the first of these two fractions. It melted at 137.5–138° after recrystallization from chloroform–methanol. A mixed m. p. with the 3-butenylamine obtained from α-allylbenzylamine (m. p. 137.5–138°) was unchanged.

Allyl Phenyl Ketone 2,4-Dinitrophenylhydrazone.—The neutral material obtained by steam distillation of the acidic solution described in the preceding section reacted with 2,4-dinitrophenylhydrazine to give what appeared to be a mixture. From 0.4 g. of the ketone and 0.54 g. of 2,4-dinitrophenylhydrazine was obtained 0.8 g. of orange-red plates melting at about 170°. Repeated recrystallization of this material from alcohol–acetic acid, glacial acetic acid and finally dilute acetic acid yielded large, shining orange-red leaflets, m. p. 201–203°.

Anal. Calcd. for $C_{16}H_{14}N_4O_4$: C, 58.89; H, 4.32. Found: C, 59.06; H, 4.32.

There was also obtained a small amount of deep red material, m. p. 190–195°. This was evidently still impure and was obtained in too small an amount to permit of further purification and analysis.

Reduction of Allyl Phenyl Ketone.—A mixture containing 0.41 g. of allyl phenyl ketone and 25 mg. of platinum oxide in 15 ml. of absolute ethanol was shaken with hydrogen at about 2 atmospheres pressure. The reduction was stopped when one mole of hydrogen had been absorbed.

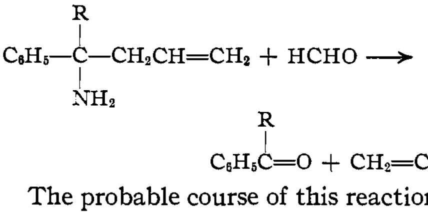
The filtered solution was divided into two equal portions. One of these was treated with 0.25 g. of 2,4-dinitrophenylhydrazine in alcohol containing a trace of hydrochloric acid. The derivative formed orange-red platelets, m. p. 189–190°. An authentic sample of *n*-butyrophenone was treated in the same way to yield a product melting at 190–191°. The mixed melting point was 189.5–190°.

Anal. Calcd. for $C_{16}H_{16}N_4O_4$: C, 58.52; H, 4.91. Found: C, 58.41; H, 5.01.

The second portion of the solution from the hydrogenation was used to prepare the semicarbazone. This melted at 180–181°, and a mixed melting point with an authentic sample (m. p. 180–181°) melted at 180–181°. Huntress and Mulliken[11] give m. p. 187–188° and 191.5°; McElvain[12] gives m. p. 184° for this derivative.

Summary

α-Allylbenzylamine and α,α-diallylbenzylamine react with formaldehyde with rearrangement and cleavage according to the general reaction



$$C_6H_5\text{—}\underset{NH_2}{\overset{R}{C}}\text{—}CH_2CH{=}CH_2 + HCHO \longrightarrow C_6H_5\overset{R}{C}{=}O + CH_2{=}CHCH_2CH_2NH_2$$

The probable course of this reaction is proposed and its analogy with the rearrangement of vinylallylmalonic acid derivatives is pointed out.

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(11) Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941.

(12) McElvain, "The Characterization of Organic Compounds." The Macmillan Co., New York, N. Y., 1945.

LOS ANGELES, CALIF. RECEIVED SEPTEMBER 20, 1949

[CONTRIBUTION FROM THE WM. H. CHANDLER CHEMISTRY LABORATORY, LEHIGH UNIVERSITY]

3-Phenylindones. I. The Synthesis of 6-Chloro-3-(*p*-chlorophenyl)-1-indenone and Some Related Compounds[1]

BY JAMES F. FEEMAN[2,3] AND E. D. AMSTUTZ

Although it is extremely difficult if not impossible, on the basis of present knowledge, to predict the insecticidal properties of a given compound, it has been noted[4] that certain structural groups appear in many of the most potent and useful insecticides. Thus, we concluded that substitution of the conjugated system –C═C–C═O for the trichloroethane grouping in the DDT molecule, either as a fused ring system, or in the form of a substituted acrylic ester, might be expected to produce compounds of value as selective insecticides. The investigations described here were concerned with the synthesis of the 3-phenylindone structurally related to DDT, and of several related reduction and halogenation products. Several of the intermediate di-(*p*-chlorophenyl)-acrylic, hydracrylic and propionic acids and esters are also of interest, both as possible insecticidal agents and as phytotoxic materials.

