[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

Reactions of Aldehydes and Ketones with Alkyl Borates[1]

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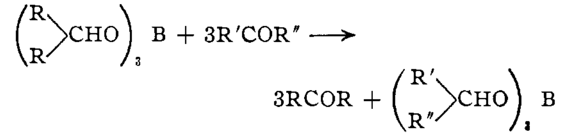
The reducing action of various metallic alkoxides on aldehydes and ketones has been examined by Meerwein and his co-workers.[2] Under the conditions of their reactions, boron alkoxides were ineffective as reducing agents. However, Wuyts and Duquesne[3] obtained what they presumed to be propionaldehyde when they heated a mixture of *n*-propyl borate and salicylaldehyde at 190°. Thus it appeared that reduction of carbonyl compounds by borates could be effected under fairly drastic conditions. This paper reports the results of an investigation of the use of borates as reducing agents for aldehydes and ketones from the standpoint of possible synthetic utility.

(I)


$$\left(\begin{matrix}R\\R\end{matrix}\!>\!\text{CHO}\right)_3 B + 3R'COR'' \longrightarrow 3RCOR + \left(\begin{matrix}R'\\R''\end{matrix}\!>\!\text{CHO}\right)_3 B$$

Results and Discussion

It will be of interest to compare our results with those obtained in the widely used Meerwein–Ponndorf–Verley reaction.[4] In the case of the borates (a) much higher temperatures (150 to 175°) are required; (b) aldehydes are reduced much more easily than ketones; (c) no Tischtschenko reaction (ester formation) occurs; (d) good yields of alcohols are obtained from aromatic aldehydes (Table I) although somewhat lower than in the Meerwein–Ponndorf–Verley reaction; aliphatic compounds appear to give uniformly poor yields; (e) polymerization of starting materials in some cases and of products in other cases occurs.

TABLE I

REDUCTIONS WITH ALKYL BORATES IN 24 HOURS AT 150–160°[a]

R'COR''	R'CHOHR'', %	R'COR'', % recovered
Benzaldehyde	70[b]	
2-Chlorobenzaldehyde	59	8.6
4-Chlorobenzaldehyde	48	24
2-Nitrobenzaldehyde	83	13
3-Nitrobenzaldehyde	86	11
Anisaldehyde	∼20[c]	
Cinnamaldehyde	∼25[c]	
Cinnamaldehyde	∼35[c,d]	
Furfural	∼57[c]	
Benzaldehyde[e]	75	5
Benzaldehyde[f]	44	22
Benzoquinone[g]	∼35[h]	
Cyclohexanone[i,g]	6	
n-Heptaldehyde[i]	19	*nil*

[a] Isopropyl borate used in all cases except where noted. [b] 78% reduction in 43 hours. [c] Polymeric product, per cent. reduction based on acetone collected. [d] Reaction carried out in xylene. [e] Allyl borate; 18 hours at 175°. [f] Isobutyl borate; 30 hours at 180°. [g] Allyl borate. [h] Polymeric product; per cent. reduction based on acrolein collected. [i] See Experimental for conditions.

Isopropyl borate brought about at least partial reduction of all of the aldehydes investigated. However, considerable aldol condensation of heptaldehyde occurred, presumably because of the acidity (in the Lewis sense) of the borate and the high temperature required. In the reductions of cinnamaldehyde, anisaldehyde and furfural only polymeric products were obtained besides acetone. The other aromatic aldehydes were reduced in good yields. Condensation of these aldehydes with acetone to form dibenzalacetones was the only side reaction observed. Although it occurred with benzaldehyde and the chlorobenzaldehydes it was not detected in the case of the nitrobenzaldehydes.

None of the ketones investigated (acetophenone, benzoquinone, cyclohexanone, benzophenone and mesityl oxide) was reduced by isopropyl borate at 160° in 24 hours.

Allyl borate proved to be somewhat more effective as a reducing agent than isopropyl borate as evidenced by the partial reductions of benzoquinone and cyclohexanone. However, only a 6% yield of cyclohexanol was obtained. The remainder of the reaction product consisted mostly of two higher boiling ketonic substances. These were not completely characterized, but are probably aldol condensation products of cyclohexanone with itself or with acrolein.

