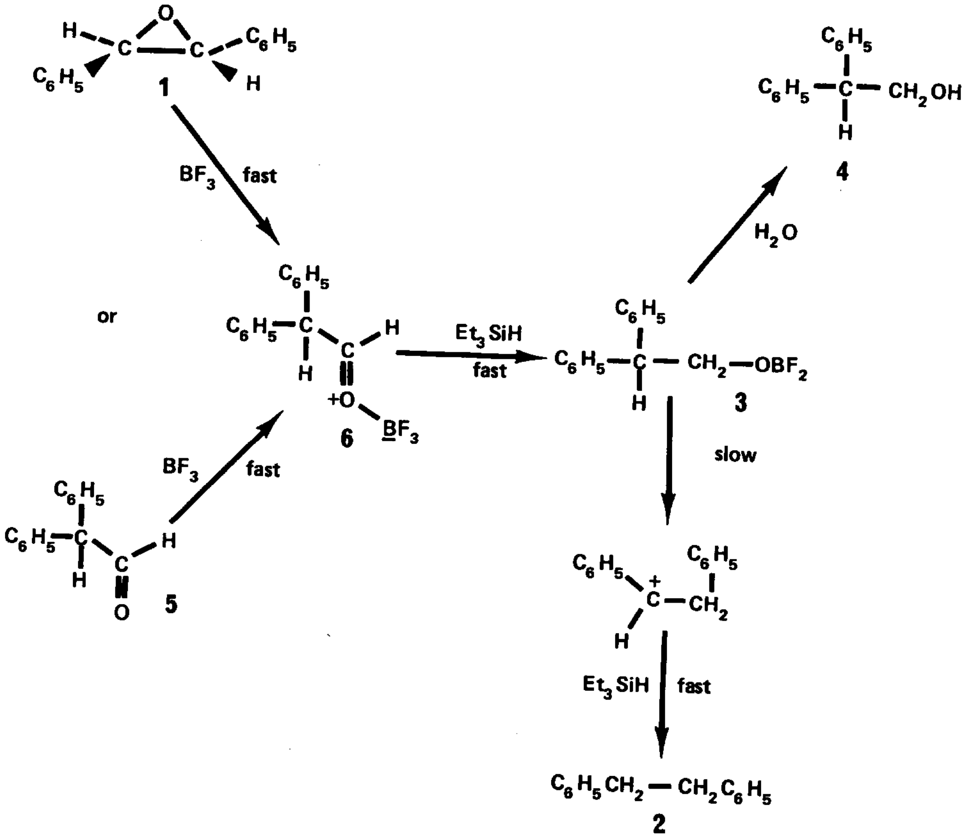


In a similar NMR experiment performed at 20 °C (CD_2Cl_2), *trans*-stilbene oxide (1) [δ 7.38 (10 H, s), 3.93 (2 H, s)] was transformed smoothly and quantitatively into 1,2-diphenylethane (2) [δ 7.25 (10 H, s), 3.00 (4 H, s)] at a rate having a half-life of approximately 24 hr. On a small preparative scale, a solution of 0.50 g (2.6 mmol) of *trans*-stilbene oxide and 1.19 g (10.2 mmol) of triethylsilane in 5 mL of dichloromethane was placed in a 10 mL flask, chilled to 0 °C, saturated with BF_3 gas, sealed and stirred at 20 °C for 7 days. Workup with saturated aqueous NaCl followed by solvent removal yielded 0.47 g (100%) of 1,2-diphenylethane which was pure by NMR.

Further investigation of this reaction revealed clearly that this seemingly simple reduction does, in fact, proceed by way of multiple phenyl migrations. The NMR spectrum of the reaction mixture taken only a few minutes after the BF_3 gas was introduced revealed the presence of but a single non-silicon-containing organic intermediate which is the species which slowly forms product 2. This reaction intermediate has NMR signals at δ 7.30 (10 H, s) and 4.49 (3 H, m). When quenched with water, it quantitatively produced 2,2-diphenylethanol (4) [δ 7.23 (10 H, s), 4.17 (3 H, s), 1.67 (1 OH, s)], consistent with the structure and expected chemical behavior of the difluoroborate ester 3.

Additional information on the nature of this reaction was obtained when it was observed that treatment of either epoxide 1 *or* 2,2-diphenylethanal (5) [δ 9.95 (1 H, d, J = 2 Hz), 7.30 (10 H, br s), 4.90 (1 H, d, J = 2 Hz)] with BF_3 gas produced immediately and quantitatively the identical BF_3 adduct 6 [δ 9.90 (1 H, d, J = 3.5 Hz), 7.57 - 7.13, most prominent at 7.40 (10 H, m), 5.48 (1 H, d, J = 3.5 Hz)].[4] Subsequent treatment of 6 from either source (1 or 5) with triethylsilane led instantly to the formation first of intermediate 3 and finally to product 2.

The reaction mechanism which evolves from these observations is summarized in Scheme 1.[5]



Scheme 1

References and Footnotes:

1. M. G. Adlington, M. Orfanopoulos, and J. L. Fry, *Tetrahedron Lett.*, 2955 (1976).
2. J. L. Fry, M. Orfanopoulos, M. G. Adlington, W. R. Dittman, Jr., and S. B. Silverman, *J. Org. Chem.*, **43**, 374 (1978).
3. See footnote 9, ref. 2.
4. The formation of this adduct is not surprising in view of the known rearrangement of **1** to **5** upon treatment with boron trifluoride etherate in either ether or benzene solvent: H. O. House, *J. Am. Chem. Soc.*, **77**, 3070 (1955).
5. This work was supported by a grant from The University of Toledo Faculty Research Awards and Fellowships Program. We thank M. Orfanopoulos for performing a preliminary experiment.

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