mocouple well and thermocouple replaced the stirrer in this case. At the end of the run, all the boron triiodide and the excess iodine were sublimed into trap no. 1, now cooled by Dry Ice and then this trap was sealed at the inlet and cut out of the system between the pair of stopcocks at the outlet of trap no. 1.

Purification of boron triiodide as obtained from the borohydrides was effected first by dissolving it and some of the excess iodine in purest carbon disulfide, reduction of the iodine by mercury and zinc dust, filtering to get a clear solution, then vacuum evaporation of the carbon disulfide to get the crude BI_3. This was then further purified by slowly subliming it over a small quantity of mercury at a pressure of about a millimeter. The resulting crystalline product was of varying shades of pink due to admixed mercuric iodide. Resublimation at low pressure in a type of molecular still (C, Fig. 1) gave colorless, glistening crystals, melting at 49.9 ± 0.5°, the melt assuming a pale pink color. The melting point previously reported for BI_3 is 43°.[6] Analysis of this purified product agreed well with the theoretical requirements of BI_3. Found: B, 2.78; I, 96.95. Calcd.: B, 2.77; I, 97.23.

Summary

1. Tetraiododiborine, B_2I_4, and a lower iodide of boron, B_xI_y, where $x > y$, have been prepared by the action of an electrodeless discharge at room temperature upon the vapors of boron triiodide at 1 to 3 mm. pressure. The decomposition is irreversible and is accompanied by a brilliant yellowish-green glow. Free iodine is formed and is trapped out by liquid nitrogen. Forty per cent. of the boron triiodide is reduced in one pass through the glow; one-third of the reduced boron triiodide is recoverable as tetraiododiborine.

2. B_2I_4 is a well-crystallized, pale yellow solid, which is slowly decomposed at room temperature, forming BI_3 and a black non-volatile residue of a polymerized monoiodide, $(BI)_x$. Decomposition is hastened by higher temperature and by the action of sunlight.

3. The lower iodides of boron are hydrolyzed by water yielding strongly reducing solutions which react with silver nitrate precipitating metallic silver and silver iodide.

4. A new and satisfactory method for the preparation of boron triiodide has been developed, in which solid sodium or lithium borohydride reacts with iodine at 200 or 120°, respectively. Yields as high as 66% on the basis of the boron involved were obtained using lithium borohydride.

5. The reduction of boron triiodide to lower iodides has been shown to occur in other ways, such as by the action of silver wool at 185° or by means of hydrogen in a "hot–cold" tube apparatus. These methods, however, are less satisfactory for preparative purposes than those employing the electrodeless discharge.

CAMBRIDGE, MASSACHUSETTS RECEIVED JULY 6, 1949

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DEPAUW UNIVERSITY]

Trichloroaminoalcohols. I. 1,1,1-Trichloro-3-aminopropanol-2 and Derivatives

BY MARYANN COMPTON,[1] HARVEY HIGGINS,[2] LORNE MACBETH,[3] JANE OSBORN[4] AND HOWARD BURKETT

In 1942 Malkiel and Mason[5] described the synthesis of a compound (I), m. p. 167.4–167.7° (cor.), by the catalytic hydrogenation of 1,1,1-trichloro-3-nitropropanol-2 (II). They reported I to be 1,1,1-trichloro-3-aminopropanol-2 (III). The synthesis of III, m. p. 123°, was first reported[6] in 1935. In addition to III, Chattaway and Witherington also described and reported analyses for its hydrochloride, sulfate and oxalate salts and the mono- and di-acetyl derivatives.