The sequence of reactions employed in the synthesis of this series of compounds has been outlined in the formula diagram. With 4,4′-dichlorobenzophenone as the starting compound, a Reformatsky reaction with either methyl or ethyl bromoacetate, employing the modification of Fieser and Johnson[5] for the preparation of active zinc, and following the suggestion of Hussey and Newman[6] for the improvement of yields by use of excess zinc and bromoester, yielded the corresponding hydracrylic esters (II, III) in over 90% yield. Difficulties encountered in separation of the unreacted dichlorobenzophenone from the esters, by means of fractional crystallization, led to direct saponification of the crude reaction product. This allowed ready separation of the β,β-bis-(*p*-chlorophenyl)-hydracrylic acid (IV). The ethyl ester has been prepared previously by means of a similar reaction.[7]

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(1) Abstracted from the dissertation of James F. Feeman, presented to the faculty of the Graduate School of Lehigh University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1949.

(2) Lehigh Institute of Research Fellow in Organic Chemistry, 1947–1949.

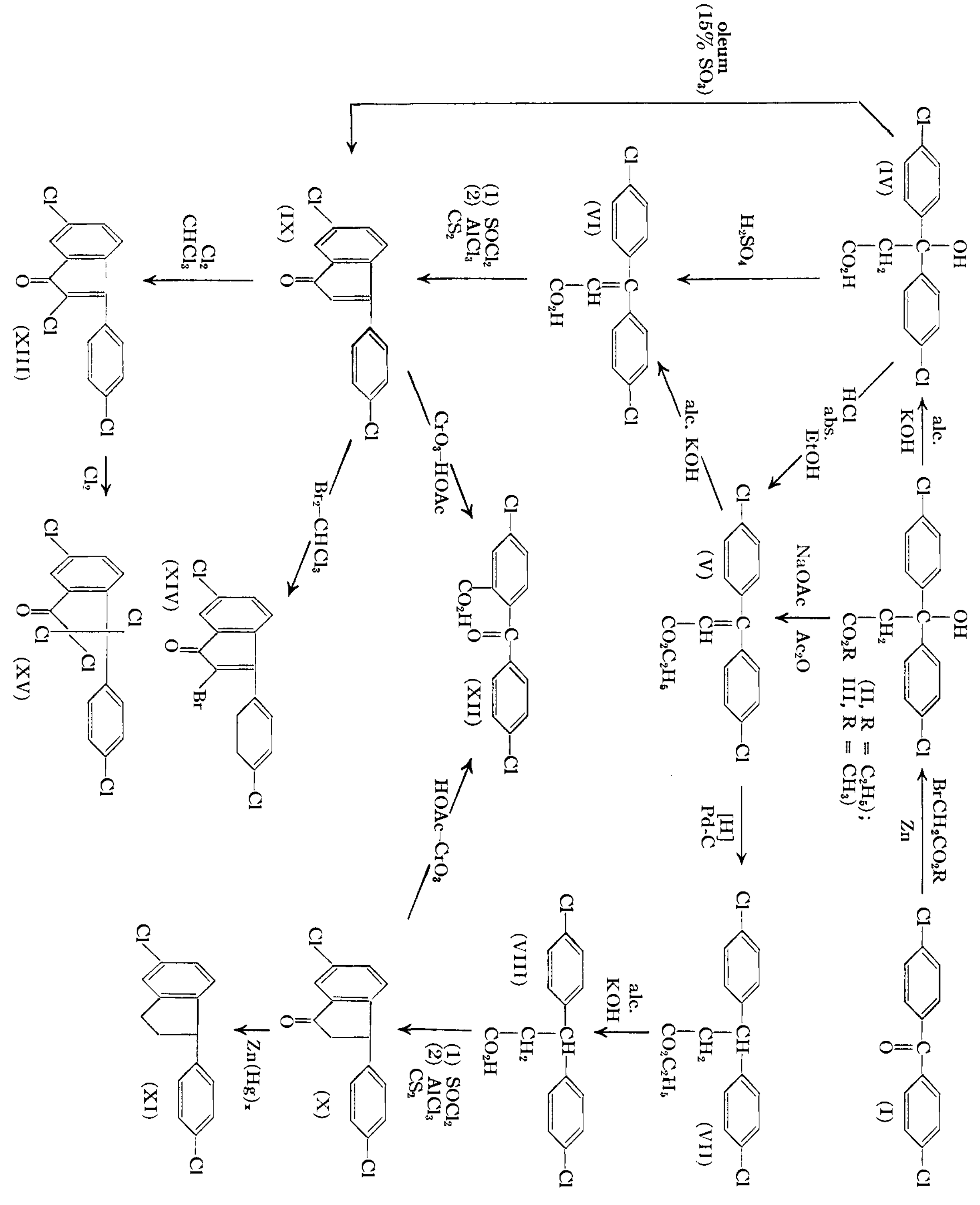
(3) Present address: Chemistry Department, The Ohio State University, Columbus 10, Ohio.

