

Competitive Reduction of Aldehyde-Ketone Mixtures by Complex Hydroborates and Hydroaluminates

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Abstract

Lithium tri-*t*-butoxyhydroaluminate, sodium tetrahydroborate and lithium tetrahydroborate, in stoichiometric amounts, reduce benzaldehyde in the presence of acetophenone or butanal in the presence of butanone. Lithium tetrahydroaluminate and lithium cyanatohydroborate are less selective.

Although all the common complex hydroborates and hydroaluminates are capable of reducing both aldehydes and ketones, Brown *et al.*¹ have shown that sodium tetrahydroborate reduces benzaldehyde about 400 times faster than acetophenone. It was decided to carry out some experiments to determine whether or not such a rate difference is more general and can be used to produce reduction of an aldehyde group selectively in the presence of a ketone.

Equimolar amounts of aldehyde and ketone were treated with one equivalent of hydride and the ratio of primary to secondary alcohol formed estimated by gas chromatographic analysis. Experiments were carried out on five reductants using butanal-butaneone and benzaldehyde-acetophenone mixtures. The results are listed in Table 1.

Table 1. The ratios of alcohols in the product mixture with various reductants

Hydride reductant	Butan-1-ol/ butan-2-ol	Benzyl alcohol/ 1-phenylethanol
Lithium tri- <i>t</i> -butoxyhydroaluminate	99 : 1	100 : 0
Sodium tetrahydroborate	96 : 4	100 : 0
Lithium tetrahydroborate	87 : 13	87 : 13
Lithium tetrahydroaluminate	63 : 37	69 : 31
Lithium cyanatohydroborate	62 : 38	91 : 9

As one would expect on electronic grounds, the degree of selectivity of the reductant was found to decrease in the order $\text{LiAlH}(\text{OBu}^t)_3$, NaBH_4 , LiBH_4 , LiAlH_4 . The enhanced selectivity in the benzaldehyde/acetophenone mixture is, no doubt, due to the lower reactivity of aryl carbonyl groups.

¹ Brown, H. C., Wheeler, O. H., and Ichikawa, K., *Tetrahedron*, 1957, 1, 214.

Lithium cyanatohydroborate was expected to be much more selective because of the observations of Drefahl and Keil² that it would reduce aldehydes but not ketones. A more recent paper³ on lithium cyanatohydroborate demonstrates that its reducing properties are very pH-dependent and so it is possible that in Drefahl and Keil's work acidic impurities in the aldehydes, which are not present in ketones, were catalysing the reduction. In support of this, butanone, which was unaffected by LiBH_3CN in the presence of potassium hydrogen carbonate, was 45% reduced after an hour when a trace of butyric acid was added to the reaction mixture.

Experimental

General

The g.l.c. machine used was a Varian series 1700 Aerograph with a 6-ft 3% SE-30 column, a column temperature of 80° and a gas flow rate of 100 ml helium/min. The product peaks were identified by comparison of the retention times with those of authentic samples and their relative areas corrected for detector response by comparison with those of standard mixtures of authentic samples. The aldehydes and ketones were freshly distilled and the tetrahydrofuran was distilled from lithium tetrahydroaluminate immediately before use. The reductants used were commercial samples apart from lithium cyanatohydroborate which was prepared by the method of Wittig and Raff.⁴

Reduction Procedure

Hydride reducing agent (0.02 mol of available H^-) in tetrahydrofuran* (10 ml) was added to a mixture of aldehyde (0.02 mol) and ketone (0.02 mol) in tetrahydrofuran (20 ml). The resultant solution was stirred at 25° for 1 h then poured into 2N hydrochloric acid (25 ml) and extracted with ether (3 × 10 ml). The extracts were washed with water then brine and dried (MgSO_4). The solution was then concentrated and examined by g.l.c.

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* This was replaced by an equal volume of absolute ethanol in the case of sodium borohydride.

² Drefahl, G., and Keil, E., *J. Prakt. Chem.*, 1958, 6, 80.

³ Borch, R. F., Bernstein, M. D., and Durst, H. D., *J. Amer. Chem. Soc.*, 1971, 93, 2897.

⁴ Wittig, G., and Raff, P., *Justus Liebigs Ann. Chem.*, 1951, 573, 202.