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SELECTIVE REDUCTION OF OXIMES WITH PYRIDINE-BORANE[1)]

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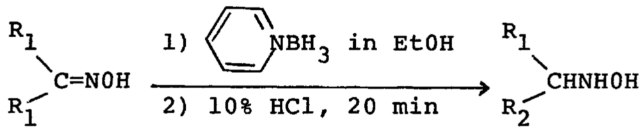
Pyridine-borane, which was readily prepared from pyridine hydrochloride and sodium borohydride, reduced oximes to the corresponding hydroxylamines in good yields with simple procedure. Other functional groups (ester, nitrile, nitro, amide, and halide) present in the same molecule of oximes were not reduced by this reagent.

The most useful methods for the preparation of hydroxylamines involve the reduction of oximes with diborane[2)] or with sodium cyanoborohydride.[3a)] Nevertheless, in the case of the diborane reduction, a careful performance under restricted conditions is necessary to obtain the desired hydroxylamines without over-reduction.[3a)] Cyanoborohydride, on the other hand, reduces oximes to hydroxylamines with no trace of over-reduction products, but the reduction of aldoximes is extremely pH-dependent.[3a,b)]

We wish to report that pyridine-borane,[4)] a weak reducing agent,[5)] can reduce oximes in good yields with simple procedure as presented in the table. A typical procedure is as follows: a mixture of benzylacetone oxime (1c) (2 mmol, 326 mg) and pyridine-borane (10 mmol, ca. 1 ml) in ethanol (4 ml) was kept below 5°. To this mixture, 10% HCl solution[6)] (10 ml) was added dropwise and the mixture was stirred for 20 min at room temperature. The solution was made alkaline with NaOH pellets with cooling, and extracted with benzene (20 ml x 3). The combined benzene extract was dried over anhydrous Na_2SO_4. After evaporation of benzene, the crystalline residue was purified by column chromatography (Polyamide-C 200,[7)] benzene for elution) to give 2c (304 mg, mp 71.5-74°, yield 92%), which was recrystallized from hexane (mp 74-75°. Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48%. Found: C, 72.52; H, 8.89; N, 8.40%).

The characteristic feature of this reduction is that oximes are reduced selectively to the corresponding hydroxylamines without reduction of other functional groups (ester, nitrile, nitro, amide, and halide) which are present in the same molecule. As pyridine-borane has not an ability to reduce further the resulting hydroxylamines, this procedure will offer a simple and versatile route for the reliable synthesis of hydroxylamines. Studies on the scope and limitation of this reduction on other oxime derivatives are in progress.

Table



1 2

1	R_1	R_2	Yield of $2^{a)}$ (%)
a	C_6H_5	H	87
b	C_6H_5	$CH_3CH_2CH_2$	91
c	$C_6H_5CH_2CH_2$	CH_3	92
d	$CH_3CH_2CH_2$	$CH_3CH_2CH_2$	91
e	m-NO_2-C_6H_4	H	91
f	p-CH_3O_2C-C_6H_4	H	74
g	p-NC-C_6H_4	H	85
h	p-Cl-C_6H_4	H	92
i	p-$(CH_3)_2NCO$-C_6H_4	H	88

a) Consistent elemental analyses and spectral data were obtained for all new compounds.

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References and Notes

1) Part I, Y. Kikugawa, J. Chem. Res.(S), 1977, 212.
2) H. Feuer, B. F. Vincent, Jr., and R. S. Bartlett, J. Org. Chem., 30, 2877 (1965).
3) a) R. F. Borch, M. D. Bernstein, and H. D. Durst, J. Amer. Chem. Soc., 93, 2897 (1971); b) C. F. Lane, Synthesis, 1975, 135.
4) Pyridine-borane is stable in air and only slightly hydrolyzed by water. It can be stored for a few months without particular care for this reduction.
5) R. P. Barnes, J. H. Graham, and M. D. Taylor, J. Org. Chem., 23, 1561 (1958).
6) Pyridine-borane cannot reduce oximes without acid. Mechanistic study of this reduction is under way.
7) Hydroxylamines are unstable and decompose on silica gel or Florisil.

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