Upon repeating the work of Malkiel and Mason, we obtained a product, m. p. 159–159.5° (uncor.), which was apparently the same as I. It was noted in our work that about 3.8–3.9 moles of hydrogen was consumed per mole of the nitro compound and that the product was much more soluble in water than was expected. Moreover, this product gives instantly a copious precipitate with aqueous silver nitrate. It was suspected that one of the chlorine atoms had been removed by hydrogenolysis, forming 1,1-dichloro-3-aminopropanol-2 hydrochloride (IV), which would give nearly the same nitrogen analysis as III. We have prepared the free amine and the N-benzoyl and O,N-dibenzoyl derivatives from this product, all of which give the correct analysis for the dichloro compound. As further confirmation of its structure, IV has also been synthesized as represented by the following equations.

$$\begin{tikzcd}
Cl_2CHCH(OC_2H_5)_2 \arrow[r] & Cl_2CHCHO \arrow[d, "CH_3NO_2"] \\
Cl_2CHCOHCH_2NH_2.HCl & Cl_2CHCHOHCH_2NO_2 \arrow[l]
\end{tikzcd}$$

The mixed melting point of this latter product with that from the catalytic hydrogenation of II is not depressed. From this evidence, it is thought that the compound reported by Malkiel and Mason was IV and not III.

Chattaway and Witherington prepared III by the reduction of II with tin and hydrochloric acid but they did not report the yield. A similar re-

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[5] Malkiel and Mason, THIS JOURNAL, **64**, 2515 (1942).

[6] Chattaway and Witherington, *J. Chem. Soc.*, **137**, 1623 (1935).

duction by us gave a poor yield. We have synthesized III in good yield, using stannous chloride and hydrochloric acid, and prepared several of its derivatives.

Malkiel and Mason describe the preparation of a benzoyl derivative, m. p. 167.4°, from their crude reduction mixture. It is confusing to note that this melting point is different from that of the mono- or di-benzoyl derivatives of either the dichloro- or trichloro-compound prepared in our work. The product obtained by us upon benzoylating the crude hydrogenation mixture, in the same manner[7] as they, was N-benzoyl-1,1-dichloro-3-aminopropanol.

Experimentation on the synthesis of II[5,8,9,10] by the base-catalyzed condensation of chloral hydrate and nitromethane has culminated in a procedure which gives a high-quality product in 92–98% yield. Attempts to make the benzoyl and *p*-nitrobenzoyl derivatives of II failed.

The N-acyl and O,N-diacyl derivatives of III are easily prepared. However, numerous attempts to synthesize O-acyl 1,1,1-trichloro-3-aminopropanol-2 hydrochloride by acylation of the hydrochloride[11–14] or by the rearrangement of the N-acyl 1,1,1-trichloro-3-aminopropanol-2[12,14] have been unsuccessful.

Pharmacology.—Several of these compounds were tested by Eli Lilly and Company for local anesthetic, pressor, analgesic and chemotherapeutic action and were found to have none.

Experimental

All melting points are uncorrected. Analyses were done by one of us (L. M.).

1,1,1-Trichloro-3-nitropropanol-2.—In a 250-ml. erlenmeyer flask were placed 165.5 g. (1 mole) of chloral hydrate and 73.2 g. (1.2 moles) of nitromethane. After the chloral hydrate had dissolved by warming to 50°, 1.9 g. of anhyd. potassium carbonate was added in portions with vigorous stirring so that the temperature remained at 70–80°, cooling in ice as necessary. The stirring was continued until the mixture had cooled to room temperature. Then, the product was washed three times with 50-ml. portions of water. The combined water washes were extracted with ether and the ether added to the main portion of the product. After the solvent had been removed under reduced pressure with warming on the steam-bath, the residue was distilled through a 15-cm. Vigreux column. The colorless fraction, boiling at 105.5–106.5° at 3.5 mm., amounted to 204.3 g. (98%). Upon standing, it gradually solidified, m. p. 44–46°.

1,1-Dichloro-3-aminopropanol-2 Hydrochloride (from 1,1,1-Trichloro-3-nitropropanol-2).—A mixture of 10.4 g. (0.05 mole) of 1,1,1-trichloro-3-nitropropanol-2, 75 ml. of ethanol and about 6 g. of Raney nickel was hydrogenated in the Adams machine, using an initial pressure of 50 p.s.i. In thirty-five minutes, a pressure drop corresponding to 0.190 mole of hydrogen was observed. The catalyst was filtered off and the filtrate evaporated to a small volume. The solid, obtained upon the addition of ethyl acetate and cooling, was recrystallized from ethanol and washed with ether, yielding 3.1 g. (34.7%) of white product, m. p. 159–159.5°.

