

(2) **The Methobromide of  $\beta$ -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  $C_{12}H_{15}O_3NBr$ : 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  $C_{12}H_{15}O_3NI$ : N, 4.0; I, 36.2. Found: N, 3.9; I, 36.0.

(3) **The Methosulfate of  $\beta$ -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  $C_{14}H_{18}O_{10}N_2S$ : N, 5.1;  $SO_4$ , 17.6. Found: N, 5.1;  $SO_4$ , 17.6.

(4)  **$\beta$ -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  $\beta$ -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.

LABORATORY OF ORGANIC CHEMISTRY  
HEBREW UNIVERSITY  
JERUSALEM, PALESTINE

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## 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  $C_{10}H_8S_3$ : C, 73.13; H, 7.37; mol. wt., 492. Found: C, 73.51; H, 7.38; mol. wt. (ebulliscope 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<sup>1</sup> converts

(1) Klinger, *Ber.*, **9**, 1893 (1876); see also Wood, Bacon and Meibohm, *This Journal*, **63**, 1334 (1941).

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°.<sup>2</sup>

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

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF ILLINOIS  
URBANA, ILLINOIS

REYNOLD C. FUSON  
CHRIS E. BEST

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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<sup>1</sup> 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.<sup>1</sup> 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

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

from 10–20 cc. of absolute ethanol gave 1.6 g. melting 91–92°; 70% of the theoretical yield. No depression was observed in a mixed m. p. with the product obtained before.

Despite the presence of a tertiary chlorine atom in the 1,1-di-(*p*-chlorophenyl)-1,2,2,2-tetrachloroethane, it does not react with 5% alcoholic silver nitrate at room temperature and only slightly with water on refluxing for fifteen minutes. With 5% sodium hydroxide at reflux for fifteen minutes appreciable hydrolysis occurs. It is readily dechlorinated by heating a mixture of 1.0 g. (0.0026 mole), 15 cc. of absolute ethanol, and 1.0 g. of zinc powder at reflux for eight hours. The hot solution was filtered, the zinc washed with hot alcohol, the filtrate poured into 75 cc. of water, and the resulting solid removed by filtration and crystallized from 8–10 cc. of absolute ethanol. The yield of 1,1-di-(*p*-chlorophenyl)-2,2-dichloroethylene was 0.6 g., 66% of the theoretical, melting 86–87° and showing no depression in a mixed m. p. with the same product prepared before.

SHERWIN-WILLIAMS LABORATORY  
WESTERN RESERVE UNIVERSITY  
CLEVELAND, OHIO

OLIVER GRUMMITT  
ALLEN BUCK  
ALBERT JENKINS

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### Di-(*p*-chlorophenyl)-acetic Acid

This compound was prepared by saponification of 1,1-di-(*p*-chlorophenyl)-2,2-dichloroethylene in an analogous manner to the preparation of diphenylacetic acid.<sup>1,2</sup> A mixture of 1.0 g. of 1,1-di-(*p*-chlorophenyl)-2,2-dichloroethylene,<sup>3</sup> 3 g. of potassium hydroxide, and 20 cc. of 95% alcohol was heated in a sealed Carius tube at 150–160° for twenty hours. The product was poured into 100 cc. of water, about 0.1 g. of Norit was added, and the mixture boiled for a few minutes. After filtering the acid was precipitated by acidifying the filtrate with 10% sulfuric acid and collected by suction filtration. The crude acid weighed 0.6 g., melting 161–164°; one crystallization from absolute ethanol gave 0.5 g. melting 163–164°; 57% of the theoretical yield.

*Anal.* Calcd. for C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>2</sub>: Cl, 25.22; neut. eq., 281.1. Found: Cl, 25.09; neut. eq., 281.4.

- (1) Fritsch and Feldmann, *Ann.*, **306**, 79 (1899).
- (2) Sheibley and Prutton, *THIS JOURNAL*, **62**, 840 (1940).
- (3) Grummitt, Buck and Jenkins, *THIS JOURNAL*, **67**, 155 (1945).

SHERWIN-WILLIAMS LABORATORY  
WESTERN RESERVE UNIVERSITY  
CLEVELAND, OHIO

OLIVER GRUMMITT  
ALLEN BUCK  
JAMES STEARNS

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## COMMUNICATIONS TO THE EDITOR

### REMOVAL OF GAS NUCLEI FROM LIQUIDS AND SURFACES<sup>1</sup>

Sir:

During a study of bubble formation in blood of animals subjected to simulated high altitudes in a low pressure chamber, it became necessary to develop methods that prevent the bubbling of liquids supersaturated with gas. If water at rest in a clean glass vessel is exhausted with an air pump, bubbles usually appear due to the growth of gas nuclei, *i. e.*, small gas masses adhering to walls of the container or particles in the water.

Experiments indicate that there is a population of gas nuclei in every liquid and container (unless special precautions have been taken to remove them) of such a character that a certain group will become unstable and grow into bubbles for each successive increase in  $\Delta P$ , where  $\Delta P$  = dissolved gas tension minus total hydrostatic pressure. The conditions for stability and growth of gas nuclei have been described in a previous paper.<sup>2</sup>

The conventional method of removing gas nuclei is prolonged boiling or evacuation, procedures which have the disadvantage of removing dissolved gas in addition to the gas nuclei. Two new methods, which do not change the gas concentration, proved satisfactory.

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

(2) E. N. Harvey, D. K. Barnes, W. D. McElroy, A. H. Whiteley, D. C. Pease and K. W. Cooper, *J. Cell. and Comp. Physiol.*, **24**, 1 (1944).

One method, strong centrifuging of liquid and container, will remove all gas nuclei which grow to bubbles at the vapor pressure of water at 22°, *i. e.*, at a  $\Delta P$  of 740 mm. Such nuclei are designated gas macronuclei. However, when the tube of centrifuged water, resting at the vapor pressure without forming bubbles, is given a light tap or blow, or is placed in a high frequency sound field, bubbles appear, due to the growth of gas *micronuclei* that have not been removed by the centrifuge treatment. The tap or blow and the supersonic waves increase  $\Delta P$  above 740 mm. as a result of the negative pressure component of the pulse or sound waves.

The second method, subjecting water and glass container to high hydrostatic pressures (1000 atmospheres), removes gas micronuclei by forcing them into solution. Water so treated has remarkable properties. It can be heated above 200° without bursting into vapor. When intense high frequency sound waves are passed through, no cavitation occurs and no bubbles arise. Finally, if exhausted to the vapor pressure of water, moderate knocks have no effect and only a very severe blow will cause bubbles to form.

The severe blow is believed to develop a sufficiently negative pressure locally to tear cavities in water free of gas nuclei. A similar procedure, which presumably also develops large local negative pressures, is to scratch the glass wall in contact with the prepressurized water at its vapor pressure, when copious bubbles form. Electrolytic gas bubbles will also appear at electrodes