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Triisopropoxy Boroxine as a Reducing Agent for Substituted Benzaldehydes

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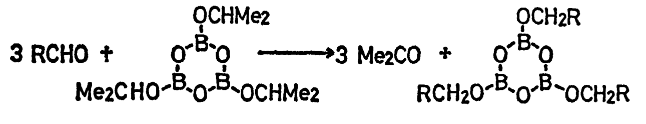
Synopsis. Substituted benzaldehydes could be reduced to corresponding benzyl alcohols in fairly good yield at 130 °C, using triisopropoxy boroxine as a reducing agent. The rates of the reduction of benzaldehyde with triisopropoxy boroxine were about ten times as large as those with triisopropyl borate at 110—130 °C.

The reducing action of various metallic alkoxides on aldehydes and ketones has been examined by Meerwein and his co-workers.1) Under their reaction conditions, boron alkoxides were ineffective as reducing agents. However, when the reaction temperatures were rasied to 150—170 °C, aromatic aldehydes were reduced to the corresponding alcohols by triisopropyl borate.2)

The ring structure of trialkoxy boroxines was confirmed in 1951,3) and a convenient synthesis of trialkoxy boroxines was published in 1966,4) but their reactivities as reducing agents have not yet been studied.

This paper will report the results of an investigation of the reducing activity of triisopropoxy boroxine toward substituted benzaldehydes and some aromatic ketones, compared with that of triisopropyl borate.



Triisopropoxy boroxine

TABLE 1. REDUCTIONS OF SUBSTITUTED BENZALDEHYDES WITH TRIISOPROPOXY BOROXINE IN XYLENE AT 130 °C FOR 22 hr

RCHO	RCH_2OH (%)
4-Nitrobenzaldehyde	90
Benzaldehyde	64
4-Chlorobenzaldehyde	63
4-Methoxybenzaldehyde	12

Table 1 shows the results obtained from the reductions of substituted benzaldehydes with triisopropoxy boroxine. The yields of alcohols in Table 1 are better than those of the reduction with triisopropyl borate,2) although they are somewhat lower than those in the Meerwein-Ponndorf-Verley reduction.5) Neither of the ketones investigated (acetophenone and *p*-nitroacetophenone) was reduced by triisopropoxy boroxine.

The effect of the reaction temperature on this reduction is remarkable. At 80 °C, the usual temperature in the Meerwein-Ponndorf-Verley reduction, practically no reduction occurred with triisopropoxy boroxine.

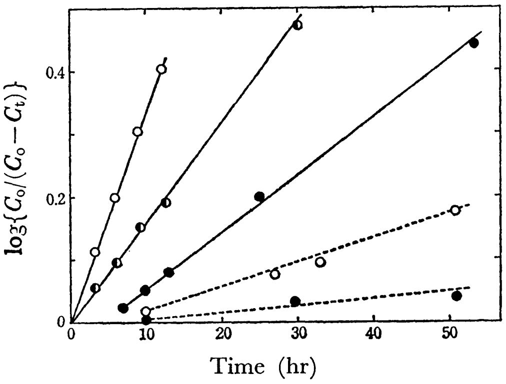


Fig. 1. Pseudo first-order rate plots for the reduction of 0.5 M benzaldehyde with 1.5 M triisopropoxy boroxine or triisopropyl borate in diglyme at these temperature: ●, 110°; ◐, 120°; ○, 130°: solid line, reduction with boroxine; dotted line, reduction with borate.

TABLE 2. THE RATE OF REDUCTION OF BENZALDEHYDE WITH TRIISOPROPOXY BOROXINE OR TRIISOPROPYL BORATE IN DIGLYME

Temp. (°C)	Rate constant, k (hr^{-1})	
	Boroxine	Borate
110	0.020	0.0020
120	0.037	
130	0.076	0.0086

In order to compare the reducing activity of triisopropoxy boroxine with that of triisopropyl borate, we measured the rate of the reduction of benzaldehyde in a diglyme solution under nitrogen, using both reducing reagents separately. A diglyme solution of benzaldehyde and an excess of triisopropoxy boroxine or triisopropyl borate was allowed to react at a constant temperature. The course of the reaction was followed by removing aliquots at appropriate intervals and by measuring the benzyl alcohol and benzaldehyde after hydrolysis by means of gas chromatography. The results are shown in Fig. 1, where C_0 is the concentration of benzaldehyde at time zero and where C_t is that of benzyl alcohol at time t (hr). The plots follow the pseudo first-order reaction for benzaldehyde. An induction period was observed in the reductions with triisopropoxy boroxine at 110 °C and with triisopropyl borate at 110 and 130 °C. The induction period may be due to the establishment of a coordination equilibrium between benzaldehyde and boroxine or borate in the same way as in the Meerwein-Ponndorf-Verley reduction.6) The psudo first-order rate constants are given in Table 2. The activation energies obtained from the Arrhenius plots were 22.6 and 20.0 kcal/mol for reductions with triisopropyl borate and with triisopropoxy boroxine respectively. From these results, it is clear that triisopropoxy boroxine is more effective than triisopropyl borate as a reducing agent.

Experimental

Materials. Triisopropoxy boroxine was prepared according to the literature[4]; mp 51—52 °C (lit, 52 °C).

Triisopropyl borate was prepared by a method modified from the literature[2] as follows: Boric anhydride (0.15 mol) and isopropyl alcohol (1 mol) were mixed in a Soxhlet extracter. In its cylindrical filter paper, calcium oxide (50 g) was placed; the mixture was refluxed for 24 hr and then distilled to obtain the borate (bp 139.5—140.5 °C).

Substituted benzaldehydes were purified by the usual method.

Reduction of Substituted Benzaldehydes. Aldehyde (0.02 mol), triisopropoxy boroxine (0.023 mol), and a solvent (25 ml) were placed in a three-necked, round-bottomed flask (50 ml) fitted with a thermometer, a nitrogen-inlet tube, and a gas-outlet tube. The mixture was heated at 130 °C for 22 hr under an atmosphere of dry nitrogen, while the acetone formed was distilled off through the gas-outlet tube. The acetone was condensed in a spiral tube cooled with an acetone-dry ice mixture and was analyzed by means of gas chromatography. After cooling, the mixture was poured into 100 ml of a 1% aqueous solution of sodium hydrogen carbonate and extracted with 400 ml of ether, after which the ethereal extract was dried over sodium sulfate. The ether was distilled off, and the product was analyzed quantitatively by means of gas chromatography.

Reaction of Ketones and Triisopropoxy Boroxine. Acetophenone (0.1 mol) and triisopropoxy boroxine (0.033 mol) were treated for 14 hr at 110 °C, and *p*-nitroacetophenone was treated similarly at 110 and 125 °C, but no reaction occurred in any case.

Kinetic Procedure. A 60-ml portion of a diglyme solution containing benzaldehyde (0.03 mol) and triisopropoxy boroxine or triisopropyl borate (0.09 mol) was placed in a four-necked, round-bottomed flask (100 ml) and the reaction was carried out as has been described above at a constant temperature. From time to time, 4-ml aliquots were removed, poured into 15 ml of a 1% aqueous solution of sodium hydrogen carbonate, and extracted with 40 ml of ether; the concentrations of benzyl alcohol and benzaldehyde were determined by means of gas chromatography.

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