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

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The Preparation of *t*-Butylamine by the Low-Pressure Hydrogenation of 2,2-Dimethylethylenimine[1]

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 Serijan[2] 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^{20}_{D} 1.3770. The amine yielded an α-naphthylthiourea, m. p. 153–154°, and a benzoyl derivative, m. p. 134–135°.

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[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).

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Bromine Analogs of DDT[1]

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 sulfuric 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 $C_{14}H_9Cl_2Br_3$: 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 $C_6H_7O_4Br_3$: 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

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[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).

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

50° for one hour. The reaction mixture was cooled and poured onto ice; the resulting solid was filtered, washed, and dried. The product was recrystallized from acetone–ethanol and melted at 181.5–183.5° (cor.).

Anal. Calcd. for $C_{14}H_7Cl_2Br_3N_2O_4$: C, 29.09; H, 1.22. Found: C, 29.32; H, 1.23.

1-Tribromo-2,2-bis-(*p*-bromophenyl)-ethane (II).—This compound was prepared in the same manner as I, with substitution of 330 g. of bromobenzene for the chlorobenzene. Three layers were formed in the ether extraction, the center layer containing about 110 g. of crude bromobenzenesulfonic acid. The ether and excess bromobenzene (210 g.) were removed under reduced pressure and the residual oil was crystallized from Skellysolve B. The yield of crude solid, m. p. 136–160°, was 34.5 g. (16.5%). Several recrystallizations from Skellysolve B gave about half of this material as pure compound melting at 173–174° (cor.) and crystallizing as rhombs or needles.

Anal. Calcd. for $C_{14}H_9Br_5$: C, 29.15; H, 1.57. Found: C, 29.19; H, 1.76.

The compound was quite unstable; ethanolic solutions became acidic rapidly, and crystallization from ethanol or from benzene–ligroin resulted in products decomposing at 140–150°.

1,1-Dibromo-2,2-bis-(*p*-bromophenyl)-ethylene was prepared by the treatment of II with ethanolic potassium hydroxide (as given above for I) in 76% yield. The product recrystallized from 95% ethanol was obtained as pale-yellow, prismatic needles melting at 121.8–122.7° (cor.).

Anal. Calcd. for $C_{14}H_8Br_4$: C, 33.91; H, 1.63. Found: C, 33.49; H, 1.36.

A hundred and ten mg. of the olefin was oxidized in 80% yield with chromic anhydride, as described above, to *p,p'*-dibromobenzophenone, m. p. 174–175° (cor.) after recrystallization from 95% ethanol, and the melting point was not depressed when the sample was mixed with an authentic sample prepared by the oxidation of bis-(*p*-bromophenyl)-methane according to Goldthwaite.[4]

Dinitro Derivative of II.—To 5 ml. of fuming nitric acid cooled in an ice-bath 500 mg. of II was gradually added. After one hour in the ice-bath and one hour at room temperature, the reaction mixture was poured onto ice. The precipitate was filtered, washed and dried. After recrystallization from acetone–ethanol, the product melted at 203–205° (cor.).

Anal. Calcd. for $C_{14}H_7Br_5N_2O_4$: C, 25.22; H, 1.06. Found: C, 25.53; H, 1.09.

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(4) Goldthwaite, *Am. Chem. J.*, **30**, 445 (1903).

BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
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Observations on the Equilibrium between *cis*- and *trans*-Stilbene

BY D. C. DOWNING AND GEORGE F WRIGHT

The thermal equilibrium between *cis*- and *trans*-stilbene has been reported as 92–94% *trans* at 340°,[1] as 96% *trans* at 214°,[2] and 93% *trans* at 25°.[3] In order to test this apparent independence with respect to temperature we applied the method of methoxymercuration[4] to a sample of *trans*-stilbene isomerized at 330–340° and found (Fig. 1) that the rate of mercury consumption *versus* time was identical (curve A) with that shown by pure stilbene (curve B), whereas a 92:8 *trans-cis* mixture and an 8:92 *trans-cis* mixture consumed mercury according to curves C and D, respectively. These data indicate that the melting point lowering observed by Kistiakowsky and Smith was not owing to the presence of 8% *cis*-stilbene.

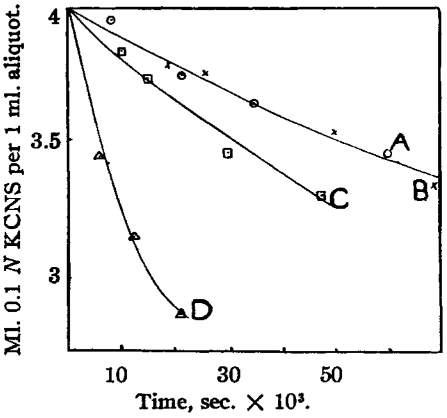

Fig. 1.—Mercury consumption by *cis-trans* mixtures *vs.* time.

The methoxymercuration was carried out without a catalyst[4] in order to accentuate the difference in reaction rate between *cis* and *trans* isomers. The slight solubility of *trans*-stilbene in the reaction medium also exaggerated this difference.

We were unable to test the 93:7 equilibrium reported at 25° because we could not repeat the catalytic isomerization of Price and Meister with boron trifluoride in carbon tetrachloride or as its etherate. In our hands no isomerization occurred with either *cis*- or *trans*-stilbene, nor did benzoyl peroxide or peracetic acid act as a co-catalyst.

It would appear that the isomerizing action of boron trifluoride is not so simple as Price and Meister supposed it to be. We are continuing to search either for a co-catalyst in their system or for an inhibitor in our own.

Experimental

Thermal Isomerization of *trans*-Stilbene.—A bomb tube, 10 × 150 mm., containing 1.80 g. (0.01 mole) of *trans*-stilbene was heated for eight hours at 330–340°. The gas was turned off and the tube was dropped from the furnace directly into ice and water. The organic material was taken up in chloroform, washed with ferrous sulfate, dried with magnesium sulfate, and the solvent evaporated under 15 mm. The residue softened at 95° and melted completely at 109°.

Analysis for Mercury.—The procedure reported previously([4c]) was adapted to a semimicro procedure employing one-tenth of the former quantities. Methoxymercuration was carried out at 35° in a fresh 0.2 *M* mercuric acetate solution freed from mercurous salt by centrifugation. The 1-ml. aliquots, diluted into aqueous potassium nitrate, were extracted five times with chloroform before titration with thiocyanate using ferric sulfate indicator.

Methoxymercuration.—When a 0.2 *M* solution of *trans*-stilbene is stirred or shaken in catalyst-free methanol suspension, also 0.2 *M* in mercuric acetate, the mercury is

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(1) G. B. Kistiakowsky and W. Smith, THIS JOURNAL, **56**, 638 (1934).

(2) T. W. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).

(3) C. C. Price and M. Meister, THIS JOURNAL, **61**, 1595 (1939).

(4) (a) G. F. Wright, *ibid.*, **57**, 1993 (1935). (b) W. H. Brown and G. F. Wright, *ibid.*, **62**, 1991 (1940). (c) A. M. Birks and G. F. Wright, *ibid.*, **62**, 2412 (1940).