The only non-volatile product obtained in the reaction of allyl borate with benzoquinone was a black polymeric solid. Neither hydroquinone nor quinhydrone could be extracted from the solid with water. No reduction of benzophenone in fourteen hours at 175° or of mesityl oxide in 48 hours at 160° could be detected.

Experimental

Preparation of Borates.—The allyl and isobutyl borates were prepared by heating a mixture of toluene, boric acid and the alcohol. The ternary azeotrope of water, alcohol and toluene distilled off through a 100-cm. Vigreux column as it formed. For the preparation of isopropyl borate, benzene was used as the third component.

Reduction Procedure.—The following general procedure was used with certain deviations as noted in Table I or as discussed below in the special Experimental section for two individual cases. Reactions were carried out on 0.1–0.3-mole batches. The carbonyl compound (1 mole) and borate (0.36 mole) were placed in a 200-ml. round-bottom flask fitted with a six-inch Vigreux type column to which was attached a condenser and receiver. An atmosphere of dry nitrogen under slight pressure was maintained in the system throughout the reaction period. The reaction mixture was heated at 150–160° for 24 to 28 hours during which time the acetone, acrolein or isobutyraldehyde which formed distilled off. After cooling, the product was poured into 100 ml. water and extracted thrice with 75-ml. portions of benzene or ether. The combined extracts were dried over sodium sulfate and the solvent distilled. Then the product was distilled at reduced pressure (10–20 mm.). (The nitro-

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(1) From theses by S. C. Slack and P. K. Siiteri presented to the Graduate School of the University of New Hampshire in partial fulfillment of the requirements for the M.S. Degree.

(2) Meerwein, von Bock, Kirschnik, Lenz and Migge, *J. prakt. Chem.*, [2] **147**, 211 (1936).

(3) Wuyts and Duquesne, *Bull. soc. chim. Belg.*, **48**, 77 (1939).

(4) A. L. Wilds in "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 178 ff.

benzyl alcohols were recovered by crystallization.) The alcohol was characterized by its melting point or that of its phenylurethan.

In several cases crystalline residues remained in the flask after distillation of the product. These were recrystallized from acetic acid and characterized as dibenzalacetones by their melting points and, in the case of dibenzalacetone, by a mixed melting point with an authentic sample. The percentages of starting aldehyde accounted for in these products based on weight of the crude dibenzalacetone were: 2-chlorobenzaldehyde, 23%; 4-chlorobenzaldehyde, 29%; benzaldehyde (43-hour reduction), 28%.

Reaction of Cyclohexanone with Allyl Borate.—The product from the reaction of 29.6 g. (0.302 mole) with cyclohexanone with 62.8 g. (0.342 mole) of allyl borate at 160–170° for 32 hours was treated in the usual manner and fractionated at 35 mm. through a 100 cm. × 0.5 cm. Podbielniak column. Three main fractions were collected: (a) 2.7 g. at 83°; (b) 5.6 g. at 106–108°; (c) 2.6 g. at 136–140°. Fraction (a) was characterized as cyclohexanol by the melting point[5] of its α-naphthylurethan, 127.5–128.0° and mixed melting point with an authentic sample. Fraction (b) yielded a semicarbazone melting at 165.5–167°. A mixed melting point with cyclohexanone semicarbazone (m.p. 165–167°) showed a great depression (m.p. 140–163°). With 2,4-dinitrophenylhydrazine a derivative melting at 141–142° after several crystallizations from ethyl acetate was obtained.

Anal. Calcd. for $C_{15}H_{16}O_4N_4$: N, 17.8. Found: N, 17.7, 17.7, 17.9.

This analysis corresponds to a one to one aldol condensation product of acrolein and cyclohexanone.

Characterization of fraction (c) was not attempted.

