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A Facile Reduction of Acid Anhydrides with Borane in the Presence of Lithium Chloride in Tetrahydrofuran

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Carboxylic acid anhydrides are rapidly reduced with borane–lithium chloride (1:0.1) system to give corresponding alcohols (diols in the case of cyclic anhydride) quantitatively in tetrahydrofuran at room temperature. This reagent tolerates aromatic acid ester, nitro, and halide functional groups, however competitively reduces aliphatic ester and nitrile groups.

Introduction

The partial reduction of cyclic acid anhydrides to the corresponding lactones can be effected readily with various metal hydrides such as NaBH_4 , LiAlH_4 , DIBAL and $n\text{-BuLi}$, LiEt_2BH , and LiSi_3BH . However the complete reduction of acid anhydrides to the corresponding alcohols (diols in the case of cyclic anhydride) has been effected with LiAlH_4 almost exclusively. Rate and stoichiometry studies revealed that $\text{Li}(\text{CH}_3\text{O})_3\text{AlH}$ and AlH_3 could be even better reducing agents, however, these are very powerful reducing agents, and many functional groups are not expected to tolerate these strong hydrides.

Sometime ago, we have observed that the rate and stoichiometry of phthalic anhydride reduction with borane could be dramatically accelerated by the addition of 10 mol percent of lithium chloride.⁹ Since borane is a much milder and more selective reducing agent than the aluminohydrides, we have decided to explore more in detail the reduction of acid anhydrides with $\text{BH}_3\text{-LiCl}$ (1:0.1) system.

Results and Discussion

First, we examined the reduction of glutaric anhydride with borane and borane–dimethyl sulfide (BMS) at room temperature, and also in the presence of 10 mol percent of

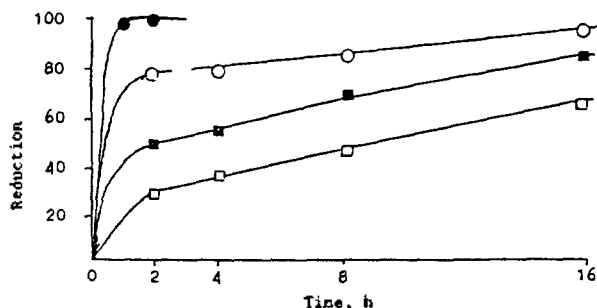
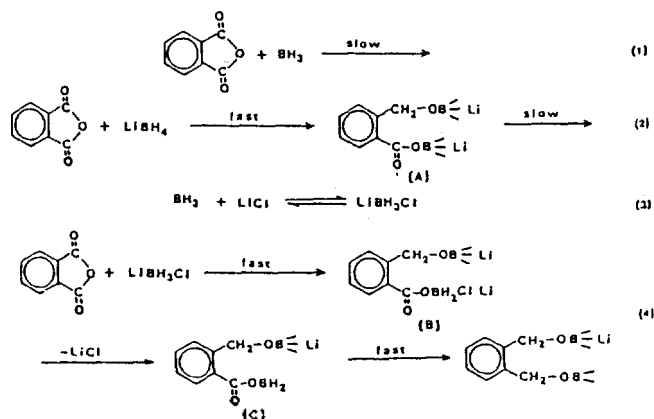


Figure 1. Reduction of glutaric anhydride to 1,5-pentanediol with BH_3 , $-\text{LiCl}$ (1:0.1); ●, BH_3 ; ○, BMS-LiCl (1:0.1); ■, and BMS ; □, at room temperature, the hydride to compound ratio being 6 in all cases.

lithium chloride in each case. The yield of the product, 1,5-pentanediol, was estimated by GLC analysis. As shown in Figure 1, glutaric anhydride was rapidly reduced with BH_3 - LiCl (1:0.1) in 1 hr, however, with BH_3 only a 80 % yield was observed in 8 hr. The reduction with BMS was slower, showing a 46 % yield with BMS and a 70 % yield in the presence of 10 mol percent of lithium chloride both in 8 hr.

We have examined eight representative acyclic and cyclic acid anhydrides and four competitive reductions with other functional groups. The reduction was typically carried out with 2 mol equivalents of BH_3 and 0.2 mol equivalents of LiCl per mol of acid anhydride (0.25 M) in THF at room temperature for two hours. As shown in Table 1, all the acid anhydride, acyclic (entries 1,2, and 3) as well as cyclic (entries 4,5, and 6), gave the corresponding alcohols or diols quantitatively in 2 hr at room temperature. As shown in entries 7, 8, 9 and 10, this system tolerates chloro, bromo, nitro and aromatic ester groups. However, aliphatic ester and nitrile (entries 11 and 12) are competitively reduced. In the case of phthalic anhydride, the reduction was also carried out in preparative



Scheme 1

scale (50 mmol), and the phthalyl alcohol was isolated in 93 % yield.

