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An Efficient Reduction of Acid Chlorides by Sodium Borohydride with Dropwise Addition of Methanol

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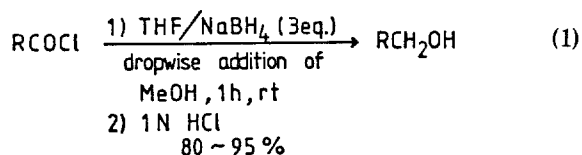
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Received June 22, 1988

The conversion of acid chlorides to the corresponding alcohols by reduction with sodium borohydride is of great practical interest because the conversion of acid or acid esters to the corresponding alcohols needs lithium aluminum hydride or other reducing agents which are more expensive and more difficult to handle than sodium borohydride.

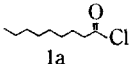
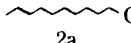
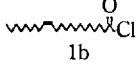
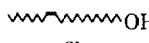
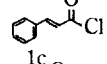
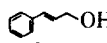
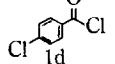
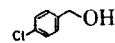
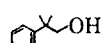
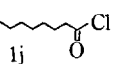
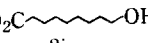
In the literature, it was reported¹ that aliphatic acid chlorides were reduced to the corresponding alcohols by employing a suspension of sodium borohydride in dioxane. But the results on the reductions of unsaturated and other polyfunctional acid chlorides were less clean-cut. It was also reported² that acid chlorides cannot be reduced to alcohols by sodium borohydride in the presence of hydroxylic solvent. In this paper², the acid chlorides react with these solvents to yield products which are unreactive towards borohydride. Recently, certain aromatic acid chlorides were reduced³ cleanly to the corresponding benzyl alcohols by sodium borohydride in a mixture of toluene and water in the presence of a phase-transfer catalyst.

We have found that acid chlorides could be easily and conveniently reduced into the corresponding alcohols by sodium borohydride in tetrahydrofuran with dropwise addition of methanol in good yields (Eq. 1). Acid chlorides were readily prepared from the corresponding acid by treatment of thionyl chloride.



Erucic acid chloride (**1b**) which could be readily prepared from erucic acid was conveniently reduced to the erucyl alcohol (**2b**) in 93% yield, which is an intermediate for the economical synthesis⁴ of muscalure⁵, the sex pheromone of the housefly, *Musca domestica* L.. From the α,β -unsaturated acid chloride (**1c**), the corresponding allylic alcohol (**2c**) was obtained as the only isolated product (Entry 3). The sterically hindered acyl chloride (**1i**) was also easily reduced in the alcohol (**2i**) (Entry 9). In the presence of ester group, acid chloride (**1j**) was selectively reduced into the corresponding

Table 1. Reduction of Acid Chlorides by Sodium Borohydride

Entry	Substrate ^a	Temp (°C)	Time(h)	Product ^b	Yield (%) ^c
1		rt	1		80
2		rt	1		93
3		rt	1		92
4		rt	1		93
5		rt	1		92
6		rt	1		94
7		rt	1		95
8		rt	1		93
9		rt	1		89
10		rt	1		92

^aAll the acid chlorides were prepared from the corresponding acids and thionyl chloride. ^bConsistent spectral data were obtained for all compounds. ^cThe yields were not optimized and represent pure isolated yields.

alcohol (**2j**) (Entry 10).

The following procedure is representative. To 3.0 ml of dry THF solution was added erucic acid chloride (0.200g, 0.60 mmol) and the sodium borohydride (0.068g, 1.8mmol) in one portion. Methanol (1.5 ml) was added to the reaction mixture drop by drop for 1h at room temperature. Then, 1N

HCl (1.0 ml) was added, and stirred for 10 min. MeOH and THF were evaporated. The reaction mixture was extracted with ether and washed with water and brine. The ether layer was dried over anhydrous MgSO_4 . The solvent was evaporated under reduced pressure to give the product in almost quantitative yield. The crude product was purified by preparative TLC (SiO_2 , CH_2Cl_2 , $R_f = 0.40$) to afford pure erucyl alcohol (0.169g, 93%).

