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FACILE REDUCTION OF BENZENETHIOL ESTER UNDER MILD CONDITIONS WITH ZINC BOROHYDRIDE

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Benzenethiol esters are efficiently reduced to alcohols under mild conditions by treatment with zinc borohydride prepared from zinc chloride and sodium borohydride.

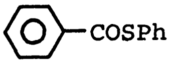
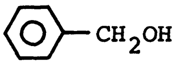
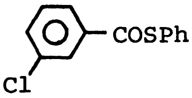
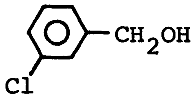
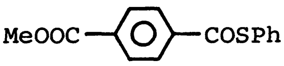
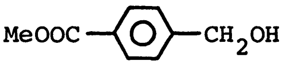
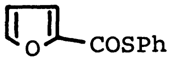
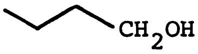
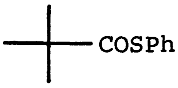
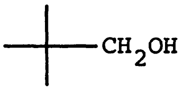
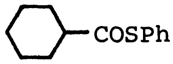
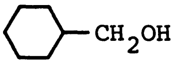
Reductive synthesis of alcohols from esters is one of the most fundamental methods in organic chemistry and several kinds of reducing agents have been developed in the past years.1) For the reduction of thiol ester group Raney Ni has been commonly used.2) Recently, however, it has been demonstrated that $NaBH_4$ could serve as a useful reagent for this type of reduction.3)

In our separate work we required a method for selective reduction of thiol ester in the presence of other functional groups. The use of $NaBH_4$ is not enough for our purpose because of its rather basic nature. On the other hand zinc borohydride prepared from $ZnCl_2$ and $NaBH_4$ is known as a neutral reducing agent and conventionally employed for the reduction of ketonic carbonyl compounds.4) However, the feasibility of extension to the esters was not apparent. Herein we wish to report the facile method for reduction of benzenethiol esters with this reagent.

Benzenethiol esters (1 mmol), which are easily available from acyl chloride and benzenethiol, were dissolved in dry Et_2O or THF (2-3 mL) and treated with ca. 1 mmol of $Zn(BH_4)_2$ (ca. 0.15 M ether solution, 6.7 mL) at room temperature or at 40 °C under N_2 for 2 days. After usual work-up, flash column or preparative layer chromatography on SiO_2 gave the corresponding alcohols in good yields (Eq. 1 and Table 1). Under the same conditions methyl benzoate or S-ethyl thiobenzoate could not be reduced. Thus, phthalic acid derivative was reduced only on the benzenethiol ester side (Table 1). We believe that the present method has a synthetic utility for selective reduction of benzenethiol ester group under neutral conditions.

$$\mathrm{RCOSPh} \xrightarrow[\mathrm{Et_2O\ or\ THF}]{\mathrm{Zn(BH_4)_2}} \mathrm{RCH_2OH} \qquad (1)$$

Table 1. Reduction of benzenethiol ester with zinc borohydride[a)]

Substrate	Solvent	Temp	Product	Yield/%[b)]
	Et_2O	RT		81 (84)
	Et_2O	RT		90
	THF/Et_2O	40 °C		92
	THF/Et_2O	40 °C		81, 84[c)]
	THF/Et_2O	RT		77[d)]
	Et_2O	RT		(89)
	Et_2O	RT		99

a) Reactions were carried out for 2 days unless otherwise noted. All the products were identified by comparing with authentic samples.

b) Yields represent pure isolated products, values in parentheses are yields determined by GLC.

c) At room temperature for 4 days.

d) Reduced yield is due to the volatile product.

References

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3) Y. Nagao, K. Kawabata, and E. Fujita, J. Chem. Soc., Chem. Commun., 1978, 330; H.-J. Liu, R. R. Bukownik, and P. R. Pednekar, Syn. Commun., 11, 599(1981).

4) M. Fieser and L. F. Fieser, "Reagents for Organic Synthesis," Wiley, New York, Vol. 11(1984), p. 599; Vol. 10(1982), p. 460; Vol. 5(1975), p. 761; Vol. 3 (1972), p. 337. See also T. Oishi and T. Nakata, Acc. Chem. Res., 17, 338 (1984).

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