

and the precipitate filtered. The filtrate was saved and the solid washed twice with 20 ml. portions of ether and air-dried. The N-(chloroacetyl)-isatin (10.0 g., 66%) consisted of fine-golden-yellow needles, m. p. 210–211° cor., suitable for use without additional purification. The reaction filtrate was replenished with fresh chloroacetyl chloride (10 ml.) and the run repeated with additional isatin (10 g.) giving more equally pure product (12.0 g., 78%). For analysis the N-(chloroacetyl)-isatin was recrystallized from ethyl acetate.

Anal. Calcd. for $C_{10}H_6O_2NCl$: C, 53.71; H, 2.71; N, 6.26; Cl, 15.85. Found: C, 53.32; H, 2.91; N, 6.41; Cl, 15.79.

On recrystallization from methanol the yellow N-(chloroacetyl)-isatin separated with one mole of solvent as fine, colorless needles, m. p. 83.0–83.5° cor.

Anal. Calcd. for $C_{11}H_{10}O_2NCl$: C, 51.68; H, 3.95; N, 5.48; Cl, 13.88. Found: C, 51.52; H, 4.09; N, 5.46; Cl, 14.02.

2,4-Dihydroxyquinoline.—Into 150 ml. of an aqueous boiling solution of potassium hydroxide (5.0 g., 0.09 mole) was added all at once 5.0 g. (0.022 mole) of yellow N-(chloroacetyl)-isatin. The straw-colored solution was refluxed for two hours and then cooled to room temperature. On acidification of the reaction mixture with concentrated hydrochloric acid a cream-colored solid separated which was filtered and washed three times with 10-ml. portions of cold water. The crude yield was 2.0–2.5 g., 56–70%. From the filtrate small amounts of isatin were isolated. The 2,4-dihydroxyquinoline was purified by dissolving in the minimum amount of 10% sodium carbonate solution, filtering, boiling the filtrate with Darco for five minutes, filtering, and then reacidifying. On recrystallizing from methanol the compound separated as fine, colorless needles; m. p. 352–354° cor., recorded m. p. 355°.¹

Anal. Calcd. for $C_8H_6O_2N$: C, 67.08; H, 4.38; N, 8.69. Found: C, 67.21; H, 4.63; N, 8.65.

The identity of the 2,4-dihydroxyquinoline was confirmed by means of its nitroso derivative, m. p. 208° dec., uncor. (recorded 208°), which melted at the same temperature when mixed with an authentic sample. In addition, the (mono) acetyl derivative was prepared; m. p. 215.0–215.5° uncor. (recorded 214–215°), mixed melting point with authentic sample was 215.0–215.5° uncor.

(5) Niementowski, *Ber.*, **40**, 4289 (1907).

(6) Baeyer and Homolka, *ibid.*, **16**, 2216 (1883); cf. Meyer, Helman, *Compt. rend.*, **203**, 335–337 (1936).

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The Synthesis of Boron Trichloride

BY DALLAS T. HURD

A well known and convenient method for preparing small amounts of boron trichloride or boron tribromide comprises passing boron trifluoride gas over aluminum chloride or aluminum bromide.¹ I recently have found that a reaction may occur at elevated temperatures between aluminum chloride and boric oxide to produce boron trichloride.

Experimental.—120 grams of anhydrous boric acid and 440 g. of aluminum chloride were ground together and placed in a steel pressure vessel. The reaction mixture was heated at 350° for sixteen hours. The bomb then

(1) Gamble, Gilmont and Stiff, *This Journal*, **62**, 1257 (1940).

was cooled and the gaseous reaction product was bled off and caught in a trap held at -80° . The collected product was a clear colorless liquid boiling at 12° (reported boiling point of boron trichloride $+12.5^\circ$). This material fumed in moist air, reacting with the moisture to produce white solid boric acid. A small amount of the liquid was dissolved in water to give a solution which, when tested with silver nitrate, gave a strong test for chloride.

The total amount of product collected was 30 g. or about 7.5% yield based on a complete conversion of boric oxide to boron trichloride.

It also was observed that a molten mixture of boric oxide and calcium chloride at $800\text{--}900^\circ$ evolved boron trichloride very slowly and became more viscous, precipitating an infusible residue in the magma. This solid residue was treated with water after it was cool and a strongly alkaline solution resulted, indicating a conversion of some of the calcium chloride to calcium oxide.

Discussion.—The low yields of boron trichloride are ascribed to: (1) the reaction between aluminum chloride and boric oxide to form aluminum oxide and boron trichloride may be an equilibrium reaction which did not go to completion in the sealed bomb; and/or (2) part of the boric oxide may become bound chemically as aluminum borate by reaction with the aluminum oxide as this material is formed. It is noteworthy that attempts to prepare boron trichloride by a reaction of sodium borate or tetraborate with aluminum chloride were unsuccessful at reaction temperatures up to 350° .

GENERAL ELECTRIC RESEARCH LABORATORY

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Reactions of Polyhaloparaffins with Grignard Reagents. 1,1,1-Trichloropentane

BY CORLISS R. KINNEY AND WILLIAM L. SPLIETHOFF

Binaghi¹ has shown that chloroform and carbon tetrachloride react readily with ethylmagnesium bromide, but that gaseous reduction products are formed for the most part. We have reexamined the reaction from the point of view of controlling its course for the production of tri- and tetrasubstituted paraffins. However, even at -78° , using the less reactive *n*-butylmagnesium chloride, and carrying the halide into the reaction flask vaporized in a stream of dry nitrogen, a vigorous reaction occurs and the products are largely gaseous.

On the other hand, the reaction may be controlled to a certain extent by using the inverse Grignard technique. Thus, adding *n*-butylmagnesium chloride to a solution of carbon tetrachloride in ether gives a small yield of the first step in the reaction, 1,1,1-trichloropentane. The new compound loses hydrogen chloride at about 140° but could be vacuum distilled without decomposition. This thermal instability further indicates activity of the vicinal chlorine atoms. No attempt was made to treat this compound with additional Grignard reagent, but instead the more available 1,1,1-trichloroethane was investigated. This compound, like chloroform, gave largely

(1) Binaghi, *Gazz. chim. Ital.*, **52**, II, 132–138 (1922); **53**, 879 (1923).