

concentrated sulfuric acid (sp. gr. 1.84). The mixture was heated on a steam-bath for four hours and then poured into 120 ml. of boiling water. After the mixture had been boiled for five minutes, the yellow precipitate was collected by filtration. The moist solid was boiled for five minutes with a solution of 3.5 g. of sodium carbonate in 45 ml. of water, collected by filtration and washed well with water. The crude product weighed 6 g. (92%). After recrystallization from glacial acetic acid the pure yellow compound melted at 315–320° (block).

Anal. Calcd. for $C_{18}H_9OCIN_2$: C, 68.46; H, 3.23. Found: C, 68.32; H, 3.21.

7,10-Dichloro-pyrid[3,2-c]acridine.—The experimental conditions were patterned after those of Albert and Ritchie⁴ for the preparation of 9-chloroacridine. In a 50-ml. three-necked flask fitted with a stirrer and reflux condenser, 25 ml. of phosphorus oxychloride was heated to 90° and 5 g. of the crude hydroxy compound was added. The temperature of the bath was then raised to 130–140° and maintained at this temperature for two hours. The excess phosphorus oxychloride was removed by distillation and the residual black tarry substance solidified on cooling. This material was added to 20 ml. of ammonium hydroxide and 50 g. of ice and the mixture was stirred vigorously and then filtered. The greenish brown solid melting at 170–200° weighed 4 g. To this material was added 100 ml. of ethyl alcohol; the mixture was heated under reflux for a few minutes and then filtered. A dilute solution of ammonium hydroxide (0.5%) was added to the brown filtrate until precipitation occurred. The mixture was cooled in an ice-bath and the solid was collected on a Büchner funnel. After three recrystallizations, the light green solid melting at 222–225° weighed 2 g. (38%).

Anal. Calcd. for $C_{16}H_5N_2Cl_2$: C, 64.23; H, 2.69. Found: C, 63.99; H, 2.76.

10-Chloro-7-(3-diethylaminopropylamino)-pyrid[3,2-c]acridine.—A mixture of 0.5 g. of the chloro compound and 2 g. of dry 3-diethylaminopropylamine (dried over solid potassium hydroxide for twelve hours and then distilled) was heated at 100–110° for two hours. To the red solution was added 3 ml. of 15% sodium hydroxide and 25 ml. of ether. After the mixture had been stirred the ether layer was separated and washed five times with 10-ml. portions of water to remove any excess 3-diethylaminopropylamine. The ether solution was dried over potassium carbonate, filtered and the solvent was removed by distillation. The residual red oil (0.3 g.) was dissolved in ethyl alcohol and to this solution was added a saturated solution of picric acid in ethyl alcohol. The dipicrate after three recrystallizations from nitromethane melted at 213–216°.

Anal. Calcd. for $C_{30}H_{31}ClN_3O_4$: C, 49.38; H, 3.67. Found: C, 49.36; H, 3.90.

(4) Albert and Ritchie, "Organic Syntheses," **22**, 5 (1942).

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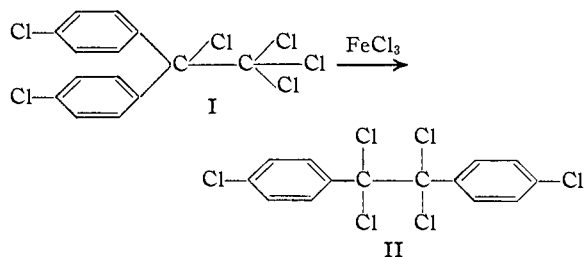
Rearrangement of 1,1,1,2-Tetrachloro-2,2-bis-(*p*-chlorophenyl)-ethane, "Chloro-DDT," to 1,1,2,2-Tetrachloro-1,2-bis-(*p*-chlorophenyl)-ethane

BY W. L. WALTON¹

It has been shown^{1a} that 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane (DDT) yields an equivalent of hydrogen chloride and 1,1-dichloro-2,2-

bis-(*p*-chlorophenyl)-ethylene when treated with ferric chloride. No rearrangement was involved in this reaction.

In our laboratories a study was made of the effect of anhydrous ferric chloride on the compound in which the tertiary aliphatic hydrogen atom of DDT had been replaced by a chlorine atom. During the course of this work with 1,1,1,2-tetrachloro-2,2-bis-(*p*-chlorophenyl)-ethane (I) the following interesting rearrangement was observed:



The product "1,1,2,2-tetrachloro-1,2-bis-(*p*-chlorophenyl)-ethane" or, systematically, *p,p'*- $\alpha,\alpha,\alpha',\alpha'$ -hexachlorobibenzyl (II) was obtained in 85% yield when molten (I) was heated for fifteen seconds with a trace of ferric chloride. The reaction was strongly exothermic. Long heating of the tetrachloroethane (I) with ferric chloride altered the course of the reaction leading to the evolution of much hydrogen chloride and a dark viscous reaction mixture from which none of (II) could be isolated.

