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Experimental

Materials.—The phenylsodium was prepared under a nitrogen atmosphere in pentane[18] in a three-necked flask fitted with a mercury-sealed stirrer, condenser and gas-inlet tube. A 10% excess of chlorobenzene was added dropwise with stirring to a suspension of sodium sand in pentane, and the mixture was heated at reflux for four hours. The pentane was decanted and replaced with fresh pentane in order to remove excess chlorobenzene and soluble by-products. Carbonation with solid carbon dioxide indicated a 84% yield of phenylsodium using this method of preparation. Crotyl chloride [b.p. 78° (630 mm.), n^{20}_{D} 1.4346–1.4354] was prepared from butadiene and hydrochloric acid using zinc chloride as catalyst[19] and converted to α-methylallyl chloride [b.p. 57° (630 mm.), n^{20}_{D} 1.4150–1.4156] by refluxing with 2 mole per cent. of ferric chloride.[20] Each chloride was distilled carefully through a center-rod column (rated at 60 theoretical plates at maximum efficiency) and center fractions were used.

Crotyl Chloride or α-Methylallyl Chloride and Phenylsodium.—Crotyl chloride (45.3 g., 0.5 mole) was added dropwise to approximately 0.6 mole of phenylsodium in 500 ml. of pentane. After the mixture had been heated at reflux for two hours, the solid material was allowed to settle, and most of the liquid was removed by decantation. Ethyl alcohol was carefully added to the remaining suspension to decompose the reaction mixture. The resulting solution was washed several times with water and was then added to the main pentane solution and dried over magnesium sulfate. A center-rod column (rated at 60 theoretical plates at maximum efficiency) was used to separate the mixture to give a 10% yield of butenylbenzenes, of which 90–95% was crotylbenzene, b.p. 172° (630 mm.), and 5–10% was α-methylallylbenzene, b.p. 157–162° (630 mm.). Better yields of the coupling products were obtained if neither reactant was in large excess during the course of the reaction. Small portions of the suspension of phenylsodium were forced by means of nitrogen pressure into a second reaction flask while the chloride was slowly dropped into the flask. Approximately 1500 ml. of pentane was required to transfer the phenylsodium. Using this method, 15.2 to 16.6 g. (23–25% yield) of the butenylbenzenes was obtained with the percentages of the two products as before. The products were identified as described earlier.[7] A higher boiling product [95–120° (50 mm.)], about twice the weight of the butenylbenzenes, which was not biphenyl, was obtained. The material did not contain an appreciable amount of chlorine, and had a density less than one. A Kuhn–Roth oxidation with chromic acid gave the following molar ratios: benzoic acid, 0.23; other volatile acid, 1; original dimer or polymer calculated as butenylbenzene, 1. If the mixture was entirely a polymer or dimer of butenylbenzene, the benzoic acid to polymer ratio should be 1.

Almost identical results were obtained with α-methylallyl chloride and phenylsodium.

Mixture of α-Methylallyl and Crotyl Chlorides with Phenylsodium.—An equal mixture by weight of crotyl and α-methylallyl chlorides (1.0 mole, 90.6 g.) was treated with phenylsodium (0.6 mole) as described previously. Approximately 70% of the unreacted chloride was recovered of which 90% was crotyl chloride and 10% was α-methylallyl chloride. Since the crotyl chloride was contaminated with benzene formed as a by-product in the reaction, the amount of chloride present was determined from refractive indices ratios and quantitative chloride analysis.

Excess α-Methylallyl Chloride with Phenylsodium.—One mole (90.6 g.) of α-methylallyl chloride reacted with 0.6 mole of phenylsodium as described above. Approximately 85% of the unreacted chloride was recovered of which 65% was crotyl chloride and 35% was α-methylallyl chloride.

BOULDER, COLO. RECEIVED NOVEMBER 24, 1950

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Sodium Borohydride as a Reducing Agent for Sugar Lactones[1]

BY M. L. WOLFROM AND HARRY B. WOOD

Sodium borohydride is an effective and convenient reagent for reducing aldonic acid lactones to the aldose or the glycitol.

