tallization of most of the β-maltose octaacetate preliminary to chromatography was also found to be undesirable.

No β-isomaltose octaacetate was found although nuclei of this substance were at hand and its isolation by chromatographic methods was an established and familiar procedure in this Laboratory.[15]

A blank on the enzyme preparation employed showed that it contained no trisaccharide isolable as the β-D-acetate by the chromatographic procedure described; neither was such isolable when the experimental procedure was repeated employing D-glucose or maltose as substrate.

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Summary

The digestion of waxy maize starch with malt amylases followed by acetylation of the hydrolyzate gave a crude product, which was essentially β-maltose octaacetate. By utilizing a chromatographic technique a second crystalline compound was obtained. By analysis, this substance was shown to be a trisaccharide hendecaacetate, m. p. 134–136°, $[\alpha]^{25}D$ + 86° (chloroform). No β-isomaltose octaacetate was found.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

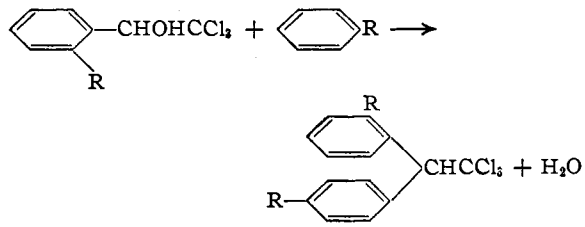
Some Positional Isomers of DDT Analogs

BY STANLEY J. CRISTOL AND DONALD L. HARMS[1]

Previous work with DDT isomers has shown that the position of the ring chlorine atoms is of utmost importance in insecticidal activity. For example, Cristol, Haller and Lindquist[2] have shown that when one of the *para* chlorine atoms in DDT [1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane] was moved to an *ortho* position to give *o,p'*-DDT [1,1,1-trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane], the dosage for equivalent toxicity against larvae of the common malaria mosquito (*Anopheles quadrimaculatus* Say) was increased approximately five- to ten-fold and the toxicity toward houseflies (*Musca domestica* L.) was almost eliminated. When the second chlorine atom was also moved to an *ortho* position, *o,o'*-DDT [1,1,1-trichloro-2,2-bis-(*o*-chlorophenyl)-ethane] was effective against mosquito larvae only at dosages approximately 1000 times greater than *p,p'*-DDT. Similar effects were noted in the dichloroethane series, 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethane being equally effective against mosquito larvae as approximately ten-fold dosages of its *o,p'* isomer, 1,1-dichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane.[3]

As the analogs of *p,p'*-DDT wherein the two *para* chlorine atoms are replaced by bromine, methyl and methoxy groups, are fairly effective insecticidally,[3,4] it seemed worthwhile to prepare the *o,p'* isomers of these compounds to test whether loss of insecticidal activity was general for such changes.

The preparations of 1,1,1-trichloro-2-*o*-bromophenyl-2-*p*-bromophenylethane, 1,1,1-trichloro-2-*o*-tolyl-2-*p*-tolylethane and 1,1,1-trichloro-2-*o*-anisyl-2-*p*-anisylethane are described in the experimental section. The general method involved the condensation of the *ortho*-substituted aryltrichloromethylcarbinol with the appropriately substituted benzene in the presence of sulfuric acid according to the equation, where R is Br, CH_3 or CH_3O.



A dinitro derivative was prepared by nitration of the bromine analog, and tetranitro derivatives were prepared of the methyl and methoxy analogs to further characterize these compounds.

Each of these compounds has been compared with its *p,p'* isomer in tests against *A. quadrimaculatus* larvae, and each required approximately ten-fold dosages for equivalent insecticidal activity. None of the *o,p'* compounds was effective against adult houseflies.[5]

Experimental

1,1,1-Trichloro-2-*o*-bromophenyl-2-*p*-bromophenylethane.—The carbinol required for this synthesis was prepared by a method analogous to that described[6] for the preparation of trichloromethyl-*o*-chlorophenylcarbinol, by the base-catalyzed condensation of *o*-bromobenzaldehyde and chloroform. The product, trichloromethyl-*o*-chlorophenylcarbinol, boiled at 134.5–135° (1.5 mm.) and was obtained in 11–18% yield. It crystallized slowly, and, after crystallization from Skellysolve B (petroleum ether, b. p. 60–70°), melted at 50°.

Anal. Calcd. for $C_8H_6OCl_3Br$: C, 31.50; H, 1.99. Found: C, 31.72; H, 2.11.

(1) Present address: Chemical Department, General Electric Company, Pittsfield, Mass.

(2) Cristol, Haller and Lindquist, *Science*, **104**, 343 (1946).

(3) Deonier, Jones, Haller, Hinchey and Incho, *Soap, Sanit. Chemicals*, **22** [11], 118 (1946).

(4) Haller, *Ind. Eng. Chem.*, **39**, 467 (1947).

(5) We are indebted to Dr. W. V. King, Dr. C. C. Deonier, and Mr. I. H. Gilbert, of the Bureau of Entomology and Plant Quarantine, U. S. Department of Agriculture, Orlando, Florida, for the biological data, which will be published in detail elsewhere.

(6) Howard and Castles, THIS JOURNAL, **57**, 376 (1935).

A solution of 7.5 g. (0.25 mole) of the carbinol in 4.7 g. (0.03 mole) of bromobenzene was added dropwise over a period of one hour to a well-stirred emulsion of 4.7 g. of bromobenzene in 30 ml. of 100% sulfuric acid. After six hours of stirring, the organic layer was separated and washed with water. The bromobenzene was removed by steam distillation. The material, after recrystallization from Skellysolve B, weighed 6.7 g. (60%), m. p. 73–74°. After several recrystallizations from 95% ethanol, the product, 1,1,1-trichloro-2-*o*-bromophenyl-2-*p*-bromophenylethane, melted at 75.5–76°.

