

quantitative. Crystallization of the material from carbon disulfide or hexane gave a purer product, m. p. 89–89.5°, but considerable loss was entailed.

CHEMICAL LABORATORY
NORTHWESTERN UNIVERSITY
EVANSTON, ILL.

RECEIVED OCTOBER 31, 1945

The Preparation of *t*-Butylamine by the Low-Pressure Hydrogenation of 2,2-Dimethylethylenimine¹

BY KENNETH N. CAMPBELL, ARMIGER H. SOMMERS AND
BARBARA K. CAMPBELL

We recently needed large amounts of *t*-butylamine, and developed a method for preparing it by the hydrogenation of 2,2-dimethylethylenimine. While our paper was being cleared by O. S. R. D., a Note by Karabinos and Serijan² appeared, in which the high-pressure hydrogenation of the imine to *t*-butylamine is described. We should like to point out that the hydrogenation can be carried out satisfactorily at low pressures, by the following procedure:

A citrate of magnesia bottle, wound for electrical heating, was charged with 100 ml. of pure dioxane, 35.5 g. of freshly-distilled 2,2-dimethylethylenimine and 9 g. of Raney nickel. The bottle was attached to a Parr low-pressure hydrogenation apparatus and flushed several times with hydrogen to remove air. Hydrogenation was carried out at 60° and an initial pressure of 60 lb./sq. in.; absorption was quantitative and complete in two hours. The solutions from two such runs were combined and distilled through a 10–15 plate Fenske-Whitmore column to give 58 g. of *t*-butylamine, b. p. 44.0–44.5°, n_D^{20} 1.3770. The amine yielded an α -naphthylthiourea, m. p. 153–154°, and a benzoyl derivative, m. p. 134–135°.

(1) The work described in this paper was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and the University of Notre Dame.

(2) Karabinos and Serijan, *THIS JOURNAL*, **67**, 1856 (1945).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA

RECEIVED OCTOBER 24, 1945

Bromine Analogs of DDT¹

BY STANLEY J. CRISTOL AND H. L. HALLER

In connection with entomological and pharmacological work on the insecticide DDT [1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane], it was necessary to prepare certain bromine-containing analogs of DDT. Of the three relatively simple analogs, that from chloral and bromobenzene and those from bromal with chlorobenzene or bromobenzene, the first, 1-trichloro-2,2-bis-(*p*-bromophenyl)-ethane, has already been described.² The preparation of the other two, 1-tribromo-2,2-bis-(*p*-chlorophenyl)-ethane (I) and 1-tribromo-2,2-bis-(*p*-bromophenyl)-ethane (II), has now been effected, although in poor yield, by the sul-

(1) The work described in this paper was carried out under a transfer of funds, recommended by the Committee on Medical Research, from the Office of Scientific Research and Development to the Bureau of Entomology and Plant Quarantine.

(2) Zeidler, *Ber.*, **7**, 1180 (1874).

furic acid-catalyzed condensation of bromal with the appropriate halobenzene.

Compound I is fairly stable, can be recrystallized from 95% ethanol, and when pure melts at 146–147°. On the other hand, II is very unstable. Recrystallization of the pure compound, m. p. 173–174°, from ethanol or from benzene-ligroin gave a mixture which melted at about 140° with decomposition. Purification of II was effected by tedious recrystallization from Skellysolve B (petroleum ether, b. p. 60–70°). I and II both eliminate the elements of hydrogen bromide in ethanolic alkali to produce the corresponding olefins. The position of the ring halogen atoms was shown by oxidation of the olefins to the *p,p'*-dihalobenzophenones. Dinitro derivatives of I and II were also prepared.

1-Tribromo-2,2-bis-(*p*-chlorophenyl)-ethane (I).—To a well-stirred mixture of 100 g. (0.36 mole) of bromal and 320 g. (5.7 moles) of chlorobenzene cooled in an ice-bath, 560 g. of 100% sulfuric acid was added dropwise over a period of one hour. The temperature of the mixture was kept below 6° during the addition, and the resulting mixture was stirred in an ice-bath for twenty-four hours. The product mixture was poured onto ice and water, and the organic fraction was extracted with ether. The ethereal solution was washed with water and dilute sodium bicarbonate solution, and then dried over anhydrous sodium sulfate. The ether and excess chlorobenzene (about 60% was recovered) were removed under reduced pressure. The residual oil was crystallized from Skellysolve B, giving 42 g. (24%) of crude I. The product was recrystallized from 95% ethanol, and when pure melted at 146–147° (cor.). About 70% recovery was obtained in the recrystallization.

Anal. Calcd. for $C_{14}H_9Cl_2Br_2$: C, 34.46; H, 1.86. Found: C, 34.68; H, 1.85.

Use of stronger or weaker acid, increase in temperature and modifications in reaction time for the condensation resulted either in poorer or unaffected yields of product. Use of acetic acid as solvent for the condensation resulted in the formation of an almost quantitative yield of the diacetate of bromal hydrate,³ m. p. 77–77.8°, rather than the desired product I.

Anal. Calcd. for $C_4H_7O_4Br_2$: Br, 62.6; mol. wt., 383. Found: Br, 61.8; mol. wt. (in benzene), 360.

1,1-Dibromo-2,2-bis-(*p*-chlorophenyl)-ethylene was obtained by heating at reflux for one hour a solution of 1.0 g. of I and 0.6 g. of potassium hydroxide in 40 ml. of 95% ethanol. The reaction mixture was poured into ice water; the product oiled out, but rapidly crystallized. The solid was separated by filtration and was recrystallized from 95% ethanol. It melted at 104–105° (cor.). The yield was not determined as a portion of the preparation was lost.

Anal. Calcd. for $C_{14}H_8Cl_2Br_2$: C, 41.32; H, 1.98. Found: C, 41.23; H, 1.90.

A solution of 125 mg. of the olefin in 5 ml. of glacial acetic acid was heated to reflux and 125 mg. of chromic anhydride was added through the condenser. Refluxing was continued for one hour. Bromine vapors were evolved during the first fifteen minutes. The product mixture was cooled and then poured into water; the oil which precipitated solidified rapidly and was filtered and dried. The yield of almost pure *p,p'*-dichlorobenzophenone was 68 mg. (88%), and the product, after recrystallization, melted at 146–147° (cor.). The melting point was not depressed upon admixture with known *p,p'*-dichlorobenzophenone.

Dinitro Derivative of I.—A mixture of 500 mg. of I and 5 ml. of fuming nitric acid was warmed in a water-bath at

(3) Gabutti, *Gazz. chim. ital.*, **30**, II, 191 (1900).