Ordinarily one reduces an aldonic lactone to an aldose by means of sodium amalgam[2,3] at acid reaction. Yields are often low and the method is time-consuming. Platinum-catalyzed hydrogenation has also been reported.[4] The lactone, ester,[5] or, preferably, the aldose,[6] may be reduced to the glycitol by high pressure catalytic hydrogenation.

We have found that sodium borohydride is an effective reagent with which to convert an aldonic lactone into either an aldose or a glycitol in *ca.* 65% yields (established for the case of D-gluco-D-*gulo*-heptonic γ-lactone). The fact that sodium borohydride[7,8] may be used in aqueous solution makes it a useful reducing agent for the water-soluble carbohydrate derivatives. Although the yield of glycitol is less than when Raney nickel is used on the aldose, the simple equipment is definitely an advantage. It may be noted that lithium aluminum hydride is not suitable for these reductions, since it must be used in ether.

Experimental

Reduction of D-Gluco-D-*gulo*-heptono-γ-lactone to D-Gluco-D-*gulo*-heptose.—A solution of sodium borohydride[9] (2 g.) in 50 ml. of water was added dropwise to a solution of D-gluco-D-*gulo*-heptono-γ-lactone (15.00 g.) in 100 ml. of water, previously cooled to near 0°, at such a rate that the temperature was maintained at 0–3°. The reaction mixture was stirred slowly and continuously by a wide sweep mechanical stirrer. Simultaneously with the addition of the so-

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[9] Metal Hydrides, Inc., Beverly, Massachusetts.

dium borohydride, a solution of N H_2SO_4 was added at such a rate that a *p*H of 3–4 (test paper) was maintained. An evolution of hydrogen gas occurred throughout a reaction period of 45–60 minutes. Ten minutes after the last addition of the reducing agent, 5 ml. of N H_2SO_4 was added to destroy any remaining hydride. The solution was diluted immediately with 2 volumes of water and passed slowly through columns containing 300 g. each of Amberlite IR-100-H[10] and IR-4-B,[10] respectively. The effluent was concentrated under reduced pressure to *ca.* 50 ml., and 100 ml. of ethanol was added. The solution was again evaporated to 50 ml. and placed in an ice-box overnight. The crystalline mass was filtered and washed with ethanol and with ether; yield 5.94 g., m.p. 191.5–192°, $[\alpha]^{27}\text{D}$ −20° (*c* 3, water, final). Upon ethanol addition and evaporation a second crop was obtained; yield 3.40 g., m.p. 191–192°, $[\alpha]^{24}\text{D}$ −19° (*c* 3, water, final); likewise a third crop; yield 0.677 g., m.p. 180–182°, $[\alpha]^{25}\text{D}$ −16° (*c* 3, water, final); total yield 10.02 g. (66.5%). Recrystallization from methanol afforded pure material; m.p. 191–192°, $[\alpha]^{23}\text{D}$ −20° (*c*, 3.5, water, final, upward mutarotation) in agreement with those recorded by Fischer[11] for β-D-gluco-D-*gulo*-heptose.

Anal. Calcd. for $C_7H_{14}O_7$: C, 40.00; H, 6.72. Found: C, 40.01; H, 7.08.

Reductions carried out in 95% aqueous methanol solution gave much lower yields than in water while in absolute methanol the reaction was extremely slow or absent.