The chief product of this rearrangement, hexachlorobibenzyl (II) is a known compound.² In our work its identity was established by synthesis from α,α,α,p -tetrachlorotoluene² and by its conversion to the known derivatives 4,4'-dichlorotoluene,² and 4,4'-dichlorobenzil.³

Experimental

Rearrangement.—Fifteen grams of 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane (I)⁴ was heated to 160° and 5 mg. of anhydrous ferric chloride was stirred into the melt. The melt turned blue, evolved hydrogen chloride, and its temperature rose rapidly to 210°. The mixture was immediately cooled to room temperature by rapidly transferring the reaction vessel to an ice-water-bath. Solidification began before the temperature indicated by the thermometer reached 170°. The crystalline mass was pulverized under 20 ml. of carbon tetrachloride while being heated on a steam-bath, and then cooled and filtered. The yield of gray-white crude product was 12.75 g. (85% of theoretical); it melted at 189–192°. One recrystallization from carbon tetrachloride raised the melting point to 193–194°. Kenner and Witham² reported m. p. 190° (apparently uncorrected).

Anal. Calcd. for $C_{14}H_8Cl_6$: Cl, 54.70. Found: Cl, 55.0.

***p,p'*-Dichlorobenzil.**—A mixture of 1 g. of the hexachlorobibenzyl (II), 40 ml. of glacial acetic acid and 10 ml. of water was placed in a sealed Pyrex tube and heated in an oil-bath at 160–175° for thirty-six hours. After cooling to room temperature, the tube was opened and the solid

(1) Present address: General Electric Company, Schenectady, N. Y.

(1a) Fleck and Haller, *THIS JOURNAL*, **66**, 2095 (1944).

(2) Kenner and Witham, *J. Chem. Soc.*, **97**, 1960 (1910).

(3) Lieberman and Homeyer, *Ber.*, **12**, 1971 (1879).

(4) Grummitt, Buck and Jenkins, *THIS JOURNAL*, **67**, 155 (1945).

product, 0.71 g. of yellow needle-like crystals, m. p. 193–194°, was collected on a filter. The product was purified by several successive crystallizations from carbon tetrachloride and ethanol to a constant melting point, 198–199°. Melting points reported previously are 200°⁵ and 193°.²

p,p'-Dichlorotoluene.—A mixture of 2.0 g. of hexachlorobiphenyl (II) and 2.0 g. of zinc dust was refluxed for forty-eight hours in 200 ml. of anhydrous ethanol. The mixture was filtered hot to remove unused zinc and the filtrate cooled to room temperature. The platelets, 0.5 g., which precipitated, melted at 178–179°. The melting point previously reported² is 175–176°.

Synthesis of *p,p',α,α',α',α'*-Hexachlorobiphenyl from *α,α,α,β*-Tetrachlorotoluene.—This reaction was carried out according to the directions of Kenner and Witham² using 12 g. of *α,α,α,β*-tetrachlorotoluene (b. p. 152–155° (70 mm.)) and 8.3 g. of copper powder which was reduced⁶ by alcohol vapor in a heated tube. The product, 3.2 g., melted at 193–194° and gave no depression in melting point when mixed with the hexachlorobiphenyl from the rearrangement.

(5) Montagne, *Rec. trav. chim.*, [iii] **21**, 19 (1902).

(6) Eiloart, *This Journal*, **12**, 239 (1890).

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Dehydrogenation of 1,5-Pentanediol

BY L. E. SCHNIEPP AND H. H. GELLER¹

Recently reported preparation of γ -butyrolactone² and γ -valerolactone³ by catalytic dehydrogenation of 1,4-butanediol and 1,4-pentanediol, respectively, suggested that δ -valerolactone might be prepared in a similar manner from the now readily available 1,5-pentanediol.⁴

Dehydrogenation was found to proceed smoothly on heating 1,5-pentanediol with a copper chromite⁵ catalyst, δ -valerolactone being obtained in 78% crude yield. It was found advantageous to stop the reaction after about 85% of the theoretical amount of hydrogen had been evolved. Attempts to carry the dehydrogenation to completion resulted in the formation of 30–35% of polymeric products.