The resulting procedure is considered to be particularly suitable for large-scale preparation.

References and Notes

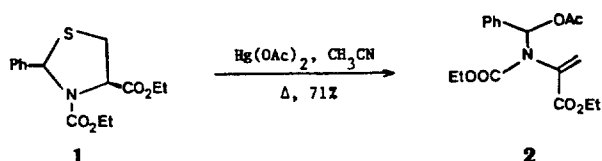
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6. The acid chloride (**11**) was prepared from benzyl cyanide in three steps (68%); (i) dimethylation (NaH , MeI , DMF) (ii) hydrolysis (KOH , ethyleneglycol) (iii) chlorination (SOCl_2 , heptane).
7. We prepared this compound (**11**) from 1,9-nonanedioic acid by esterification (EtOH , H^+), partial hydrolysis (KOH , H_2O), followed by chlorination (SOCl_2 , heptane) in 67% yield.

Selective Cleavage of Thiazolidines I. Mercuric Acetates in Aprotic Media

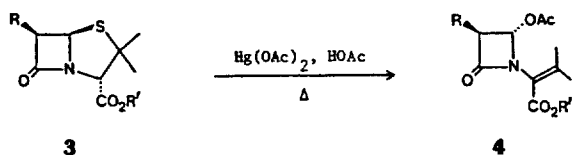
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During the course of our attempts to cleave thiazolidines with thiophilic metal salts in the presence of external nucleophiles, it was found that mercuric salts, especially mercuric acetate, in acetonitrile was very effective for the cleavage of the compound **1** without incorporation of external nucleophile, which was rather unexpected by two accounts stated below.

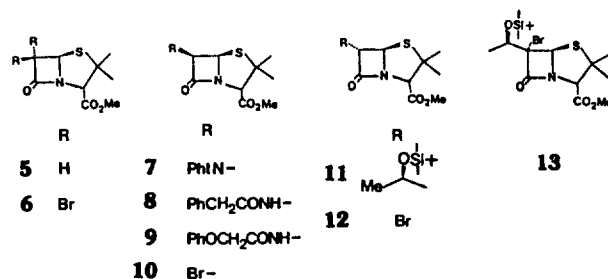


First of all, mercuric acetate is almost insoluble in acetonitrile. Also, the closely related Stoodley fragmentation, which is very useful in penicillin chemistry, is carried out universally in acetic acid where external nucleophiles are present in great excess.¹

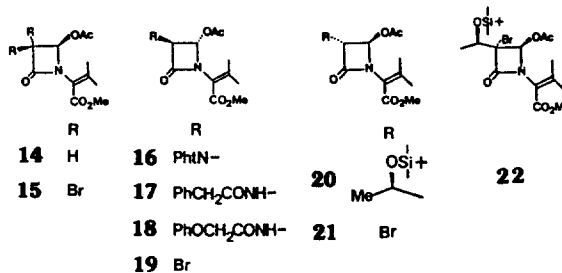


Consequently, a detailed study was undertaken to elucidate the scope and utility of the reaction especially in penams. Thus the following substrates were prepared according to procedures reported elsewhere.

And each substrate was subject to the reaction condition described below for the siloxyethyl derivative **11**. A mixture of mercuric acetate (0.238g, 0.75 mmol), calcium carbonate (as



an acid scavenger, 0.041 g, 0.41 mmol) and the penam **11** (0.140 g, 0.37 mmol) in acetonitrile (1.9 mL) was refluxed for 6 h. After cooling to rt, the white solid was filtered off with aid of methylene chloride. Aqueous work-up followed by chromatography provided the corresponding acetate **20** (0.108 g, 78%). But it was found later that the aqueous work-up could be omitted even for pure product (94%).



However; extension to other penams revealed the characteristic of the present reaction; although the non-halogenated species, **5**, **7** and **11**, gave good yields of the corresponding acetate (**5**→**14**, 81%; **7**→**16**, 56%; **11**→**20**, 78%), halo-