

## Methylal as a Solvent in Lithium Aluminium Hydride Reductions

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The number of solvents used in lithium aluminium hydride reductions is very limited and only one of them — diethyl ether — has found more general use. Tetrahydrofuran has proved quite a good medium and a few other solvents such as di-*n*-butyl ether, N-ethyl-morpholine, bis ( $\beta$ -ethoxyethyl)ether (diethyl carbitol) and dioxan have been used for special purposes.

In the course of some other work the need arose for a lowboiling solvent with solvent properties differing from those of diethyl ether. It seemed that methylal (formaldehyde dimethyl acetal), well known as an excellent solvent for a number of organic substances, was a suitable choice. The nonreduction of the acetal group by lithium aluminium hydride has been established by Prins<sup>1</sup>, Julian, Meyer and Ryden<sup>2</sup> and Marwel and Hill<sup>3</sup>. The low boiling point of methylal (42°) allows the rapid removal of the solvent from the products and makes it less apt to cause rearrangements. As a solvent it is superior to diethyl ether in a great many instances. *E. g.* does it dissolve to an appreciable extent polycarboxylic acids and polycarbonyl compounds. Glycols and other polyhydric alcohols which often are the reaction products in the reductions concerned are also generally more soluble in methylal than in ether and thus the isolation of products is facilitated. Another advantage is that the set-up with a Soxhlet or continuous extractor often can be omitted. (For experimental details in general

see Brown, W. G. *Organic Reactions* 6 (1951) 469.)

Like acetals in general methylal is stable towards alkaline aqueous solutions but is rapidly hydrolyzed by acid solutions especially by mineral acids. This would seem to be a serious drawback in the use of methylal as the aluminium hydroxide formed in the decomposition of the intermediate compounds by water very often is dissolved in dilute sulphuric acid. If, however, the reaction products are stable towards alkali the aluminium hydroxide may be dissolved in dilute aqueous sodium hydroxide. Otherwise it may be dissolved in a solution of sodium potassium tartrate. As mentioned below it is in some cases not necessary to dissolve the hydroxide at all.

The total solubility of lithium aluminium hydride in methylal has not been determined but on refluxing a slurry of the hydride for four hours and clarifying the resulting solution by sedimentation a reagent was obtained containing 5.6 g hydride per 100 g methylal, *i. e.* about a 1.3 *M* solution. This concentration is usually more than adequate for normal purposes. In practice, however, it is more convenient to use a slurry as is the case when ether is the solvent.

A few reductions which we have performed in order to determine the yields are listed in Table 1.

As will be seen the yields are about the same as when the reduction takes place in diethyl ether. It should be mentioned in this connection that methylal apparently has good solvent characteristics for the intermediate metal complexes, a fact which contributes to the good overall yields. It seems therefore safe to recommend methylal as a solvent for lithium aluminium hydride reductions especially in those cases where reactants or products are sparingly soluble in ether.

The methylal used was purified in the following way: A good commercial grade

Table 1.

Reactant	Product	Per cent yield	
		in methylal	in ether
Anthranilic acid	<i>o</i> -Aminobenzyl alcohol	95	97 <sup>4</sup>
Phenylacetic acid	$\beta$ -Phenylethyl alcohol	98—99	92 <sup>4</sup>
Phthalic anhydride	Phthalyl alcohol	99—100	87 <sup>5</sup>
Adipic acid	Hexanediol-1,6	78	Not reported
Sorbic acid	Sorbyl alcohol	92	92 <sup>4</sup>
Cyclopentanone	Cyclopentanol	92	85 <sup>6</sup>
Benzamide	Benzylamine	82	85 <sup>7</sup>

methylal was distilled through a 40 cm Widmer column rejecting head and tail fractions. The distillate was treated overnight with metallic sodium and thereafter refluxed for four hours with freshly cut sodium. Finally it was treated with a small amount of lithium aluminium hydride and distilled through the Widmer column, again rejecting small head and tail fractions.

A typical reduction was performed as follows: 0.01 mole of the substance to be reduced was dissolved in 50 ml methylal. This solution was added to a briskly stirred slurry of lithium aluminium hydride (the calculated amount with 100 % excess) in 25 ml methylal at a rate so as to keep the reaction mixture in gentle reflux. Thereafter was refluxed for one hour, cooled and the excess hydride decomposed by cautiously adding water. A further amount of water was added dropwise until a granular white mass had formed at the bottom of the flask. The methylal layer was decanted and the residue extracted with

further amounts of methylal. The extracts were collected, dried with anhydrous sodium sulphate and the solvent distilled off. Usually the residue consisted of a very pure reduction product having nearly the correct melting point or refractive index.

1. Prins, D. A. *J. Am. Chem. Soc.* **70** (1948) 3955.
2. Julian, P. L., Meyer, E. W. and Ryden, I. *Ibid.* **71** (1949) 756.
3. Marwel, C. S. and Hill Jr., H. W. *Ibid.* **73** (1951) 481.
4. Nystrom, R. F. and Brown, W. G. *Ibid.* **69** (1947) 2548.
5. Nystrom, R. F. and Brown, W. G. *Ibid.* **69** (1947) 1197.
6. Roberts, J. D. and Sauer, C. W. *Ibid.* **71** (1949) 3925.
7. Matlow, unpublished work. See *Organic Reactions* **6** (1951) 479.

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