Anal. Calcd. for $C_3H_7ONCl_2\cdot HCl$: N, 7.75. Found: N, 7.49.

In another experiment, in which 3.9 moles of hydrogen was consumed per mole of compound, an aliquot of the reduced mixture was treated with an excess of silver nitrate solution. The amount of precipitated silver chloride indicated 1.19 equivalents of chloride ion per mole of compound reduced.

1,1-Dichloro-3-aminopropanol-2.—A small sample of the hydrochloride described in the previous section was recrystallized from butanol-1. This material, m. p. 162–163°, was dissolved in abs. alcohol and an excess of dry ammonia was added. Addition of anhyd. ether caused the precipitation of ammonium chloride, which was removed by filtration. The filtrate was evaporated to dryness at room temperature under reduced pressure. The residue was extracted with anhyd. ether and this solution evaporated to a small volume. After cooling in the refrigerator, the white crystalline product, m. p. 57–58°, was filtered off. It was somewhat hygroscopic and began to turn yellow in a few days.

Anal. Calcd. for $C_3H_7ONCl_2$: N, 9.69. Found: N, 9.49.

A sample of this amine was dissolved in anhyd. ether and dry hydrogen chloride was added. The resulting precipitate melted at 162–163° and gave no depression of the mixed melting point with the original hydrochloride, proving that there were no deep-seated changes in the compound.

1,1-Dichloro-3-aminopropanol-2 Hydrochloride (from Dichloroacetaldehyde).—To a mixture of 12.7 g. (0.112 mole) of dichloroacetaldehyde[15] (obtained from dichloroacetal[16]), 2.03 g. (0.112 mole) of water and 8.25 g. (0.135 mole) of nitromethane was added 0.22 g. of anhydrous potassium carbonate in portions. After an initial exothermic reaction, the temperature was kept at 80° for a few minutes. The cool reaction mixture was washed twice with small portions of water. The aqueous portions were extracted with ether and the combined organic materials were dried for a few seconds over anhyd. sodium carbonate and distilled. The portion (6.13 g.) boiling at 103–107° at 5 mm. was added to a solution of 47.6 g. of stannous chloride (hydrated) in 33 ml. of concd. hydrochloric acid. The reaction mixture was heated to 90°, at which temperature it darkened considerably. It was evaporated to dryness at 60° under reduced pressure and the residue was dissolved in water. The tin was removed by adding ammonium hydroxide and hydrogen sulfide and filtering. The solid residue, obtained upon evaporating the filtrate to dryness, was extracted thoroughly with boiling butanol-1. After evaporation to one-fourth volume and cooling, a crude product was obtained. One crystallization from butanol-1 yielded 0.24 g. of pure white product, m. p. 161–162°. The melting point of this product with that from the hydrogenation of 1,1,1-trichloro-3-nitropropanol-2 was 161–162°.

N-Benzoyl-1,1-dichloro-3-aminopropanol-2.—The reaction mixture from a hydrogenation identical to that described previously was evaporated to dryness under reduced pressure. The residue was mixed with a little water and 10 ml. of benzoyl chloride; then, with continuous stirring and cooling as necessary, 75 ml. of 10% sodium hydroxide was added in 20-ml. portions. After cooling and filtering, the solid was thoroughly extracted with warm ethyl acetate. The crude product, precipitated by adding petroleum ether, was crystallized twice from ethyl acetate-

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(7) Private communication.

(8) Henry, *Bull. Acad. Roy. Belg.*, **32**, 17 (1896).

(9) Chattaway and Witherington, *J. Chem. Soc.*, **137**, 1178 (1935).

