(2) **The Methobromide of β-Dimethylaminoethyl Salicylate.**—The bromide I (36.8 g.), salicyloyl chloride (45 g., large excess) and dried benzene (75 g.) are heated on the water-bath until the evolution of gaseous hydrochloric acid ceases. The benzene is decanted, replaced by anhydrous acetone and the mixture boiled for one hour. This procedure is repeated and the solid phase subsequently recrystallized from alcohol as white prisms, m. p. 176°, readily soluble in water, difficultly in alcohol; yield, 80%. *Anal.* Calcd. for $C_{12}H_{18}O_3NBr$: Br, 26.3. Found: Br, 26.4.

The corresponding iodide, prepared analogously from II, forms, after recrystallization from alcohol, white needles, m. p. 147–148°; yield, 88%. *Anal.* Calcd. for $C_{12}H_{18}O_3NI$: N, 4.0; I, 36.2. Found: N, 3.9; I, 36.0.

(3) **The Methosulfate of β-Dimethylaminoethyl Salicylate.**—To a solution of the methobromide (61 g.) in water (300 cc.), silver sulfate (35 g.) was added and the mixture shaken for four hours. Upon evaporation *in vacuo*, microscopic needles of m. p. 300° were obtained. *Anal.* Calcd. for $C_{24}H_{36}O_{10}N_2S$: N, 5.1; SO_4, 17.6. Found: N, 5.1; SO_4, 17.6.

(4) **β-Iodo-ethyl Allophanate.**—Cyanuric acid (35 g.) is heated in a current of dry carbon dioxide and the gaseous cyanic acid formed absorbed at 0° in ethylene iodohydrin (255 g.). During this operation, which requires approximately one hour, a voluminous precipitate is formed which is collected and recrystallized from alcohol or boiling water: needles, m. p. 182°; yield, 60%. *Anal.* Calcd. for $C_4H_7O_3N_2I$: N, 10.8; I, 49.0. Found: N, 10.8; I, 49.5.

(5) **The Methiodide of β-Dimethylaminoethyl Allophanate.**—A suspension of the preceding substance (5 g.) in water (60 cc.) is saturated with gaseous trimethylamine at room temperature. The mixture is heated for ten hours at 100° in a sealed tube, filtered from traces of solid material and evaporated to dryness *in vacuo*. By recrystallization from alcohol, the residue is obtained in form of needles, m. p. 254–255° (dec.); yield, 4 g. *Anal.* Calcd. for $C_7H_{16}O_3N_3I$: N, 13.3; I, 40.1. Found: N, 13.2; I, 40.0.

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RECEIVED JULY 31, 1944

NEW COMPOUNDS

Thiomesitaldehyde

Because of the excessive crowding about the functional group there was some question as to whether mesitaldehyde could be converted to thiomesitaldehyde by the general method for transforming aromatic aldehydes to their sulfur analogs. Moreover, it was of interest to determine whether thiomesitaldehyde, once formed, would exist in the monomeric or the trimeric form.

A solution of 24 g. of mesitaldehyde in 250 ml. of absolute ethanol was saturated with dry hydrogen chloride. Hydrogen chloride and hydrogen sulfide were then passed into the solution for two hours at 0–5°. The white powder, produced in this way, was isolated and recrystallized from nitromethane; m. p. 184–185°; yield 8.5 g. Recrystallization from glacial acetic acid yielded a pure sample of thiomesitaldehyde in the form of beautiful white crystals; m. p. 186–187°.

Anal. Calcd. for $C_{30}H_{36}S_3$: C, 73.13; H, 7.37; mol. wt., 492. Found: C, 73.51; H, 7.38; mol. wt. (ebullioscopic in chloroform), 483.