Reaction of *n*-Heptaldehyde with Isopropyl Borate.—A mixture of 68 g. (0.306 mole) of isopropyl borate and 62 g. (0.544 mole) of *n*-heptaldehyde was heated at 150–160° for 44 hours. The product was hydrolyzed, extracted with ether and dried. Fractionation at 15 mm. yielded: (a) 11.6 g. at 82–85°; (b) 11.7 g. at 150–153°; and (c) 18.8 g. residue. Fraction (a) was shown to be 1-heptanol: 3-nitrophthalate m.p. 125–126° (lit.[6] 127°). Fraction (b), $n^{28}\text{D}$ 1.4515, had a molecular weight of 210 (benzene, cryoscopic); calcd. for $C_{14}H_{26}O$, 211. This compound is probably the aldol condensation product of two molecules of heptaldehyde, **2-*n*-amyl-2-nonenal**. Its 2,4-dinitrophenylhydrazine derivative melted at 127–128° after crystallization from ethyl acetate.

Anal. Calcd. for $C_{20}H_{18}O_4N_4$: N, 14.6. Found: N, 14.6, 13.8, 14.4.

Distillation of fraction (c) at about 1 mm. yielded further fractions: 5.5 g. at 130–175°; mol. wt., 380; 4.2 g. at 175–185°, mol. wt., 410, 398; 8.9 g. at 185–205°. The mol. wt. of the condensation product of four moles of *n*-heptaldehyde, $C_{28}H_{50}O$, would be 402.

Summary

The reactions of several aldehydes and ketones with alkyl borates have been investigated. Reduction, aldol condensation of starting material or polymerization of the product may be the main reaction depending upon the carbonyl compound and borate used.

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(5) All melting points are uncorrected.

(6) Dickinson, Crosson and Copenhaver, THIS JOURNAL, **59**, 1095 (1937).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF NORTHWESTERN UNIVERSITY AND THE UNIVERSITY OF ILLINOIS]

The Reaction of Trimethylene Oxide with Grignard Reagents and Organolithium Compounds

BY SCOTT SEARLES

The reaction of ethylene oxide with Grignard reagents and organolithium compounds is a well known method of preparing certain primary alcohols and lengthening the carbon chain by two carbon atoms. The analogous reaction of trimethylene oxide, however, appears to be but little known. This situation is no doubt largely due to the low yields previously reported for the synthesis of trimethylene oxide, but with recent improvements in the latter synthesis the reaction is of some interest as a synthetic method for adding three carbon atoms at one time.

The reaction of trimethylene oxide with the Grignard reagent was first reported by Derick and Bissell.[1] These workers obtained from the reaction of *n*-propylmagnesium bromide and trimethylene oxide a 49% yield of *n*-hexanol, which was rather incompletely characterized. The only other example of the reaction in the literature appears to be the corresponding one with ethylmagnesium bromide, which was reported to yield both *n*-pentanol and 3-bromopropanol (each in about 30% yield).[2] The present work was carried out to investigate the course of the reaction with a variety of other Grignard reagents and with organolithium compounds.

As shown in Table I, trimethylene oxide reacted with aromatic and primary aliphatic Grignard reagents and organolithium compounds to give, after hydrolysis, the expected 3-substituted propanols in generally good yields. The products were characterized with some care, so that there is no question about the course and generality of the reaction. The method represents a more convenient synthesis than has previously appeared in the literature for several of these compounds, such as 4-phenylbutanol[3] and 3-(2-naphthyl)-propanol-1.[4]

The experimental conditions and procedures are similar to those employed with the analogous reaction of ethylene oxide with Grignard reagents.[5] Further similarity to the ethylene oxide reaction[6] is observed in the formation of trimethylene halohydrin in the reaction of trimethylene oxide with secondary and tertiary Grignard reagents. This formation of halohydrin by the competing reaction (B) of trimethylene oxide with magnesium halide present in the Grignard reagent is supported by the formation of trimethylene bromohydrin upon

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(1) Derick and Bissell, THIS JOURNAL, **38**, 2478 (1916).

(2) Bermejo and Aranda, *Anales soc. españ. fis. quim.*, **27**, 798 (1929); *Chem. Centr.*, **101**, I, 2382 (1930).

(3) von Braun, *Ber.*, **44**, 2871 (1911); Conant and Kirner, THIS JOURNAL, **46**, 241 (1924).

(4) Manske and Ledingham, *Can. J. Research*, **17B**, 19 (1939).

(5) For example, Dreger in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 306.

(6) Huston and Agett, *J. Org. Chem.*, **6**, 123 (1941).