(10) Studies on the condensation of aldehydes with nitro compounds have been carried out by Vanderbilt and Hass, *Ind. Eng. Chem.*, **32**, 34 (1940); Lindal, *ibid.*, **33**, 65 (1941); Sprang and Degering, THIS JOURNAL, **64**, 1063 (1942); Nightingale, *ibid.*, **66**, 352 (1944).

(11) Cope and Hancock, THIS JOURNAL, **66**, 1448, 1453 (1944).

(12) Cope and Hancock, *ibid.*, **66**, 1738 (1944).

(13) Hancock, Hardy, Heyl, Wright and Cope, *ibid.*, **66**, 1747 (1944).

(14) Day, *J. Org. Chem.*, **5**, 515 (1940).

(15) Wohl and Roth, *Ber.*, **40**, 217 (1907).

(16) Magnani and McElvain, THIS JOURNAL, **60**, 2210 (1938).

petroleum ether, yielding 2.3 g. of white product, m. p. 131.3–132.5°.

Anal. Calcd. for $C_{10}H_{11}O_2NCl_2$: N, 5.67. Found: N, 5.87.

O,N-Dibenzoyl-1,1-dichloro-3-aminopropanol-2.—To 0.694 g. (0.0038 mole) of 1,1-dichloro-3-aminopropanol-2 hydrochloride suspended in 8 ml. of dry benzene was added, with cooling and stirring, 1.40 g. (0.0138 mole) of triethylamine; then, 1.94 g. (0.0138 mole) of benzoyl chloride, keeping the temperature below 30°. After the addition of the benzoyl chloride, the mixture was warmed to 40–45° for one hour. Filtration of the warm reaction mixture and addition of petroleum ether to the filtrate gave an oil, which upon two crystallizations from ethanol-water afforded 0.211 g. of white solid, m. p. 87–88°. The filtrates yielded 0.6 g. more of slightly less pure product.

Anal. Calcd. for $C_{17}H_{15}O_3NCl_2$: N, 3.95. Found: N, 3.75.

Treatment of the N-benzoyl-1,1-dichloro-3-aminopropanol-2, obtained from the crude hydrogenation mixture, in a similar manner gave the same product, m. p. 87–88° (mixed m. p. 87–88°).

1,1,1-Trichloro-3-aminopropanol-2.—In an erlenmeyer flask 580 g. (2.57 moles) of stannous chloride (hydrated) was dissolved in 400 ml. of concd. hydrochloric acid. With good stirring, 82.3 g. (0.394 mole) of 1,1,1-trichloro-3-nitropropanol-2 was added in one portion. The temperature rose spontaneously to 106°. When the temperature began to drop, the mixture was heated to boiling (114°) for a few minutes; then allowed to cool slowly. After finally cooling for three hours in an ice-bath, the tin-containing salt was filtered off and air-dried. A solution of this in 800 ml. of water was saturated with hydrogen sulfide and filtered. The filtrate was evaporated to dryness. To a solution of the resultant white solid in 85 ml. of water was added concd. ammonium hydroxide until no more precipitate formed. After cooling in an ice-bath and filtering, there was obtained 48.7 g. (69.4%) of product, m. p. 115.3–116.5°. Sublimation at 2 mm. pressure gave a pure product, m. p. 118–119°.

Anal. Calcd. for $C_3H_6ONCl_3$: N, 7.85. Found: N, 7.66.

In another preparation the tin-containing salt was thoroughly dried and analyzed.

Anal. Calcd. for $C_3H_6ONCl_3 \cdot H_2SnCl_4$: N, 3.28. Found: N, 3.40.

N-Benzoyl-1,1,1-trichloro-3-aminopropanol-2.—To a suspension of 5 g. (0.028 mole) of 1,1,1-trichloro-3-aminopropanol-2 in 50 ml. of benzene was added 3.75 g. (0.037 mole) of triethylamine; then, dropwise with stirring, 4.14 g. (0.029 mole) of benzoyl chloride. When the odor of benzoyl chloride was gone, the cooled reaction mixture was filtered. Thorough washing with water, followed by crystallizing from ethanol-water, yielded 6.65 g. (84%) of product, m. p. 144–144.5°.