(4) Frear, "A Catalogue of Insecticides and Fungicides, Vol. I. Chemical Insecticides," Chronica Botanica Company, Waltham, Mass., 1947.

(5) Fieser and Johnson, THIS JOURNAL, **62**, 575 (1940).

(6) Hussey and Newman, *ibid.*, **70**, 3024 (1948).

(7) Bergmann, Hoffmann and Meyer, *J. prakt. Chem.*, **135**, 245 (1932).



Methods given in the literature[7,8] for dehydration of β-hydroxy esters were found to give inconsistent results. Anhydrous hydrogen chloride in ethanol was found to dehydrate and esterify the hydracrylic acid (IV), affording an excellent yield of V. Saponification of the latter produced the desired β,β-bis-(p-chlorophenyl)-acrylic acid (VI) in nearly quantitative yield. The use of dry hydrogen chloride for the dehydration of Reformatsky products has been employed by Natelson and Gottfried with very good results.[9]

DeFazi[10,11] has proposed concentrated sulfuric acid at room temperature as a cyclization agent for diaryl-hydracrylic esters substituted in the α-position. Ivanoff and Ivanoff[12] also have used

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(8) Rupe and Busolt, *Ber.*, **40**, 4537 (1907).

(9) Natelson and Gottfried, THIS JOURNAL, **61**, 970 (1939).

(10) DeFazi, *Gazz. chim. ital.*, **45**, II, 143 (1915); **46**, I, 256 (1916).

(11) DeFazi, *Atti II congresso naz. chim. pura applicata*, 1285 (1926); *C. A.*, **22**, 2165 (1928).

(12) Ivanoff and Ivanoff, *Compt. rend.*, **226**, 1199 (1948).

this method recently for the preparation of indones from 2,3,3-triaryl-substituted hydracrylic acids in excellent yield. The action of cold concentrated sulfuric acid on β,β-bis-(*p*-chlorophenyl)-hydracrylic acid or its ethyl ester, however, gave no indone formation, but, in both cases, produced the intermediate acrylic acid derivative (VI) in nearly quantitative yield. Cyclization to the indone was effected by means of oleum (15% sulfur trioxide). Preparation of the indone (IX) has also been effected by means of the action of anhydrous aluminum chloride on the acid chloride of VI, but this method is less satisfactory because of tar formation.

Preparation of 6-chloro-3-(*p*-chlorophenyl)-1-indanone (X) has been carried out readily through hydrogenation over palladium-charcoal catalyst of ethyl β,β-bis-(*p*-chlorophenyl)-acrylate (V), saponification of the ester to the diarylpropionic acid (VIII), and cyclization by means of an intramolecular Friedel–Crafts reaction employing aluminum chloride on the acid chloride.

