

12. A 9 : 1 mixture of 1,2- and 2,4-isopropylidenebutane-1,2,4-triol was used. Meyers, A. I.; Lawson, J. P. *Tetrahedron Lett.* **1982**, *23*, 4883-4886.
13. The isomeric ratios of oxazolines and dihydro-1,3-oxazines were the same as those of aziridines.
14. The product generated from the hydride attack to aziridine **19** was formed in 10% yield (*i.e.* R=H).
15. All new compounds showed satisfactory spectral data.

Chemoselective Reduction of Carbonyl Compounds with Diisobutylethoxyalane

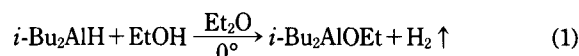
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Received November 30, 1995

Very recently, we reported that diisobutylchloroalane (*i*-Bu₂-AlCl) is a highly selective reducing agent for the competitive reduction between carbonyl compounds¹ and for the 1,2-reduction of α,β -unsaturated carbonyl compounds.² In continuation of our efforts to explore new reducing systems for such transformations, we prepared a series of diisobutylalkoxyalane (*i*-Bu₂AlOR) and examined the reducing action toward general organic functional groups. In the course of this systematic investigation, we found that the ethoxy derivative, diisobutylethoxyalane (*i*-Bu₂AlOEt), reduces aldehydes in a fast rate but ketones only slowly. Accordingly, we applied this reagent for the competitive reduction between carbonyl compounds. Herein, we report the results for such selective reduction by *i*-Bu₂AlOEt in ethyl ether.

The reagent can be readily prepared by alcoholysis of diisobutylaluminum hydride (*i*-Bu₂AlH) in ether solution (Eq. 1). The reagent is effective for the reduction of aldehydes and ketones at 25°. As in the case of *i*-Bu₂AlCl,^{1,2} the reduction with *i*-Bu₂AlOEt involves hydride shift from the β -carbon atom of isobutyl group.



The reduction of representative aldehydes and ketones with 10% excess reagent at 25° in ethyl ether is listed in Table 1. Aldehydes are reduced readily in less than 1 or 3 h, while ketones are reduced slowly requiring 48 hrs for completion.

The chemoselectivity of this reagent was tested with twenty-four representative pairs in competition experiments. Equimolar amounts of two compounds were allowed to compete for a limited quantity of *i*-Bu₂AlOEt (1 equivalent). A standard solution of the reagent (*ca.* 1 M) in ethyl ether was added to the equimolar mixture of two compounds (*ca.* 1 M in each compound) in ethyl ether maintained at 25°.

Table 1. Reduction of Representative Aldehydes and Ketones with Diisobutylethoxyalane in Ethyl Ether at 25 °C^a

Compound	Product	Time (h)	Yield (%) ^b
Butanal	1-Butanol	1.0	96
		3.0	100
Benzaldehyde	Benzyl alcohol	0.5	98
		1.0	100
2-Butanone	2-Butanol	24	90
		48	100
Acetophenone	1-Phenyl ethanol	24	95
		48	100

^aTen % excess reagent was utilized. Reaction mixtures were *ca.* 1 M in substrates. ^bDetermined by GC using internal standard.

Table 2. Chemoselective Reduction of Carbonyl Compounds with Diisobutylethoxyalane in Ethyl Ether at 25 °C^a

Entry	Starting mixture	Time (h)	Ratio of redn products ^b
1	Butanal/Hexanal	12	60 : 40
2	Butanal/Benzaldehyde	3	5 : 95
3	Butanal/Anisaldehyde	6	95 : 5
4	Hexanal/Benzaldehyde	3	2 : 98
5	Hexanal/Anisaldehyde	6	92 : 8
6	Benzaldehyde/Anisaldehyde	3	99.5 : 0.5
7	Butanal/Cyclohexanone	6	100 : 0
8	Hexanal/Cyclohexanone	6	100 : 0
9	Hexanal/2-Heptanone	6	100 : 0
10	Hexanal/Acetophenone	6	100 : 0
11	Hexanal/Benzophenone	6	100 : 0
12	Anisaldehyde/Cyclohexanone	12	99 : 1
13	Cyclohexanone/2-Heptanone	24	100 : 0
14	Cyclohexanone/Acetophenone	24	95 : 5
15	Cyclohexanone/Benzophenone	24	100 : 0
16	Acetophenone/2-Heptanone	48	100 : 0
17	2-Heptanone/Benzophenone	96	95 : 5
18	Acetophenone/Benzophenone	48	100 : 0
19	Cyclohexanone/Cyclopentanone	24	90 : 10
20	Hexanal/Hexanoyl Chloride	6	100 : 0
21	Hexanal/Benzoyl Chloride	6	100 : 0
22	2-Heptanone/Benzoyl Chloride	96	99 : 1
23	Hexanal/Hexanenitrile	6	100 : 0
24	Hexanal/Ethyl Hexanoate	6	100 : 0

^aReaction mixtures were *ca.* 1 M in substrates. One equivalent of reagent was utilized for competitive reduction of equimolar mixture of two carbonyl compounds. ^bNormalized ratio determined by GC with appropriate internal standard; the total yields of product alcohols were \geq 99%.

After appropriate time intervals, the mixture was hydrolyzed with 3 N HCl. The results obtained by GC analysis of the reaction mixture with an internal standard are summarized in Table 2.

Both aliphatic and aromatic aldehydes examined are selec-

tively reduced in the presence of ketones (Entries 9-11): a wide variety of aldehydes is selectively reduced in the presence of a more reactive ketone, cyclohexanone (Entries 7, 8 and 12). Even more remarkable is the chemoselective discrimination between aldehydes. Thus, benzaldehyde can be selectively reduced in the presence of hexanal (Entries 2 and 4) or anisaldehyde (Entries 6). Hexanal is much more reactive than anisaldehyde toward this reagent (Entries 3 and 5). Furthermore, the reagent can discriminate between structurally different ketones (Entries 13-18). Even cyclohexanone can be selectively reduced in the presence of cyclohexanone in a 90:10 selectivity (Entry 19). In addition, various representative functional groups, such as ester, lactone, amide, nitrile, alkene, alkyne, and anhydride, are not affected by *i*-Bu₂AlOEt. Furthermore, even acid chlorides are inert to the reagent. Such a remarkable inertness toward most of the reducible functional groups, combined with a high selectivity for the reduction of aldehydes and ketones, has already been realized with *i*-Bu₂AlCl.^{1,2} However, the reducing power of *i*-Bu₂AlOEt is much weaker than that of *i*-Bu₂AlCl and, hence, seems to be more applicable for such transformations in complex molecules.

Acknowledgment. This study was supported by the Yeungnam University research grants in 1995.

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