1-Chloro-2,3-dimethylbutane

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A convenient synthesis of 1-chloro-2,3-dimethylbutane is described. The key step is the hydroboration-oxidation of 2,3-dimethyl-1-butene. The conversion of 2,3-dimethyl-1-butanol to the desired product proceeds without isomerization.

THE UTILITY of 2,3-dimethylbutane (I) as a substrate for assessing the relative reactivity of primary and tertiary hydrogen atoms in free radical processes is well known. From chlorination studies the isomeric derivatives, 1-chloro- and 2-chloro-2,3-dimethylbutane (II and III, respectively), usually are identified by comparison (vapor phase chromatography) with authentic samples. Only III, however, is easily prepared for characterization. The infrequent preparation of II has always involved the photochlorination of I followed by the separation of the isomeric products by fractional distillation (*9*) or selective hydrolysis of the tertiary chloride over a period of days (*5, 8*). In other studies a simpler procedure for product analysis has been to determine the retention time (VPC) for authentic III and assign the second peak to II (*1, 6, 10*). The present work was undertaken to develop an alternate route to II.

It was found that hydroboration of 2,3-dimethyl-1-butene (IV), oxidation with alkaline hydrogen peroxide, and treatment of the resulting primary alcohol with thionyl chloride constituted a convenient and unambiguous synthesis of 1-chloro-2,3-dimethylbutane. The hydroboration of IV proceeded, as expected, with almost exclusive addition of the boron atom to the terminal carbon atom (*2*). The product consisted of 99% 2,3-dimethyl-1-butanol (V) and 1% 2,3-dimethyl-2-butanol (VI). The simple hydroboration of IV has not previously been reported, although optically active V was recently prepared by the treatment of IV with (+)-diisopinocampheylborane followed by oxidation (*11*). The conversion of V to II was effected without rearrangement; a sample of III was prepared for comparison purposes.

The complexity of the NMR spectrum of II was a function of its molecular dissymmetry. The asymmetric carbon atom at C-2 rendered nonequivalent the two hydrogens at C-1 as well as the two methyl groups at C-3. The protons at C-1 and C-2 thus became an ABX system, and each peak of the methylene doublet was further split. The same situation obtained for the methyl groups at C-3; in addition, this latter pair of doublets was superimposed on the C-2 methyl doublet.

EXPERIMENTAL

Boiling points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 237B spectrometer. NMR spectra were determined at 60 MHz. with a Varian DA-60-IL spectrometer and data are expressed in parts per million downfield from a tetramethylsilane external standard. Analytical VPC was accomplished with an Aerograph 202B instrument.

Materials. 2,3-Dimethyl-1-butene (minimum purity 99.6%) and 2,3-dimethyl-2-butanol were obtained from the Chemical Samples Co. Boron trifluoride etherate (Eastman White Label) and sodium borohydride (Metal Hydrides, Inc.) were used as received. Diethylene glycol dimethyl ether (diglyme) was distilled at reduced pressure from lithium aluminum hydride immediately prior to use.

2,3-Dimethyl-1-butanol (V). The hydroboration procedure of Brown and Zweifel was used (*4*). To a nitrogen-swept flask were added a 0.5*M* solution of sodium borohydride (2.1 grams, 0.056 mole) in diglyme (115 ml.) and IV (16.8 grams, 0.20 mole). To the stirred solution maintained at 20° C. was added dropwise over 1.5 hours a solution of boron trifluoride etherate (10.7 grams, 0.075 mole) in diglyme (20 ml.). The oxidation with 30% hydrogen peroxide (21.5 ml.) and work-up were the same as previously described (*4*). The ethereal extract was dried, concentrated, and distilled through a 40-cm. Vigreux column, giving 15.6 grams (76.2%) of V {b.p. 84–87° C. (65 mm.); n_D^{20} 1.4162 [lit. (*7*) b.p. 85.7–85.9° C. (68.6 mm.); n_D^{20} 1.4206]}. VPC analysis showed only two peaks: V (99%) and VI (1%).

1-Chloro-2,3-dimethylbutane (II). Thionyl chloride (24.1 grams, 0.21 mole) was added dropwise with cooling during 0.5 hour to a stirred solution of V (15 grams, 0.15 mole) in dry pyridine (12 ml.). The reaction mixture was heated 2 hours at 85° C., cooled, and treated with 3*M* hydrochloric acid (25 ml.). The organic phase was washed with 3*M* hydrochloric acid and cold saturated sodium chloride solution, dried, and distilled through a 12-cm. Vigreux column, giving 5.2 grams (30%) of clear, colorless II {b.p. 59.5–60.0° C. (86 mm.), n_D^{25} 1.4200 [lit. (*8*) b.p. 124°, n_D^{20} 1.4235]; infrared (neat) no OH absorption; NMR (CCl_4)δ 3.45 (*d*, 1) and 3.38 (*d*, 1, J_{AB} = 10.7 Hz., J_{AX} = 5.0 Hz., J_{BX} = 6.2 Hz., —CH_2Cl), 1.81 (*m*, 1, $>$CH—CH_2Cl), 1.55 [*m*, 1, $(CH_3)_2CH$—], 0.96 (*d*, 3, CH_3CH—CH_2Cl), 0.93 (*d*, 3) and 0.86 [*d*, 3, $(CH_3)_2CH$—]; 99.7% purity by VPC analysis}.

