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EFFICIENT REDUCTION OF ACYL CHLORIDES WITH ZINC BOROHYDRIDE/N,N,N',N'-TETRAMETHYLETHYLENEDIAMINE

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Abstract: Various acyl chlorides are efficiently reduced to the corresponding alcohols under mild conditions by treatment with zinc borohydride in the presence of N,N,N',N'-tetramethylethylenediamine.

Zinc borohydride($Zn(BH_4)_2$), prepared from zinc chloride and sodium borohydride,1) is uniquely mild reducing agent because of its almost neutral character and has been conveniently employed for the reduction of ketonic carbonyl compounds.2) Recently we have reported that this one is also useful for the mild reduction of benzenethiol ester function.3) In order to extend the reducing ability of $Zn(BH_4)_2$ we have studied the reduction of acyl chlorides. Herein we wish to report on our successful results.

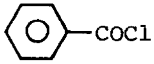
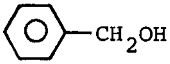
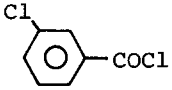
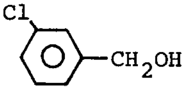
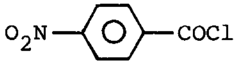
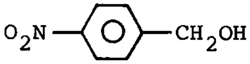
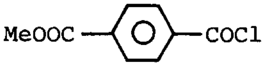
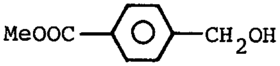
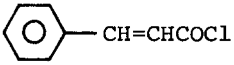
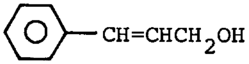
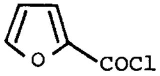
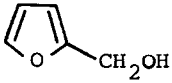
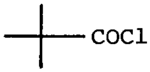
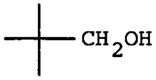
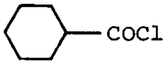
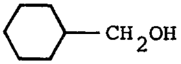
In spite of the description on the reactivity of $Zn(BH_4)_2$ towards acyl halides,4) in our practice the reaction was usually quite slow and had less synthetic utility. Fortunately, however, we have found that clean reduction was achieved by using $Zn(BH_4)_2$ with one equivalent of N,N,N',N'-tetramethylethylenediamine(TMEDA) (Eq. 1). Under these conditions a wide variety of aliphatic and aromatic acyl chlorides was readily reduced into the corresponding alcohols in good yields except for the unexpectedly slow reduction of 2-furoyl chloride. Instead of TMEDA the use of triethylamine gave also a comparable result but was rather less effective. The results are summarized in Table 1.

$$\mathrm{RCOCl} \xrightarrow{Zn(BH_4)_2/\mathrm{TMEDA}} \mathrm{RCH_2OH} \qquad (1)$$

From these results it would be apparent that the electron-withdrawing groups enhance the rate of reduction. And also it would be worth to note the selective reduction of acyl chlorides in the presence of other functional groups, such as chloro, nitro, ester, and conjugated double bond.

The following procedure is representative. To 1.8 ml of dry THF solution of m-chlorobenzoyl chloride(1 mmol) were added successively at 0 °C 6.7 ml of $Zn(BH_4)_2$(ca. 0.15 M ether solution) and TMEDA(1 mmol). During the reaction a white insoluble substance was gradually formed. After stirring for 30 min at

Table 1. Reduction of acyl chlorides with zinc borohydride/TMEDA[a)]

Substrate	Temp.	Time	Product	Yield, %[b)]
	40 °C 40 °C	4.5 h 18 h		95 87[c)]
	0 °C	30 min		98, 94[c)]
	0 °C	15 min		93
	0 °C -78 °C	15 min 1 h		95 90
	0 °C	30 min		86
	40 °C	3 days		80[d)]
	RT	6 h		96
	RT	2 h		(88)
	0 °C	5 h		93

a) All the products were identified by comparing with authentic samples. b) Yields represent pure isolated products, value in parenthesis was determined by GLC. c) Triethylamine was used instead of TMEDA. d) After 92 % conversion.

0 °C, the mixture was quenched by addition of dilute HCl, dried(Na_2SO_4), filtered through Celite, and evaporated. The crude product was purified by preparative TLC to give m-chlorobenzyl alcohol(139 mg, 98 %).[5)]

References and notes

1) W. J. Gensler, F. A. Johnson, and A. D. B. Sloan, J. Am. Chem. Soc., 82, 6074(1960).

2) For example see: T. Oishi and T. Nakata, Acc. Chem. Res., 17, 338(1984); T. Nakata, Yakugaku Zasshi, 105, 619(1985).

3) H. Kotsuki, N. Yoshimura, Y. Ushio, T. Ohtsuka, and M. Ochi, Chem. Lett., 1986, 1003.

4) E. R. H. Walker, Chem. Soc. Rev., 5, 23(1976).

5) In some cases the contaminated $ZnCl_2$•TMEDA complex was hard to remove. In this case the product was isolated once after trimethylsilylation.

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