The effect of LiCl may be rationalized as shown in Scheme 1. Cyclic anhydrides are reduced slowly with BH_3 ,⁹ (eq. 1) but rapidly to the lactone stage [A] with borohydride¹⁰ (eq. 2). Therefore, the small amount of basic borohydride, LiBH_3Cl ,¹¹ formed from BH_3 and LiCl (eq. 3) should be responsible for the fast reduction to the intermediate [B], an acyloxychloroborohydride which is expected to give acyloxyborane [C] according to the similar equilibrium (eq. 3). Acyloxyborane is known to be reduced rapidly to the corresponding alcohol.¹²

Experimental

Hypodermic syringes with a 6-inch needle were used at all times to introduce and transfer liquid materials. All glass apparatus were dried in a drying oven at 120°C for more than 5 h and then cooled under a stream of dry nitrogen. All the

Table 1. Reduction of Acid Anhydrides with BH_3 - LiCl (1:0.1) System in Tetrahydrofuran at Room Temperature

Entry	Compound ^a	H/Cpd	Product	Yield, % ^a
1	hexanoic anhydride	6	1-hexanol	100
2	benzoic hexanoic anhydride	6	benzyl alcohol	99.6
			1-hexanol	98.6
3	benzoic anhydride	6	benzyl alcohol	97
4	succinic anhydride	6	1,4-butanediol ^b	99
5	glutaric anhydride	6	1,5-pentanediol ^b	100
6	phthalic anhydride	6	phthalyl alcohol ^b	97(93) ^c
7	chloroacetic anhydride	6	2-chloroethanol	100
8	4-nitrobenzoic anhydride	6	4-nitrobenzyl alcohol ^b	99.8
9	glutaric anhydride	5	1,5-pentanediol ^b	100
	1-bromooctane		1-bromooctane	100
10	glutaric anhydride	5	1,5-pentanediol ^b	99.7
	ethyl benzoate		ethyl benzoate	99.5
11	glutaric anhydride	5	1,5-pentanediol ^b	100
	ethyl hexanoate		ethyl hexanoate	50
		4	1,5-pentanediol ^b	70
			ethyl hexanoate	70
12	glutaric anhydride	5	1,5-pentanediol ^b	98
	hexanenitrile		hexanenitrile	58

^aOne mmol of compound was added to 2 mmol of borane and 0.2 mmol of LiCl in 4 ml of solution, 0.25 M in compound and 1.5 M in hydride.

^bYields were estimated by GLC. ^cThese products were checked by GLC after silylation. ^dIsolated yield.

compounds used were commercial products of the highest purity available. Some acid anhydrides, not available commercially, were prepared according to the standard procedures.^{13,14} Gas chromatographic (GLC) analysis was performed on a Varian Model 3700 instrument. All of the yield of products were determined by utilizing suitable internal standards and authentic samples.

Reduction of Acid Anhydride with $\text{BH}_3\text{-LiCl}$ (1:0.1) System.

The reduction of phthalic anhydride is described as a representative. Into an oven-dried hot flask, equipped with a rubber stopple, and a magnetic stirring bar, was introduced 8.5 mg (0.2 mmol) of pre-dried lithium chloride. The flask was cooled to room temperature under dry nitrogen, and then there were added 0.9 ml of THF and 1.1 ml (6 mmol hydride) of 1.8 M $\text{BH}_3\text{-THF}$ solution. The reaction was started by the addition of 2 ml (1 mmol) of 0.5 M phthalic anhydride solution in THF. This makes the reaction mixture 0.5 M in BH_3 (i.e. 1.5 M in hydride), 0.05 M in LiCl, and 0.25 M in compound. After 2 hr at room temperature, 2 ml of dry methanol was added and the solution was evaporated to dryness. This procedure was repeated for several times to remove methyl borate. The crude phthalyl alcohol was silylated by stirring with 0.25 ml hexamethyldisilazane and 0.15 ml of trimethylchlorosilane in the presence of 1 ml of pyridine.¹³ After 20 min, the solid deposit was removed by centrifuge. The GLC analysis of the supernatant liquid revealed a 97% yield of phthalyl alcohol.

Preparation of Phthalyl Alcohol. For the preparative run, 7.4 g (50 mmol) of phthalic anhydride was treated with 0.42 g (10 mmol) of LiCl and 55.5 ml (300 mmol hydride) of 1.8 M $\text{BH}_3\text{-THF}$ solution. After 2.0 hr, 50 ml of H_2O was added to destroy residual hydride, and dissolve LiCl and boric acid. The aqueous solution was transferred to a continuous ether extractor and the extraction was continued for 3 hr. The extract was dried over anhydrous MgSO_4 and the solvents were evaporated. The residue was saturated in dry ether, and by the addition of dry hexane, 6.86 g (93%) of colorless crystal of phthalyl alcohol was obtained: mp 62–64°C [Lit.⁶⁻⁸ 63–65°C].

Selective Reduction of Acid Anhydride with $\text{BH}_3\text{-LiCl}$ (1:0.1) System in the Presence of Other Functional Groups.

The selective reduction of glutaric anhydride in the presence of ethyl benzoate is representative.

Into a oven dried 50 ml hot flask, equipped with a rubber stopple and a magnetic stirring bar, was introduced 8.5 mg (0.2 mmol) of pre-dried hot lithium chloride, and the flask was cooled to room temperature under dry nitrogen. And then

there were added 0.89 ml of THF and 1.11 ml of 1.8 M BH_3 solution (2 mmol in BH_3 , 6 mmol in hydride) with stirring. To this, a mixture of glutaric anhydride (0.1141 g, 1 mmol), ethyl benzoate (0.1502 g, 1 mmol), and dodecane (0.1703 g, 1 mmol, as an internal standard) in 2 ml THF was added. After 2 h, 2 ml of dry methanol was added and the solution was evaporated to dryness. This procedure was repeated for several times to remove the boric acid as methyl borate. To this product, 1 ml of pyridine and 0.5 ml of hexamethyldisilazane were added with stirring. After 5 h, the GLC analysis of the supernatant liquid showed that 99.9% of glutaric anhydride was reduced to 1,5-pentanediol and 99.5% of ethyl benzoate remained intact.

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