2-Chloro-2,3-dimethylbutane (III). The procedure of Brown and Fletcher was used (*3*). The product from VI (0.10 mole) was distilled through a 12-cm. Vigreux column, giving 9.1 grams (75%) of III; {b.p. 51–52° C. (100 mm.); n_D^{25} 1.4169 [lit. (*3, 9*) b.p. 67.6–70.0° C. (108 mm.), n_D^{25} 1.4171]; infrared (neat) no OH absorption.}

VPC Analyses. A 12-foot ×⅛-inch column of 10% Dow 710 on Chromosorb W was operated at 83° C. for the alcohols and 50° C. for the alkyl chlorides. Under the conditions employed (helium at 40 ml. per minute), compounds VI and V had retention times of 2.2 and 4.0 minutes, respectively. Similarly, III and II had retention times of 5.0 and 8.2 minutes. Prepared mixtures of the isomeric alcohols and chlorides were used to calibrate the procedure.

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Solubility and Spectra of Cadmium in Dilute Cadmium Chloride–Molten Salt Mixtures

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The solubility of cadmium in dilute mixtures of cadmium chloride with LiCl, 59 mole % LiCl–41 mole % KCl, and 50 mole % $MgCl_2$–30 mole % NaCl–20 mole % KCl was measured at 500° and 650° C. Absorption spectra of the species produced when cadmium dissolves in the three salt systems are reported.

THE solution of cadmium metal in cadmium chloride has been the subject of a large amount of investigation. Older work, reviewed by Bredig (*2*) and Corbett (*3*), and a recent e.m.f. study (*6*) indicate that cadmium dissolves by a reaction with cadmium chloride to form the cadmium (I) species, Cd_2^{2+}, perhaps solvated by an unknown number of cadmium (II) chloride entities. Other research (*4, 5, 8*) has shown that Cd_2^{2+}, unsolvated by cadmium chloride, is produced when cadmium dissolves in aluminum chloride-based salts containing cadmium chloride. Several workers have studied the effects on the cadmium solubility of diluting cadmium chloride with other chlorides (*7, 9-12*). The present work reports an investigation of cadmium solubility in dilute mixtures of cadmium chloride in several molten salts. The absorption spectra of the dissolved cadmium subchloride species in these systems are presented.

EXPERIMENTAL

Purification of Materials. Cadmium metal sticks of 99.99% purity (American Smelting and Refining Co.) were cleaned with dilute nitric acid, distilled water, and acetone, and then vacuum sublimed at about 1 micron pressure and 450° C. Immediately before use, the cadmium was filtered through a coarse fritted quartz disk on a vacuum line to remove any insoluble impurities. Anhydrous cadmium chloride (Mallinckrodt AR grade) was purified by sparging at 650° C. first with chlorine gas for about 1 hour, then with hydrogen chloride for about 2 hours, and finally filtering the purified salt after the system was evacuated. The solvent chloride salts, LiCl, 59 mole % LiCl-41 mole % KCl, and 50 mole % $MgCl_2$-30 mole % NaCl-20 mole % KCl, were prepared from the individual reagent grade alkali metal chlorides and from anhydrous magnesium chloride. These salts were purified by bubbling hydrogen chloride through the molten salts at 500° to 650° C. for about 3 to 4 hours, removing dissolved hydrogen chloride under vacuum, and filtering. The purified salts were sealed in quartz ampoules and then transferred to a glovebox containing a purified helium atmosphere. All manipulations involving the purified reagents were performed either in the helium-filled glovebox or on a vacuum line.

Measurements. Spectral measurements were made using a Cary Model 14 Recording Spectrophotometer equipped with a high temperature furnace similar to that described by Young and White (*13*). The absorbance of a solution of solvent salt and cadmium chloride was measured as the base line, then cadmium metal in excess of its solubility was added and the absorbance measured again. An inert argon atmosphere was maintained in the cells during these operations. Air was the reference in both cases. The absorption cells had a path length of 1 cm., but an 8-mm. insert was used in some cases to shorten the light path. The absorbance due to dissolved cadmium was obtained by