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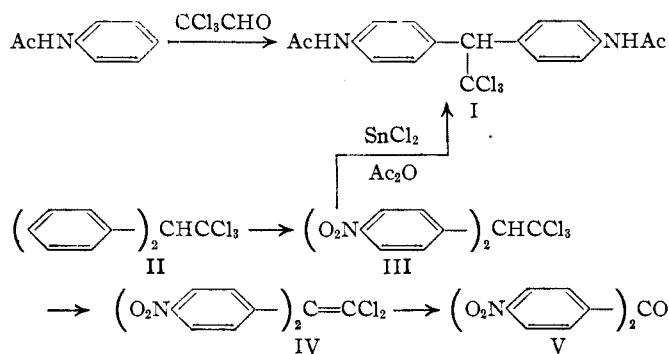
Derivatives of 1,1,1-Trichloro-2,2-diphenylethane

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Publications by Stephenson and Waters² and Burger, Graef and Bailey³ prompt us to report additional observations concerning analogs of DDT prepared in the course of an investigation that is being continued.

Stephenson and Waters² report the condensation of chloral with α -chloronaphthalene, presumably in the 4-position, but report no yield; conditions have now been found permitting preparation of the reaction product in 71% yield. Biphenyl was condensed with chloral to a substance identified as 1,1,1-trichloro-2,2-di-(4'-biphenyl)-ethane by dehydrohalogenation and oxidation of the ethylene to 4,4'-diphenylbenzophenone. A condensation product was isolated from fluorene and chloral, but the position of substitution was not determined. 1,1,1-Trichloro-2,2-di-(3'-nitro-4'-hydroxyphenyl)-ethane was obtained from chloral and *o*-nitrophenol more conveniently than by the method of Elbs,⁴ and it was found to undergo normal dehydrohalogenation. Phenyl thiocyanate also condenses with chloral, probably in the para position; the product suffered deep-seated decomposition on treatment with alkali.

Burger and co-workers³ explored the condensation of chloral with acetanilide as a possible route to the di-(acetylaminophenyl)-trichloroethane (I) but isolated only amongst other products a small amount of a substance, m. p. 239–246° dec. We



isolated an apparently identical high-melting substance (245–250° dec.) in 11% yield and characterized it as the 4,4'-diacetylmino derivative I by independent synthesis: 1,1,1-Trichloro-2,2-diphenylethane (II) was converted in 53% yield into a dinitro derivative. The latter was dehydrohalogenated to 1,1-dichloro-2,2-di-(nitrophenyl)-ethylene, corresponding in melting point to the

p,p'-isomer (IV) prepared by Lange and Zufall⁵ by a different method. The dinitrobenzophenone (V) obtained by oxidation melted at the temperature recorded for the 4,4'-isomer but, since 2,2'-dinitrobenzophenone has the same melting point, the substance was reduced to the diamine; this corresponded in melting point to the 4,4'-derivative (239°) and not the 2,2'-isomer (135°).⁶ The conversion of III by reduction and acetylation into a di-(acetylaminophenyl)-trichloroethane (I) identical with the product of condensation of chloral with acetanilide proves that this condensation occurs in the 4-position.

Experimental

1,1,1-Trichloro-2,2-di-(4'-chloronaphthyl-1')-ethane⁸ was prepared by slowly adding 225 g. of concentrated sulfuric acid to a cooled mixture of 51.5 g. of α -chloronaphthalene and 25 g. of chloral hydrate; the mixture was shaken for seven hours at 10° and poured on ice and the product triturated with boiling alcohol and crystallized from xylene; m. p. 223–224° dec.; yield 71%; dichloroethylene derivative,² m. p. 190° from propyl alcohol.

1,1,1-Trichloro-2,2-di-(4'-biphenyl)-ethane.—To a cold solution of 62 g. of biphenyl and 33 g. of chloral hydrate in 60 cc. of chloroform a cooled mixture of 100 g. of concentrated sulfuric acid and 40 g. of fuming sulfuric acid was added slowly with stirring. The cooling bath was removed after two hours, and after stirring for three hours longer the homogeneous material was poured onto a mixture of ice and chloroform. The chloroform layer was washed with water and soda solution and the solvent evaporated. Trituration of the residual oil with methanol gave a solid that was freed from biphenyl by steam distillation and crystallized from butanol. The product formed white needles, m. p. 151.5–152.5°; yield 41%.

