Tetrahedron Letters,Vol.24,No.43,pp 4711-4712,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

DIISOBUTYLALUMINUM HYDRIDE
A NOVEL REAGENT FOR THE REDUCTION OF OXIMES

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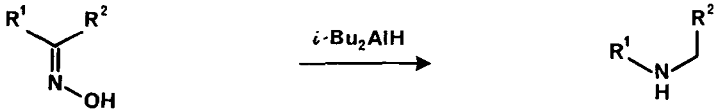
Summary: A simple procedure for converting oximes to rearranged secondary amines is described.

Although the direct transformation of oximes to rearranged secondary amines is an important synthetic operation, it has never been developed to a useful level due to the lack of a satisfactory reagent for selectivity. For example, the lithium aluminum hydride (LAH) reduction of oximes is known to produce the corresponding primary amines, isomeric secondary amines, and aziridines depending on the nature of oxime substrates and the reduction conditions.[1~3] During an investigation into the chemistry of tandem Beckmann rearrangement-alkylation sequence,[4] we have found a simple and highly convenient procedure for obtaining secondary amines exclusively from oximes[5] by the use of diisobutylaluminum hydride (DIBAH) (eq 1).

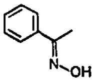
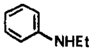
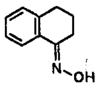
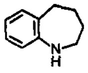
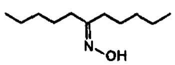
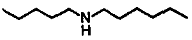
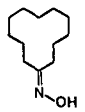
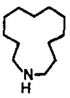
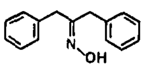
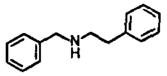
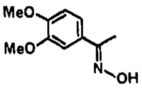
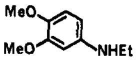


(1)

A typical experimental procedure follows. DIBAH (5 mL of a 1 M hexane solution, 5 mmol) was added dropwise to a solution of acetophenone oxime (135 mg, 1 mmol) in dry CH_2Cl_2 (10 mL) at 0°C, and the mixture was stirred at 0°C for 2 h. Then the reaction was quenched by dilution with CH_2Cl_2 (~20 mL), followed by successive treatment with sodium fluoride (840 mg, 20 mmol) and water (0.27 mL, 15 mmol). Vigorous stirring of the resulting suspension was continued at 0°C for 30 min. Filtration, washing with CH_2Cl_2, and removal of solvent left a colorless oil, which was subjected to column chromatography on silica gel (ether-hexane, 1:3) to give N-ethylaniline (111 mg, 92% yield).

Several examples are listed in Table I. A striking feature of the reaction is the general applicability to a wide variety of oxime substrates,[6] particularly aliphatic ketoximes, which normally provide the primary amines almost exclusively by usual aluminum hydride type reagents.[1] Notably, the reduction of 1,3-diphenylacetoxime afforded solely the rearranged secondary amine (entry 5). This lies in sharp

Table I. Reduction of Oximes with Diisobutylaluminum Hydride[a]

entry	oxime	conditions temp (°C), time (h)	product	yield (%)[b]
1		0, 2		92
2		0, 1; 20, 2		92
3		0, 1; 20, 2		85
4		0, 1; 20, 2		70
5		0, 1; 20, 2		71
6		0, 3		74

a) Reaction was performed on a 1–2 mmol scale using 5 equiv of DIBAH. b) Isolated yield.

contrast to the reduction by LAH which provides 2-benzyl-3-phenylaziridine predominantly.[3,7]

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5. With the exception of aliphatic oximes substantial amounts of rearranged amine have been obtained only from aromatic ketoximes, when an electrophilic "mixed hydride" prepared from LAH and aluminum chloride was employed. See ref 1.
6. Neither primary amines nor aziridines were detected by TLC analysis.
7. This work was supported in part by a grant from the Ministry of Education, Japanese Government (Grant-in-aid, No. 118006) and the Toyo Stauffer Chemical Co., Ltd.

(Received in Japan 4 July 1983)