LITHIUM TRI-*t*-BUTOXYALUMINOHYDRIDE—A NEW REAGENT FOR CONVERTING ACID CHLORIDES TO ALDEHYDES

Sir:

Lithium aluminum hydride in ether solution reacts readily with four moles of methyl, ethyl or isopropyl alcohol to liberate four moles of hydrogen. In the case of *t*-butyl and *t*-amyl alcohols only three moles of hydrogen are evolved at room temperature, even in the presence of excess alcohol.

$$3t\text{-BuOH} + \text{LiAlH}_4 \longrightarrow \text{Li}(t\text{-BuO})_3\text{AlH} + 3\text{H}_2$$

Lithium tri-*t*-butoxyaluminohydride precipitates from the ether as a white, finely-divided solid. It is very stable. Samples have been sublimed at 360° at low pressures without significant decomposition. It is soluble in tetrahydrofuran and the dimethyl ether of diethylene glycol (diglyme) forming solutions of 1.2 *M* and 1.3 *M* at 25°, respectively. In these solvents it exhibits a much milder reducing behavior than lithium aluminum hydride. Thus, at 0° it reduces aldehydes, ketones, and acid chlorides, but fails to react with esters and nitriles.

We have discovered that at low temperatures lithium tri-*t*-butoxyaluminohydride in tetrahydrofuran or diglyme solution serves as a convenient reagent for the reduction of acid chlorides to aldehydes. Thus we have reduced *p*-nitrobenzoyl chloride to *p*-nitrobenzaldehyde in 80% yield, benzoyl chloride to benzaldehyde in 78% yield, and terphthalyl chloride to terphthalyl aldehyde in 85% yield. Other acid chlorides have been reduced to aldehydes in somewhat lower yields. However, these have been the results of single experiments and we believe that the yield may be improved to those realized for *p*-nitro-, benzoyl, and terphthalyl chlorides with further study. The results are summarized in Table I.

TABLE I

REDUCTION OF ACID CHLORIDES TO ALDEHYDES BY LITHIUM TRI-*t*-BUTOXYALUMINOHYDRIDE

		Yield of aldehyde		
		Tetrahydrofuran by analysis	Diglyme	
Acid chloride	Moles		By analysis	By isolation
p-Nitrobenzoyl	0.244	..	..	80^a
Benzoyl	.256	65	78	73^b
Terphthalyl	.200	..	..	85^a
p-Toluyl	.056	..	61	..
m-Chlorobenzoyl	.074	..	63	..
o-Chlorobenzoyl	.174	..	36	20^b
Pivaloyl	.033	60	44	..

[a] Isolated by precipitation with water. [b] Isolated through bisulfite addition compound.

The following procedure was utilized. Dry *t*-butyl alcohol, 60 g. (0.81 mole), was added with stirring to 500 ml. of a 0.5 *M* solution of lithium aluminum hydride in ether. The white precipitate of lithium tri-*t*-butoxyaluminohydride was allowed to settle, the ether decanted, and the solid dissolved in 200 ml. of diglyme. This solution was added over a period of one hour to 45.3 g. (0.244 mole) of *p*-nitrobenzoyl chloride (recrystallized from hexane, m.p. 74–75°) in 100 ml. of diglyme maintained at approximately −75° by a Dry-Ice bath. The mixture was then permitted to warm to room temperature (1 hour) and poured onto crushed ice. The mixture was filtered, and the solid pressed dry and extracted several times with 95% ethanol. Evaporation of the solvent yielded the crude product, m.p. 103–104° (29.4 g., 80%). After recrystallization from aqueous ethanol the pure aldehyde was obtained in the form of light tan crystals, m.p. 104–105° (25.4 g., 69%).

Alternatively, a solution of lithium aluminum hydride in tetrahydrofuran may be treated with three moles of *t*-butyl alcohol and the resulting solution added slowly to the acid chloride in tetrahydrofuran at −75°. In preliminary experiments this procedure has given slightly lower yields than that utilizing diglyme, so that the latter has been preferred. We are currently engaged in an examination of the scope of this new aldehyde synthesis.

The most general method in the past for the conversion of acid chlorides to aldehydes has been the Rosenmund reduction.[1] This has not been satisfactory because of the difficulties in reproducing the catalyst. Consequently many other procedures for converting acid derivatives to aldehydes have been investigated in recent years.[2,3]

It appears that lithium tri-*t*-butoxyaluminohydride may provide a highly convenient synthetic route from acid chlorides to the corresponding aldehydes.

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(1) K. W. Rosenmund, *Ber.*, **51**, 585 (1918); Erich Mosettig, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 362.

(2) A. Reissert, *Ber.*, **38**, 1610 (1905); J. M. Grosheintz and H. O. L. Fisher, THIS JOURNAL, **63**, 2021 (1941); R. B. Woodward, *ibid.*, **62**, 1626 (1940); G. Wittig, M. Jesaitis and M. Glos, *Ann.*, **577**, 4 (1953); H. Stephen, *J. Chem. Soc.* (*London*), **127**, 1874 (1925); J. S. MacFadyen and T. S. Stevens, *ibid.*, 1936, 584; C. H. Grundmann, *Ann.*, **524**, 31 (1936); A. Sonn and E. Müller, *Ber.*, **52**, 1927 (1919); J. von Braun and W. Rudolf, *ibid.*, **67**, 269, 1735 (1934); Paul Brandt, *Acta. Chem. Scand.*, **3**, 1050 (1949); G. Wittig and P. Hornberger, *Ann.*, **577**, I, 11 (1952); F. Weygand, *et al.*, *Angew. Chem.*, **65**, 525 (1953).

(3) A general review of this field is provided by Erich Mosettig, "Organic Reactions," Vol. VIII, Chap. 5, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 218.