Anal. Calcd. for $C_{26}H_{19}Cl_3$: C, 71.4; H, 4.3. Found: C, 71.5; H, 4.6.

Conversion to 1,1-dichloro-2,2-di-(4'-biphenyl)-ethylene was accomplished by refluxing 4.4 g. of the trichloride with 0.3 g. of sodium in 25 cc. of butanol for five hours; the product that crystallized on cooling formed white needles from acetone-petroleum ether, m. p. 153.5° (95% yield).

Anal. Calcd. for $C_{26}H_{18}Cl_2$: C, 78.0; H, 4.5. Found: C, 78.3; H, 4.6.

Oxidation of the ethylene (2 g.) with chromic acid (1.3 g.) in acetic acid (20 cc., refluxed three hours) gave a crude product that was triturated with ether to remove starting material, and crystallized from acetic acid. The product, m. p. 239°, gave no depression when mixed with authentic 4,4'-diphenylbenzophenone.

The condensation of chloral hydrate with fluorene was conducted in the same way in a more dilute chloroform solution and afforded in 22% yield a product, m. p. 162.5°, that on dehydrohalogenation gave 1,1-dichloro-2,2-di-(x'-fluorenyl)-ethylene; m. p. 220.5° from toluene, yield 79%.

Anal. Calcd. for $C_{28}H_{18}Cl_2$: C, 79.1; H, 4.2. Found: C, 79.6; H, 4.5.

(1) From a thesis by D. Lavie in presenting to the Hebrew University, Jerusalem.

(2) Stephenson and Waters, *J. Chem. Soc.*, 339 (1946).

(3) Burger, Graef and Bailey, *THIS JOURNAL*, **68**, 1725 (1946).

(4) Elbs, *J. prakt. Chem.*, [2], **39**, 500 (1889); **47**, 61 (1893).

(5) Lange and Zufall, *Ann.*, **271**, 1 (1892).

(6) Staedel and Haase, *Ber.*, **23**, 2578 (1890).

1,1,1-Trichloro-2,2-di-(*x'*-thiocyanophenyl)-ethane was obtained by stirring an ice cold mixture of phenyl thiocyanate (5 g.), chloral hydrate (3 g.) and a 1:3 mixture (20 g.) of concentrated and fuming sulfuric acid for two hours and pouring the material onto ice. Crystallization of the product from acetic acid gave white needles, m. p. 234.5–235°, dec.; yield 40%.

Anal. Calcd. for $C_{16}H_9N_2Cl_3S_2$: N, 7.0; Found: N, 7.2.

1,1,1-Trichloro-2,2-di-(3'-nitro-4'-hydroxyphenyl)-ethane was prepared by slowly adding 150 g. of concentrated sulfuric acid to a solution of 27 g. of *o*-nitrophenol and 16.5 g. of chloral hydrate in 15 cc. of chloroform and shaking the mixture for eight hours at 15°. The product was freed of solvent and unchanged *o*-nitrophenol by steam distillation and crystallized from methanol: yellow prisms m. p. 158–159°, yield 41%.

Anal. Calcd. for $C_{14}H_9O_3N_2Cl_3$: C, 41.4; H, 2.2; N, 6.9. Found: C, 41.4; H, 2.3; N, 7.3.

When the substance was refluxed with potassium hydroxide in methanol a salt separated; acidification of an aqueous solution of the salt gave the ethylene in the form of yellow needles, m. p. 131.5–132° from methanol (55%).

1,1,1-Trichloro-2,2-di-(4'-acetaminophenyl)-ethane (I).—A mixture of 13.5 g. of acetanilide, 8.2 g. of chloral hydrate and 60 g. of a mixture of equal parts of concentrated and fuming sulfuric acid was heated at 75–80° for six hours and poured onto ice. A yellow oil separated, and trituration with boiling water gave a solid product that was purified by crystallization from 60% ethanol or methanol; m. p. 245–250° (dec.), depending on the rate of heating; yield 11%.

Anal. Calcd. for $C_{18}H_{17}O_2N_2Cl_3$: N, 7.0. Found: N, 7.2.

