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 $C_{10}H_6O_3NCl$: 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 $C_{11}H_{10}O_4NCl$: 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°.[5]

Anal. Calcd. for $C_9H_7O_2N$: 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°[6]), 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°[3]), 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**, Heimann, *Compt. rend.*, **203**, 335–337 (1936).

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

RECEIVED NOVEMBER 3, 1948

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 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°). 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 800–900° 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°.

---

(1) Gamble, Gilmont and Stiff, THIS JOURNAL, **62**, 1257 (1940).

GENERAL ELECTRIC RESEARCH LABORATORY
SCHENECTADY, N. Y.

RECEIVED OCTOBER 25, 1948

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

BY CORLISS R. KINNEY AND WILLIAM L. SPLIETHOFF

Binaghi[1] 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 reëxamined 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).

gaseous products and the reaction appeared to be unsuited as a synthetic method. To complete the series, methylene chloride also was tried but did not react at the boiling point of ether. These results indicate a marked difference in the reactivity of vicinal chlorides at the trichloro level. This is of interest in connection with the behavior of chloral for which only reduction at the carbonyl group with aliphatic Grignard reagents containing β-hydrogen atoms has been reported[2] and the behavior of monochloroacetone which was found to react with isoamylmagnesium bromide at the chlorine atom as well as adding on the reagent at the carbonyl group.[3]

Considering the violence of the reaction of carbon tetrachloride, even at −78°, carbon tetrafluoride was also treated with *n*-butylmagnesium chloride at the boiling point of ether. However, no reaction was observed.

Experimental

1,1,1-Trichloropentane.—*n*-Butylmagnesium chloride was prepared from one mole of *n*-butyl chloride, one gram atom of magnesium and 300 ml. of dry ether. The solution was forced by means of dry nitrogen under pressure, into a stirred mixture of 2 moles of carbon tetrachloride and 300 ml. of dry ether cooled in a bath of Dry Ice and acetone. A vigorous reaction occurred with the formation of a white precipitate and a gas which decolorized bromine in carbon tetrachloride. White fumes were also formed which settled on the walls of the flask as a white solid. Since this was very soluble in water it was concluded that it was magnesium chloride. After the reagent had been added the cooling bath was removed and the mixture allowed to come to room temperature and stand for two hours. It was then refluxed gently for forty-five minutes and after cooling was decomposed with ice-water. Some basic magnesium precipitate was filtered out with suction and the organic layer separated, dried with calcium chloride and distilled to 100° to remove ether and excess carbon tetrachloride. The residue weighed about 30 g. and constituted a crude yield of 16.5%. On continuing the distillation, hydrogen chloride was evolved copiously at about 140°; consequently, the residue was vacuum distilled. Refractionation at 20 mm. through a 10-plate column packed with glass helices gave a heart-cut boiling at 56–57°. The index of refraction was $n^{20}D$ 1.4540.

Anal. Calcd. for $C_5H_9Cl_3$: Cl, 60.5. Found: Cl, 60.2, 60.1.

Acknowledgments—The authors are indebted to Mr. H. L. Lovell for the analysis reported above and to the Fluorine Laboratories of The Pennsylvania State College for the sample of carbon tetrafluoride used.

DIVISION OF FUEL TECHNOLOGY
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA

RECEIVED OCTOBER 4, 1948

---

[2] Gilman and Abbott, *J. Org. Chem.*, **8**, 224 (1945); Floutz, THIS JOURNAL, **67**, 1615 (1945).

[3] Kinney and Spliethoff, to be published in the *Journal of Organic Chemistry*.

Decomposition of Aliphatic Azo Compounds

BY FREDERICK M. LEWIS AND MAX S. MATHESON

Certain aliphatic azo compounds have several properties which make them especially suitable as sources of free radicals for kinetic investigations. These properties include stability, clean first order decompositions nearly independent of reaction media, and the ability to act as efficient photosensitizers in the near ultraviolet.

The decomposition rates (Table I) as measured by nitrogen evolution, were in all cases first order after a short induction period, probably due to a thermal adjustment after sample addition and to the disappearance of oxygen traces introduced with the sample. Thiele and Heuser[1] and Dox[2] have described the method of preparation of these compounds. Further, it has been shown that 2-azo-bis-isobutyronitrile heated at 110° in high boiling petroleum ether quantitatively splits out nitrogen, tetramethyl succinonitrile being formed in 50% yield.[1] Of course such fragments of the azo compound as initiate polymerization in the presence of monomer will not appear as tetramethyl succinonitrile.

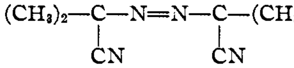
TABLE I

DECOMPOSITION OF AZO COMPOUNDS IN XYLENE AT 80°

Material, 0.1–0.3 mole/l.	*k*, min.$^{-1}$	*Ea*, kcal.
2-Azo-bis-isobutyronitrile	0.0092	31.3
2-Azo-bis-2-methylbutyronitrile	.00598	29.4
2-Azo-bis-2-methylheptonitrile	.0107	30.2
1-Azo-bis-1-cyclohexanecarbonitrile	.000282	39.9
Dimethyl-2-azo-bis-isobutyrate	.00653	35.8
4-Azo-bis-4-cyanopentanoic acid	.00538[a]	34.0

[a] In water, insoluble in xylene.

Table II shows that there is little change in rate for 2-azo-bis-isobutyronitrile (sold as Porofor N by Naugatuck Chemical Division of U. S. Rubber Co.) with widely different reaction solvents, and even a powerful inhibitor (tetrachloroquinone) has little effect. Accordingly these materials offer several advantages over peroxides as free radical sources when a constant rate of production of radicals is desired. (As an example of free radical activity 0.096 g./l. of Porofor N in purified vinyl acetate induces 4.7% polymerization per hour at 50°.) Several authors[3] have shown that



$$(CH_3)_2\underset{\displaystyle CN}{\underset{|}{C}}—N{=}N—\underset{\displaystyle CN}{\underset{|}{C}}—(CH_3)_2$$

TABLE II

SOLVENT EFFECT IN THE DECOMPOSITION OF 2-AZO-BIS-ISOBUTYRONITRILE

(~0.3 mole/l.) at 80°

Solvent	*k*, min.$^{-1}$
Xylene	0.0092
Xylene contg. 0.012 mole/l. tetrachloroquinone	.00898
Glacial acetic acid	.00914
N-Dimethylaniline	.011
Dodecyl mercaptan	.00875
Carbon tetrachloride	.00725 (77°)

---

[1] Thiele and Heuser, *Ann.*, **290**, 1 (1896).

[2] Dox, THIS JOURNAL, **47**, 1473 (1925).

[3] Nozaki and Bartlett, *ibid.*, **68**, 1686 (1946); Cass, *ibid.*, **68**, 1976 (1946).