Anal. Calcd. for $C_{10}H_{10}O_2NCl_3$: N, 4.96. Found: N, 4.96.

N-*p*-Nitrobenzoyl-1,1,1-trichloro-3-aminopropanol-2.—To a solution of 4.5 g. (0.025 mole) of 1,1,1-trichloro-3-aminopropanol-2 in 15 ml. of pyridine was added 4.6 g. (0.025 mole) of *p*-nitrobenzoyl chloride in small portions with stirring and cooling. After standing overnight, the mixture was warmed gently for thirty minutes, cooled and poured into water. The tan solid was filtered and was crystallized three times from ethanol-water and once from methanol, furnishing 1.6 g. (19.5%) of white solid, m. p. 134–136°.

Anal. Calcd. for $C_{10}H_9O_4N_2Cl_3$: N, 8.54. Found: N, 8.37.

O,N-Di-*p*-nitrobenzoyl-1,1,1-trichloro-3-aminopropanol-2.—To a solution of 4.0 g. (0.0224 mole) of 1,1,1-trichloro-3-aminopropanol-2 in 40 ml. of dry benzene and 4.95 g. (0.049 mole) of triethylamine was added 8.7 g. (0.047 mole) of *p*-nitrobenzoyl chloride in small portions with stirring so that the temperature did not rise above 30°. After standing for two days at room temperature, the mixture was refluxed for thirty minutes, cooled and filtered. The solid was washed thoroughly with water and crystallized twice from acetone-water, affording 6.8 g. (63.9%) of white product, m. p. 207.5–208.5°,

Anal. Calcd. for $C_{17}H_{12}O_6N_3Cl_3$: N, 8.81. Found: N, 8.70.

N-Phenylacetyl-1,1,1-trichloro-3-aminopropanol-2.—Handling 3.7 g. (0.0208 mole) of 1,1,1-trichloro-3-aminopropanol-2, 7.0 ml. (0.05 mole) of triethylamine and 5.6 ml. (0.042 mole) of phenylacetyl chloride by the same procedure as the preceding experiment yielded a product which sintered at 120° and melted at 129°.

Anal. Calcd. for $C_{11}H_{12}O_2NCl_3$: N, 4.74. Found: N, 4.86.

O,N-Di-diphenylacetyl-1,1,1-trichloro-3-aminopropanol-2.—This compound was made in the same manner as the preceding one from 1.78 g. (0.01 mole) of 1,1,1-trichloro-3-aminopropanol-2, 3 ml. of triethylamine and 4.9 g. (0.021 mole) of diphenylacetyl chloride. After one crystallization from ethanol, there was obtained 4.3 g. (77%) of white product, m. p. 142–143°.

Anal. Calcd. for $C_{31}H_{26}O_3NCl_3$: N, 2.47. Found: N, 2.32.

N-Benzenesulfonyl-1,1,1-trichloro-3-aminopropanol-2.—To a suspension of 3.56 g. (0.02 mole) of 1,1,1-trichloro-3-aminopropanol-2 in 15 ml. of water was added 7.77 g. (0.044 mole) of benzenesulfonyl chloride and 24 ml. of 10% aqueous sodium hydroxide in small portions alternately with stirring so that the temperature did not rise above 30° and the mixture was at no time strongly basic. When the odor of the benzenesulfonyl chloride was almost gone, the product was filtered, washed with water and crystallized from ethanol-water, yielding 3.7 g. (58%) with m. p. 162–163°.

Anal. Calcd. for $C_9H_{10}O_3NSCl_3$: N, 4.41. Found: N, 4.52.

Summary

Evidence for the identity of 1,1-dichloro-3-aminopropanol-2 hydrochloride was presented.

The synthesis of 1,1,1-trichloro-3-aminopropanol-2 and several of its derivatives were described.

GREENCASTLE, INDIANA RECEIVED DECEMBER 21, 1948