Oxidation of the indenone (IX) and of the indanone (X) by means of chromium trioxide in glacial acetic acid produced the same acid, presumably 5-chloro-2-(*p*-chlorobenzoyl)-benzoic acid. All attempts to convert this degradation product to the known 2,7-dichloroanthraquinone thus far have failed.

Reduction of the indanone (X) by the Clemmensen method, using toluene as the solvent, proceeded smoothly, affording the indan (XI) in 81.8% yield.

Halogenation experiments performed on the indenone (IX) produced unexpected results. Addition of bromine and chlorine in chloroform at low or room temperatures gave the colorless addition products initially; however, these were quite unstable, decomposing with loss of one mole of hydrogen halide and formation of the brilliantly orange colored 2-halo-indenones (XIII, XIV). Addition of chlorine to 2,6-dichloro-3-(*p*-chlorophenyl)-1-indenone produced the completely chlorinated derivative, 2,2,3,6-tetrachloro-3-(*p*-chlorophenyl)-1-indenone (XV).

Acknowledgments.—The authors wish to thank the Lehigh Institute of Research for the funds which permitted carrying out these investigations.

Experimental[13]

4,4′-Dichlorobenzophenone (I).—Methods given in the literature were followed for the preparation of this compound. Reaction of *p*-chlorobenzoyl chloride with chlorobenzene in the presence of anhydrous aluminum chloride[14] afforded I in 66% yield, m. p. 145–147°, colorless hexagonal plates. Oxidation of 2,2-bis-(*p*-chlorophenyl)-1,1-dichloroethylene (prepared by hydrolysis of DDT) by means of chromium trioxide in glacial acetic acid[15] gave the same compound in 56.2% over-all yield.

Reformatsky Reactions of 4,4′-Dichlorobenzophenone and Bromoacetic Esters

A. β,β-Bis-(*p*-chlorophenyl)-hydracrylic Acid (IV).—A one mole excess of ethyl bromoacetate (133.6 g., 0.08 mole) and 100.44 g. (0.04 mole) of 4,4′-dichlorobenzophenone (I) were dissolved with heating in a mixture of 300 ml. each of distilled, anhydrous benzene and toluene. Special precautions were observed to keep the apparatus free from moisture.

After solution was complete, 65.4 g. (1.0 mole) of 30-mesh zinc, activated according to Fieser and Johnson,[5] and a crystal of iodine were added. The mixture was refluxed with stirring for about thirty minutes, when a vigorous reaction started. External cooling by means of a cold water-bath was used to control the reaction during the next twenty minutes. After the exothermic phase of the reaction had passed, refluxing was continued for an additional two hours. Then the hot solution was decanted over 500 g. of cracked ice and 200 ml. of 20% sulfuric acid with good stirring.

Separation of the organic layer, drying over anhydrous magnesium sulfate, and removal of the solvents *in vacuo*, left a solid product which was then treated with a solution of 44.8 g. (0.80 mole) of potassium hydroxide in 100 ml. of water and 1 l. of 95% ethanol. The solution was refluxed for two hours, poured into cold water, the insoluble dichlorobenzophenone filtered off and the filtrate acidified with 20% sulfuric acid. The slightly yellow powder, after drying, weighed 114.9 g. (92.3%), m. p. 187–192°, dec. Trituration with benzene gave colorless solid, m. p. 196.5–197.5°, dec. Recrystallization of 4.0 g. from benzene gave 3.45 g. of fine, colorless needles, m. p. 197.5–198.5°, dec.

Anal. Calcd. for $C_{15}H_{12}Cl_2O_3$: C, 57.90; H, 3.88; neut. equiv., 311.2. Found: C, 58.10; H, 3.96; neut. equiv., 312.0.

B. Ethyl β,β-Bis-(*p*-chlorophenyl)-hydracrylate (II).—A similar procedure to that given above was followed, except for the saponification of the crude product. Repeated recrystallization of the latter from methanol yielded colorless needles, m. p. 101.0–101.6° (reported in the literature,[7] m. p. 102°).

C. Methyl β,β-Bis-(*p*-chlorophenyl)-hydracrylate (III).—A similar procedure to that given above for IV was followed, with the exceptions that methyl bromoacetate was used, and the crude product was not hydrolyzed. Recrystallization of the crude product from methanol gave colorless prisms, m. p. 125–126°, in 35.2% yield.