1,1,1-Trichloro-2,2-di-(4'-nitrophenyl)-ethane (III).—Forty grams of 1,1,1-trichloro-2,2-diphenylethane was added slowly with vigorous stirring to 160 cc. of fuming nitric acid cooled to –30° and the temperature was not allowed to rise above –15°. The mixture was poured onto ice and the semisolid product was washed with cold water and dilute soda solution, filtered, trituated with methanol containing 5% acetone, and crystallized from glacial acetic acid. The dinitro derivative was obtained as yellowish needles, m. p. 169°, in 53% yield.

Anal. Calcd. for $C_{14}H_9O_4N_2Cl_3$: C, 44.9; H, 2.4; N, 7.5. Found: C, 44.8; H, 2.1; N, 7.6.

After this paper had been submitted to the Editor, a communication appeared by Kirkwood, Phillips and McCoy (*THIS JOURNAL*, **68**, 2405 (1946)), who also nitrated 1,1,1-trichloro-2,2-diphenylethane and reduced the *p,p'*-dinitro derivative formed to the corresponding diamine. For the latter, they record a m. p. of 92–95°, as compared

with our figure of 144–144.5° dec. Frequent repetition of our procedure has invariably led to a product of the same high melting point, and we are unable to account for the discrepancy. Our product was colorless and gave satisfactory analytical figures.

Anal. Calcd. for $C_{14}H_{13}N_2Cl_3$: C, 53.3; H, 4.1; N, 8.9. Found: C, 53.5; H, 4.3; N, 8.7.

We have, furthermore, prepared the well-defined dibenzylidene derivative (from the components in benzene by azeotropic removal of the water formed; yield, 66%; from butyl alcohol, platelets, m. p. 172–172.5°).

Anal. Calcd. for $C_{26}H_{21}N_2Cl_3$: C, 68.4; H, 4.3; N, 5.7. Found: C, 68.3; H, 4.4; N, 5.9.

Additional proof is afforded by the observation that the 1,1,1-trichloro-2,2-di-(*p*-aminophenyl)-ethane could be dehydrohalogenated in 86% yield to 1,1-dichloro-2,2-di-(*p*-aminophenyl)-ethylene, which was identical with the product obtained from the dinitro compound IV by reduction with stannous chloride and hydrochloric acid (yield, 62%). The aminated ethylene formed white needles and melted at 145.5° (dec.); it gave a strong depression of the melting point upon admixture of 1,1,1-trichloro-2,2-di-(*p*-aminophenyl)-ethane.

Anal. Calcd. for $C_{14}H_{12}N_2Cl_2$: C, 60.2; H, 4.3; N, 10.0. Found: C, 60.6; H, 4.2; N, 9.8.

The dichloroethylene derivative, obtained in 84% yield by the action of refluxing methanolic potassium hydroxide, crystallized from acetic acid in needles, m. p. 171.5–172°. Oxidation of the ethylene with chromic acid in acetic acid at the boiling point gave a dinitrobenzophenone, m. p. 187–188° (4,4'-derivative, 189°; 2,2'-derivative, 188°). Reduction with stannous chloride and crystallization of the neutralized reaction product from dilute alcohol gave needles, m. p. 240°, corresponding in properties to the known 4,4'-diaminobenzophenone.⁵

The conversion of the dinitro derivative III into the diacetylamino derivative I was accomplished as follows: 32 g. of stannous chloride and 10 cc. of concentrated hydrochloric acid were added slowly to a boiling solution of 7.4 g. of III in 25 cc. of alcohol. After thirty minutes the solution was diluted with water and made alkaline and the product collected and crystallized from 50% alcohol and obtained as clusters of needles, m. p. 144–144.5° (dec.). Acetylation of the diamine with acetic anhydride at the boiling point and crystallization of the product from nitrobenzene afforded fine needles, m. p. 245–250°, dec., that showed no depression in m. p. when mixed with the product of the condensation of chloral hydrate with acetanilide.

Anal. Calcd. for $C_{18}H_{17}O_2N_2Cl_3$: C, 54.1; H, 4.2; N, 7.0. Found: C, 54.2; H, 4.2; N, 7.0.

Summary

Procedures have been developed for the preparation of certain analogs of DDT.

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