

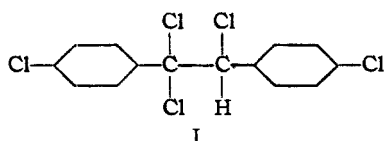
[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

## The Preparation of $\alpha,\alpha,\alpha',4,4'$ -Pentachlorobibenzyl, an Isomer of DDT

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Various attempts have been made to correlate the insecticidal action of DDT and related compounds with the presence of the *p*-chlorophenyl groups<sup>1</sup> or the trichloromethyl group<sup>2</sup> and with the ease with which hydrogen chloride is eliminated from the molecule.<sup>3</sup> Martin<sup>4</sup> has stated that, while high toxicity was not found in all the DDT analogs that are readily dehydrohalogenated, all the analogs that showed high toxicity dehydrohalogenated readily in dilute alcoholic alkali.

It was thought to be of interest to prepare an isomer of DDT which retained the *p*-chlorophenyl groups and was readily dehydrochlorinated, but in which both carbon atoms of the ethyl group were substituted with a *p*-chlorophenyl group. Such a compound has been prepared by the chlorination of *cis*- $\alpha,4,4'$ -trichlorostilbene to form *dl*- $\alpha,\alpha,\alpha',4,4'$ -pentachlorobibenzyl (I). This com-



pound melted at 97–98°. When refluxed for fifteen minutes with 0.1 *N* alcoholic alkali, it readily lost hydrogen chloride to form *cis*- $\alpha,\alpha,\alpha',4,4'$ -tetrachlorostilbene (II). Anhydrous ferric chloride also dehydrochlorinated I, in the molten condition, to form II, just as DDT is dehydrochlorinated.<sup>5</sup>

The identity of II was established by chlorinating it to form the known compound  $\alpha,\alpha,\alpha',\alpha',4,4'$ -hexachlorobibenzyl.

Insecticidal tests<sup>6</sup> show that I is ineffective, against house flies, pea aphids, celery leaf tiers, red spider mites, and European corn borers. These results provide evidence that insecticidal action is due to the molecule as a whole rather than to the presence of toxic groups or specific reactions.

(1) Luger, Martin and Muller, *Helv. Chim. Acta*, **27**, 892 (1944).

(2) Martin and Wain, *Nature*, **154**, 512 (1944).

(3) Busvine, *ibid.*, **155**, 169 (1945); Domenjoz, *Helv. Chim. Acta*, **29**, 1317 (1946); Muller, *ibid.*, **29**, 1560 (1946); Metcalf and Gunther, *This Journal*, **69**, 2579 (1947).

(4) Martin, *J. Soc. Chem. Ind.*, **65**, 405 (1946).

(5) Fleck and Haller, *This Journal*, **66**, 2095 (1944).

(6) Unpublished.

### Experimental

**Preparation of *dl*- $\alpha,\alpha,\alpha',4,4'$ -Pentachlorobibenzyl.**—Chlorine was passed through a solution of 7 g. of *cis*- $\alpha,4,4'$ -trichlorostilbene<sup>7</sup> in 75 ml. of carbon tetrachloride for two hours at room temperature. The solution was then concentrated on a steam-bath to a volume of about 15 ml. The prisms that separated, when this solution was cooled in ice, were collected and dried at room temperature in a vacuum; yield, 6.1 g. After recrystallization from alcohol the product melted at 97–98°. No yellow color was given with tetranitromethane.

*Anal.* Calcd. for  $C_{14}H_3Cl_5$ : C, 47.43; H, 2.56; Cl, 50.01. Found: C, 47.63; H, 2.92; Cl, 50.32.

***cis*- $\alpha,\alpha,\alpha',4,4'$ -Tetrachlorostilbene.**—A solution of 0.5 g. of *dl*- $\alpha,\alpha,\alpha',4,4'$ -pentachlorobibenzyl in 50 ml. of 0.1 *N* alcoholic sodium hydroxide was refluxed for two hours. Water was then added to the hot solution until crystallization occurred. The cooled solution yielded 0.45 g. of material that melted at 83–85°. Repeated recrystallization from acetone yielded needles which melted at 166–167°. With tetranitromethane a yellow color was obtained.

When this experiment was repeated quantitatively with a 100-mg. sample and a fifteen-minute reflux period, titration of the chloride ion formed indicated that 0.92 mole of hydrogen chloride was removed per mole of *dl*- $\alpha,\alpha,\alpha',4,4'$ -pentachlorobibenzyl.

The same compound was prepared by the catalytic removal of hydrogen chloride. A mixture of 1 g. of *dl*- $\alpha,\alpha,\alpha',4,4'$ -pentachlorobibenzyl and 1 mg. of anhydrous ferric chloride was heated in a current of air in a U-tube at 90–95° for half an hour.<sup>8</sup> Gas evolution was complete at the end of five minutes. Recrystallization of the product yielded needles that melted at 166–167°. Mixed melting points showed this product to be identical with that obtained by alkaline hydrolysis.

A quantitative determination showed that 0.98 mole of hydrogen chloride was eliminated by the catalyst.

**$\alpha,\alpha,\alpha',\alpha',4,4'$ -Hexachlorobibenzyl.**—Chlorine was passed through a solution of 0.1 g. of *cis*- $\alpha,\alpha,\alpha',4,4'$ -tetrachlorostilbene (obtained by hydrolysis) in 5 ml. of carbon tetrachloride for two hours at room temperature. The solution was evaporated to dryness on a steam-bath, and the residue was recrystallized from chloroform. The product melted at 191–192°, and no depression of the melting point was found when this material was mixed with authentic  $\alpha,\alpha,\alpha',\alpha',4,4'$ -hexachlorobibenzyl.<sup>9</sup>

### Summary

A DDT isomer, *dl*- $\alpha,\alpha,\alpha',4,4'$ -pentachlorobibenzyl, has been prepared which has two *p*-chlorophenyl groups, a hydrolyzable chlorine atom, and sensitivity to the catalytic action of anhydrous ferric chloride similar to DDT, but which has little insecticidal action.

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(7) Fleck, *J. Org. Chem.*, **12**, 708 (1947).

(8) Analysis by N. Green.

(9) Kenner and Witham, *J. Chem. Soc.*, **97**, 1965 (1910).