Anal. Calcd. for $C_{16}H_{14}Cl_2O_3$: C, 59.09; H, 4.34. Found: C, 58.82; H, 4.27.

Ethyl β,β-Bis-(*p*-chlorophenyl)-acrylate (V).—Anhydrous hydrogen chloride was passed for four hours through a solution of 86.0 g. (0.276 mole) of IV (m. p. 196.5–197.5°) in 700 ml. of absolute ethanol, and the solution was refluxed during the last hour. The product was obtained, by dilution with water and cooling, as slightly yellow prisms, m. p. 55–61°. Recrystallization from 200 ml. of ethanol afforded 74.0 g. (83.5%) of colorless prisms, m. p. 61–63°. A sample recrystallized for analysis melted at 64–65° (reported in the literature,[7] m. p. 65°).

Anal. Calcd. for $C_{17}H_{14}Cl_2O_2$: C, 63.57; H, 4.39. Found: C, 63.46; H, 4.70.

β,β-Bis-(*p*-chlorophenyl)-acrylic Acid (VI).—Saponification of 64.0 g. (0.20 mole) of V by means of 22.4 g. (0.40 mole) of potassium hydroxide in 500 ml. of ethanol under reflux for one and a half hours, yielded 58.0 g. of acid (98.8%), m. p. 176–178°. Recrystallization from benzene–petroleum ether did not change the melting point, but yielded colorless prismatic rods.

The same compound was obtained by stirring 73.8 g. (0.261 mole of β,β-bis-(*p*-chlorophenyl)-hydracrylic acid (IV) gradually and at room temperature into 500 ml. of concentrated sulfuric acid. The solution was allowed to stand for thirty minutes before pouring it with good stirring into ice-water. The gummy mass soon solidified yielding 67.0 g. (87.6%) of nearly colorless material.

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[13] All melting points have been corrected for thermometer stem-emergence unless otherwise noted.

[14] Dittrich, *Ann.*, **264**, 175 (1891).

[15] Cristol and Haller, THIS JOURNAL, **68**, 140 (1946).

Recrystallization from benzene afforded 60.7 g. (79.4%) of colorless rods, m. p. 176–178° (reported in the literature,[16] m. p. 175°).

Ethyl β,β-Bis-(*p*-chlorophenyl)-propionate (VII).—Hydrogenation of 64.14 g. (0.20 mole) of ethyl β,β-bis-(*p*-chlorophenyl)-acrylate (V) was carried out in ethanol at two atmospheres pressure and room temperature employing 3.0 g. of a commercial 5% palladium–carbon catalyst (Baker and Company, Newark, N. J.). After twenty-five minutes the pressure had dropped 17.2 pounds per sq. in. Working up the product in the usual manner, and distillation of the oil obtained, under diminished pressure, gave a colorless, viscous oil, 55.45 g. (85.8%), b. p. 205–209° at 7 mm.

Anal. Calcd. for $C_{17}H_{16}Cl_2O_2$: C, 63.17; H, 4.99. Found: C, 63.06; H, 5.19.

β,β-Bis-(*p*-chlorophenyl)-propionic Acid (VIII).—Saponification of 44.0 g. (0.136 mole) of VII was carried out by means of 16.9 g. (0.30 mole) of potassium hydroxide in 350 ml. of 95% ethanol under reflux for one and a half hours. The crude product weighed 40.2 g. (100%), m. p. 175–184°. Recrystallization from benzene (350 ml.) gave 24.4 g., m. p. 184–188°. Several recrystallizations of a 4.0-g. sample from benzene–petroleum ether yielded 2.85 g. of colorless rhombic prisms, m. p. 189–191° (reported in the literature, m. p. 187°,[16] 188–189°[17]).

Anal. Calcd. for $C_{15}H_{12}Cl_2O_2$: C, 61.03; H, 4.10. Found: C, 61.26; H, 4.14.