Vacuum distillation of the dehydrogenation reaction mixture yielded a product which analyzed about 90% δ -valerolactone and 10% 1,5-pentanediol. Refractionation improved the purity up to 97–98%. Complete removal of contaminating diol was effected by adding a slight excess of phenyl isocyanate to the mixture, decomposing the excess with water and distilling the pure lactone from the residue of the bis-phenylurethan and diphenylurea. A 71% yield of pure δ -valerolactone was obtained by this procedure. This com-

(1) Formerly Chemist, Industrial Chemical Section, Agricultural Residues Division.

(2) (a) J. W. Reppe, *Chem. Industries*, **57**, 458 (1945). Condensation of translated report on advances in acetylene chemistry by Dr. J. W. Reppe, ORR Report No. G-1, Rubber Reserve Co. (July 25, 1945); (b) I. G. Callomon and G. M. Kline, *Modern Plastics*, **23**, No. 6, 174 (1946); (c) Krizikalla, OPB Report No. 11431, U. S. Department of Commerce (February 19, 1943).

(3) L. P. Kyrides and F. B. Zienty, *This Journal*, **68**, 1385 (1946).

(4) L. E. Schiepp and H. H. Geller, *ibid.*, **68**, 1646 (1946).

(5) "Organic Syntheses," Coll. Vol. II, p. 142.

pared favorably with the method involving the hydrolysis of δ -chlorovaleronitrile.⁶

Dehydrogenation of 1,5-Pentanediol.—1,5-Pentanediol, 52 g. (0.50 mole), was thoroughly mixed with 1.5 g. of copper chromite and the mixture was heated under reflux. The top of the reflux condenser was connected to a gas-washing bottle, containing water, which was in turn connected to a wet-test meter. Vigorous evolution of hydrogen began when the temperature of the reaction mixture reached 210° and continued for about thirty minutes. At the end of this time the temperature had risen to 245° and gas evolution slowed down considerably. Meter readings showed that 21 liters of gas had been evolved. Heating was stopped and the reaction mixture subjected to vacuum distillation. The distillate, 43.2 g., was analyzed by saponification with 0.4 *N* sodium hydroxide and found to consist of 90.6% δ -valerolactone. Treatment of another sample with phenyl isocyanate yielded a precipitate of the bis-phenylurethan of 1,5-pentanediol. The weight of urethan obtained was roughly equivalent to 9.4% of diol in the original sample. Refractionation of this crude product gave a distillate analyzing 97–98% pure as the lactone. The yield of crude lactone based on the analysis of the original distillate was 78.3% of the theoretical.

Purification of δ -Valerolactone.—A sample of the crude distillate from the dehydrogenation was treated with a 10% excess of phenyl isocyanate over that calculated as necessary to react with the 1,5-pentanediol in the sample. This mixture was shaken and allowed to stand for thirty minutes after which sufficient water to react with the excess phenyl isocyanate was added. The resulting mixture was distilled under reduced pressure. The distillate analyzed as 100% δ -valerolactone by saponification and the yield calculated back to the original 1,5-pentanediol was 71.2% of the theoretical. The pure lactone had the following properties: b. p. 105° (8 mm.) (227° (750 mm.)), n_D^{20} 1.4553, d_4^{20} 1.104.

The structure of the lactone was established by converting a sample to δ -iodovaleric acid, m. p. 56–57°. Mixed melting point with an authentic sample showed no depression.

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(6) H. Kroper and Bretschneider, OPB Report No. 645, U. S. Department of Commerce (April 25, 1942).

(7) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

Estrogenic Action and Isomorphism

BY HERBERT E. UNGNADE AND FRANCIS V. MORRIS

The extraordinary agreement in the molecular dimensions of stilbestrol and estrone¹ and the dihydrostilbestrol isomers and estrone² as determined from crystallographic data has prompted a study of the melting behavior of mixtures of natural and synthetic estrogens.

The results prove that mixed crystals are formed between α -estradiol and the synthetic estrogens stilbestrol (Fig. 1) and *meso*-dihydrostilbestrol (Fig. 2) and hence the isomorphism of these substances, but it is uncertain whether the solid solutions are continuous or not at the melting temperatures. The same uncertainty holds for the system of mixed crystals between stilbestrol and *dl*-dihydrostilbestrol (Fig. 3), whereas the dia-

(1) Giacomello and Bianchi, *Gazz. chim. ital.*, **71**, 667 (1944).

(2) Carlisle and Crowfoot, *J. Chem. Soc.*, 5 (1941).