Reduction of D-Gluco-D-*gulo*-heptono-γ-lactone to *meso*-Gluco-*gulo*-heptitol.—A solution of D-gluco-D-*gulo*-heptono-γ-lactone (15.00 g.) in 30 ml. of water was added dropwise to a mechanically stirred solution of sodium borohydride (3 g.) in 50 ml. of water at room temperature. This was the reverse addition to that for reduction of the lactone to the aldose. The reaction time was 10 minutes. The temperature was not allowed to exceed 50°. A *p*H of 8 was observed on complete addition of the lactone. After standing for an additional 10 minutes, a few drops of 6 N H_2SO_4 were added until no further evolution of hydrogen gas occurred. The solution was then diluted to 300 ml. with water and passed through columns containing 300 g. each of Amberlite IR-100-H[10] and IR-4-B.[10] The effluent was treated with decolorizing charcoal, filtered and the filtrate was evaporated to a thin sirup under reduced pressure. Ethanol (100 ml.) was added and the volume was again reduced to *ca.* 40 ml., whereupon crystallization occurred. After standing at ice-box temperature overnight, the crystalline mass was filtered and washed with ethanol and ether; yield 9.2 g., m.p. 123–127°. A second crop was obtained on further concentration of the filtrate; yield 1.01 g., m.p. 115–125°; total yield 10.21 g. (67.2%). Recrystallization from methanol gave pure material; m.p. 126.5–128° (accepted value[11] 127–128°).

Anal. Calcd. for $C_7H_{16}O_7$: C, 39.60; H, 7.60. Found: C, 39.61; H, 7.72.

Qualitative Experiments with Other Lactones.—Under the above described conditions for reducing the lactone to the aldose, D-galactono-γ-lactone, D-ribono-γ-lactone and D-manno-D-*gala*-heptono-γ-lactone all gave final reaction mixtures strongly reducing to Benedict solution. From the first there was isolated some dulcitol; yield *ca.* 35%, m.p. 185° (accepted 188.5–189°).

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Structure of Barium Titanate at Elevated Temperatures

BY JAMES W. EDWARDS, RUDOLPH SPEISER AND HERRICK L. JOHNSTON

The crystal structure of barium titanate has been investigated over the temperature range 200 to 1372°. The structure remains cubic perovskite throughout this range. Unit cell dimensions were observed as a function of temperature, and are listed in Table I. The 200° value of a_0 is in close agreement with that obtained by Megaw.[1]

Introduction

$BaTiO_3$ has been shown by Megaw[1] to exist in a tetragonal structure up to 120° and to have the cubic perovskite structure between 120 and 200°. Megaw[2] and other workers[3] have also reported hexagonal modifications.

The object of the present work was to study the structure of $BaTiO_3$ from 200° to near its melting point. A series of X-ray diffraction powder patterns made in the temperature range 200 to 1372° show the perovskite modification to exist over this entire range.

Experimental

The specimen was prepared from a sample of $BaTiO_3$ obtained from Linde Air Products Co., Buffalo, New York. At room temperature, patterns obtained agreed with Megaw's[2] tetragonal polymorph. The material was ground to a fine powder in a mullite mortar then moistened with distilled water to make a thick paste. This paste was forced through 0.020 inch i.d. glass capillary to form a small rod which was subsequently dried in air and fired at 1100° for 3 hours. The rod was then cemented into a platinum specimen holder with a paste made of finely ground $BaTiO_3$ and distilled H_2O. This was finally placed in the high temperature camera.[4] The camera was fitted with platinum furnace elements and was not evacuated during heating and exposure. Copper $K\alpha$ radiation was used with the value[5] λ 1.537395 Kx.

The temperature of the interior of the furnace was measured with a platinum–platinum–10% rhodium thermocouple, which was calibrated (before mounting) at the freezing points of tin, zinc, aluminum and copper. The metal samples used were standard samples from the National Bureau of Standards. The thermal gradient between specimen and thermocouple hot junction was determined to be less than 10° at the gold point (1063°) by melting a pure gold wire at the specimen position.

Results

Visual examination and intercomparison of

TABLE I

Temperature, °C.	Unit cell edge, a_0, Kx.
201	4.0037
401	4.0136
601	4.0239
901	4.0415
1114	4.0539
1301	4.0658
1372	4.0701

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(5) See Table I, p. 586 "Internationale Tabellen zur Bestimmung von Kristallstrukturen."