6-Chloro-3-(*p*-chlorophenyl)-1-indenone (IX).—Cyclization of β,β-bis-(*p*-chlorophenyl)-acrylic acid was carried out in the following manner. The acid (8.79 g., 0.03 mole) was warmed on the steam-bath with 7.14 g. (0.06 mole) of thionyl chloride and a drop of pyridine, in a 50-ml. flask fitted with condenser and drying tube. After two hours excess thionyl chloride was removed under diminished pressure, and the acid chloride was dissolved in 25 ml. of dry carbon disulfide. Then 8.0 g. (0.06 mole) of anhydrous aluminum chloride was added and the mixture warmed on the steam-bath for twenty hours. Decomposition of the complex with cracked ice (200 g.) and hydrochloric acid (10 ml.) left an orange colored solid, after removal of the carbon disulfide. Unreacted acid was removed by means of 10% sodium hydroxide solution and recrystallization of the insoluble product from benzene gave 5.0 g. (60.6%) of orange needles, m. p. 152–155°, dec. Recrystallization from isopropyl alcohol or benzene, with decolorization with active charcoal, gave yellow needles, m. p. 160–162°, dec.

Anal. Calcd. for $C_{15}H_8Cl_2O$: C, 65.48; H, 2.93; Cl, 25.78. Found: C, 65.41; H, 3.09; Cl, 25.81.

The **2,4-dinitrophenylhydrazone**, a dark red powder, melted at 290–291°, dec.

Anal. Calcd. for $C_{21}H_{12}Cl_2N_4O_4$: C, 55.40; H, 2.65. Found: C, 55.29; H, 2.60.

This compound has also been prepared by cyclization of β,β-bis-(*p*-chlorophenyl)-hydracrylic acid, or its ethyl ester, by a solution of 2.0 g. in 10 ml. of oleum (15% sulfur trioxide) at room temperature. After ten minutes the dark solution was poured over cracked ice (100 g.) and the yellow precipitate filtered off. Unreacted acid was extracted by means of 5% sodium hydroxide solution, and the insoluble material washed well with water. This gave 0.8 g. (45.2%), m. p. 157–160°. Recrystallization from benzene afforded yellow needles, m. p. 161–162°.

6-Chloro-3-(*p*-chlorophenyl)-1-indanone (X).—The acid chloride was prepared from 27.4 g. (0.0928 mole) of β,β-bis-(*p*-chlorophenyl)-propionic acid by treatment with 21.4 g. (0.18 mole) of thionyl chloride and 1 ml. of pyridine. After two hours of heating on the steam-bath, the excess thionyl chloride was removed under reduced pressure, and 25 ml. of dry carbon disulfide and 12.7 g. (0.095 mole) of anhydrous aluminum chloride (granular) were added. The mixture was warmed for one and a half hours and then decomposed with 400 g. of cracked ice. The carbon disulfide was removed and the remaining solid triturated with 200 ml. of 5% sodium hydroxide solution. The orange colored product weighed 25.0 g., m. p. 101–112°. Recrystallization from ethanol with decolorization yielded 20.0 g. (77.7%), m. p. 105–115°, of orange-yellow prisms. Two further recrystallizations from ethanol gave light orange prisms, 12.3 g., m. p. 116–118°. Further recrystallization of 1.37 g. afforded 1.0 g. of nearly colorless (salmon-colored) prisms, m. p. 117.0–118.5°.

Anal. Calcd. for $C_{15}H_{10}Cl_2O$: C, 65.00; H, 3.64; Cl, 25.69. Found: C, 64.78; H, 3.75; Cl, 25.82.

The **2,4-dinitrophenylhydrazone** was an orange-red solid, m. p. 259–261°.

Anal. Calcd. for $C_{21}H_{14}Cl_2N_4O_4$: C, 55.16; H, 3.09. Found: C, 55.27; H, 3.25.