Thiomesitaldehyde not only exists as a trimer but behaves normally in other respects. For example, heating with copper–bronze by the method of Klinger[1] converts it to 1,2-dimesitylethylene. An intimate mixture of 1.64 g. of the thioaldehyde and 1.4 g. of copper–bronze powder was heated for thirty minutes in an oil-bath at 220–230°. The crude stilbene, obtained by extracting the resulting mass with high-boiling petroleum ether, was purified by recrystallization from aqueous acetic acid and then from ethanol; m. p. 125–128°; yield 0.55 g. Repeated recrystallization from ethanol and the use of Norite gave pure 1,2-dimesitylethylene; m. p. 131–132°.[2]

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[1] Klinger, *Ber.*, **9**, 1893 (1876); see also Wood, Bacon and Meibohm, THIS JOURNAL, **63**, 1334 (1941).

[2] Fuson, Denton and Best, *J. Org. Chem.*, **8**, 64 (1943).

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1,1-Di-(*p*-chlorophenyl)-1,2,2,2-tetrachloroethane

1,1-Di-(*x*-chlorophenyl)-2,2,2-trichloroethane prepared from chlorobenzene and chloral according to Zeidler[1] was dehydrochlorinated by refluxing for ten hours a solution of 15 g. (0.042 mole) in 400 cc. of absolute ethanol containing 8.0 g. (0.14 mole) of potassium hydroxide. About half of the alcohol was removed by distillation and the residue poured into 600 cc. of cold water, the crystalline precipitate was collected by suction filtration, washed with water until free of hydroxide and chloride ions, dried in air and crystallized from about 75 cc. absolute ethanol; yield, 11 g., 81% of the theoretical, melting 86–87°.

Anal. Calcd. for $C_{14}H_8Cl_4$: Cl, 44.61. Found: Cl, 44.64, 44.64.

This product corresponds to the 1,1-di-(*x*-chlorophenyl)-2,2-dichloroethylene obtained by a similar procedure by Zeidler.[1] The structure of this compound was established by oxidizing 1.0 g. in a mixture of 5 g. of chromic acid and 30 cc. of glacial acetic by refluxing for four hours. This solution was poured into 200 cc. of cold water, suction filtered and the solid washed with water, dried in air and crystallized from absolute ethanol; 0.8 g. of *p,p*′-dichlorobenzophenone, m. p. 143–144°, mixed melting point with an authentic sample, 143–144°, was obtained. This product proves the structure of the ethylene derivative to be 1,1-di-(*p*-chlorophenyl)-2,2-dichloroethylene which in turn establishes Zeidler's 1,1-di-(*x*-chlorophenyl)-2,2,2-trichloroethane as 1,1-di-(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT). Several attempts to oxidize the latter with chromic acid in acetic acid to *p,p*′-dichlorobenzophenone gave no identifiable products.

1,1-Di-(*p*-chlorophenyl)-1,2,2,2-tetrachloroethane is readily made either by chlorination of the trichloroethane compound or the dichloroethylene derivative. Ten grams (0.028 mole) of 1,1-di-(*p*-chlorophenyl)-2,2,2-trichloroethane (m. p. 105–106°) in 65 cc. of carbon tetrachloride containing 0.5 g. phosphorus trichloride was placed in a cylindrical flask 1.5″ o.d. and 7.5″ high. A 45° side-arm near the top was attached to a reflux condenser. Chlorine gas was passed vigorously for three hours through a sintered-glass gas bubbler with an outlet 1″ in diameter placed near the bottom of the flask while the solution was refluxed gently. To accelerate the chlorination a 150-watt bulb was located about 8″ from the flask. On evaporation of the solution with vacuum a semi-solid residue of 16 g. remained. This was crystallized from 100 cc. of absolute ethanol and 0.2 g. of Norit. The crude product was twice recrystallized with 60 and 50 cc. portions of absolute alcohol to yield 8 g. of colorless crystals, resembling granulated sugar in appearance, m. p. 91–92°; yield 73%.

Anal. Calcd. for $C_{14}H_8Cl_6$: Cl, 54.76. Found: Cl, 54.38, 54.46.

Two grams (0.006 mole) of 1,1-di-(*p*-chlorophenyl)-2,2-dichloroethylene in 20 cc. of chloroform was chlorinated in the same way as before but without radiation. Additional solvent was added to replace that evaporated. Evaporation of the solution with vacuum and two crystallizations

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[1] Zeidler, *Ber.*, **7**, 1181 (1874).