Anal. Calcd. for $C_{14}H_9Cl_3Br_2$: C, 37.92; H, 2.05. Found: C, 37.75; H, 2.07.

When 1.55 g. of this material was treated with 10 ml. of fuming nitric acid at 65° for one-half hour, and the product isolated by precipitation with ice-water and recrystallization from 95% ethanol, a dinitro compound, presumably 1,1,1-trichloro-2-[2-bromo-5-nitrophenyl]-2-[4-bromo-3-nitrophenyl]-ethane, was obtained, m. p. 168.5–169°.

Anal. Calcd. for $C_{14}H_7O_4N_2Cl_3Br_2$: N, 5.25. Found: N, 5.47.

1,1,1-Trichloro-2-*o*-tolyl-2-*p*-tolylethane.—Trichloromethyl-*o*-tolylcarbinol was prepared in 83% yield by the condensation of *o*-tolylmagnesium bromide and chloral.[7] A mixture of 65 g. (0.27 mole) of this carbinol and 99.5 g. (1.08 mole) of toluene was added dropwise over a period of one hour to 250 ml. of vigorously stirred concd. sulfuric acid at 0°. The reaction mixture was then allowed to come to room temperature, and stirring was continued for eight hours. The mixture was decomposed with ice and water, and the resulting oil was extracted with ether. The ether extract was washed with water, aqueous sodium bicarbonate, and saturated brine, and then filtered through cotton. The ether was removed under reduced pressure, and the resulting oil taken up in methanol at 40°, decolorized with charcoal and allowed to crystallize slowly, finally, in a refrigerator. After a week, the crystals were removed by filtration. This crude material, m. p. 42–43°, weighed 55 g. (65%). Several recrystallizations from methanol gave 1,1,1-trichloro-2-*o*-tolyl-2-*p*-tolylethane, m. p. 44–44.2°.

Anal. Calcd. for $C_{16}H_{15}Cl_3$: C, 61.26; H, 4.82. Found: C, 61.46; H, 4.91.

Nitration of 300 mg. of this material with 3 ml. of fuming nitric acid and 3 ml. of concd. sulfuric acid for ninety minutes at 70° gave a tetranitro derivative, presumably 1,1,1-trichloro-2-(2-methyl-3,5-dinitrophenyl)-2-(4-methyl-3,5-dinitrophenyl)-ethane, m. p. 217–217.5°, after several recrystallizations from ethanol–acetone mixtures.

(7) Jozitsch, *J. Russ. Phys.-Chem. Soc.*, **34**, 97 (1902); Beilstein, "Handbuch der org. Chem.," Suppl. 1, v. 6, Berlin, 1931, p. 254.

Anal. Calcd. for $C_{16}H_{11}O_8N_4Cl_3$: C, 38.93; H, 2.65; N, 11.35. Found: C, 39.01; H, 2.45; N, 11.50.

1,1,1-Trichloro-2-*o*-anisyl-2-*p*-anisylethane.—The required carbinol, trichloromethyl-*o*-anisylcarbinol, was prepared by the Grignard synthesis starting with 46.7 g. (0.25 mole) of *o*-bromoanisole, 5.6 g. (0.23 mole) of magnesium and 32.4 g. (0.22 mole) of chloral to give 49.5 g. (80%) of product, b. p. 168–172° (11 mm.). The product could not be induced to crystallize, although Lebedev,[8] who prepared this compound in 40% yield by the base-catalyzed condensation of *o*-methoxybenzaldehyde and chloroform, reported an m. p. of 53°. We were able to obtain a solid acetate, m. p. 58°, by the action of acetyl chloride on the alcohol as reported.[8]

A mixture of 45 g. (0.15 mole) of this carbinol and 39 g. (0.36 mole) of anisole was added dropwise during a period of forty-five minutes to a well-stirred mixture of 150 ml. of concd. sulfuric acid and 100 ml. of glacial acetic acid maintained at 0°. The reaction mixture was allowed to come to room temperature, and stirring was continued for eight hours. The reaction mixture was decomposed with ice and water, and the crude product, m. p. 73–75°, was removed by filtration. The crude yield was 50 g. (85%). Several recrystallizations from 95% ethanol gave 1,1,1-trichloro-2-*o*-anisyl-2-*p*-anisylethane, m. p. 79.5–80°.

Anal. Calcd. for $C_{16}H_{15}O_2Cl_3$: C, 55.59; H, 4.37. Found: C, 55.72; H, 4.58.

Nitration of 1 g. of this material with 10 ml. of fuming nitric acid at 0° gave a tetranitro derivative, presumably 1,1,1-trichloro-2-(2-methoxy-3,5-dinitrophenyl)-2-(4-methoxy-3,5-dinitrophenyl)-ethane, m. p. 175–175.5°, after several recrystallizations from acetone–ethanol mixtures.

Anal. Calcd. for $C_{16}H_{11}O_{10}N_4Cl_3$: C, 36.56; H, 2.49; N, 10.66. Found: C, 36.43; H, 2.47; N, 10.64.

Summary

The *o,p'* position isomers of the analogs of DDT in which the ring chlorine atoms are replaced by bromine, methyl and methoxyl groups are described. Nitro derivatives of these compounds have been prepared.

These compounds are insecticidally less effective than their *p,p'* isomers against *A. quadrimaculatus* larvae and adult houseflies.

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(8) Lebedev, *J. Russ. Phys.-Chem. Soc.*, **32**, 197 (1900); *Chem. Zentr.*, **71**, II, 326 (1900).