Oxidation of 6-Chloro-3-(*p*-chlorophenyl)-1-indenone (IX) and of 6-Chloro-3-(*p*-chlorophenyl)-1-indanone (X): 5-Chloro-2-(*p*-chlorobenzoyl)-benzoic Acid (XII).—A. A solution of 1.0 g. of 6-chloro-3-(*p*-chlorophenyl)-1-indenone in 20 ml. of glacial acetic acid was treated with 2.0 g. of chromium trioxide at room temperature. A vigorous reaction took place and after an hour the mixture was poured over cracked ice, the insoluble material filtered off, washed, and extracted with 25 ml. of 10% potassium hydroxide solution. After filtering the basic solution gave 0.3 g. of yellow solid which was recrystallized from benzene–petroleum ether. The product crystallized as prisms, m. p. 149–155°. Recrystallization again yielded 0.05 g. of colorless prims, m. p. 158–159°.

B. A solution of 1.0 g. of 6-chloro-3-(*p*-chlorophenyl)-1-indanone in 10 ml. of glacial acetic acid was treated at room temperature with 2.0 g. of chromium trioxide. After ten minutes the reaction was completed and the mixture was worked up as above, yielding 0.3 g. of colorless solid. Recrystallization from benzene–petroleum ether gave 0.16 g. of colorless prisms, m. p. 157–157.5°. A mixed melting point determination with the degradation product isolated in (A) above from (IX) showed no depression, m. p. 158.0–158.6°.

Anal. Calcd. for $C_{14}H_8Cl_2O_3$: C, 56.97; H, 2.73; neut. equiv., 295.1. Found: C, 56.71; H, 2.94; neut. equiv., 292.0.

5-Chloro-1-(*p*-chlorophenyl)-indan (XI).—Fourteen grams of 30-mesh zinc, cleaned with concentrated sulfuric acid at 100° for fifteen minutes, and then washed well with water, was amalgamated by shaking for five minutes in 20 ml. of water and 1 ml. of concentrated hydrochloric acid with 0.7 g. of mercuric chloride. The liquid was decanted from the zinc, and to the latter were added 4 ml. of water and 10 ml. of concentrated hydrochloric acid.

Then 4.0 g. (0.0144 mole) of 6-chloro-3-(*p*-chlorophenyl)-1-indanone (X) in 10 ml. of toluene were added, and the mixture refluxed for a total of fifteen hours. Five-ml. portions of concentrated hydrochloric acid were added after four, eight and twelve hours. The toluene layer was separated, the aqueous layer extracted with ether, and the extract combined with the toluene solution. After washing with 10% sodium carbonate solution and water, the solution was dried over magnesium sulfate and the solvents removed. The remaining oil, distilled under reduced pressure, came over almost entirely at 170–172° at 3 mm. as a colorless viscous oil which did not solidify, 3.1 g. (81.8%).

Anal. Calcd. for $C_{15}H_{12}Cl_2$: C, 68.46; H, 4.60; Cl, 26.95. Found: C, 67.56; H, 4.66; Cl, 27.35.

Halogenation of 6-Chloro-3-(*p*-chlorophenyl)-1-indenone (IX)

A. **Bromo Addition: 2-Bromo-6-chloro-3-(*p*-chlorophenyl)-1-indenone (XIV).**—One gram (0.0036 mole) of 6-chloro-3-(*p*-chlorophenyl)-1-indenone suspended in 10 ml. of anhydrous chloroform was treated with 0.58 g. (0.0036 mole) of bromine. The solution became colorless

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[16] Bergmann, Weizmann, Dimant, Patai and Szmuszkowicz, THIS JOURNAL, **70**, 1612 (1948).

[17] Fuson, Kozacik and Eaton, *ibid.*, **55**, 3799 (1933).

rapidly, but upon removal of the solvent on the steam bath an orange solid remained. Recrystallization from glacial acetic acid–ethanol yielded 1.0 g. (78.4%) of orange needles, m. p. 209–211°.

Anal. Calcd. for $C_{15}H_7BrCl_2O$: C, 50.89; H, 1.99. Found: C, 50.35; H, 2.21.

The dark orange **2,4-dinitrophenylhydrazone** melted at 257–258°.

B. Chlorine Addition. 2,6-Dichloro-3-(*p*-chlorophenyl)-1-indenone (XIII).—One gram (0.0036 mole) of IX was suspended in 15 ml. of chloroform, and dry chlorine gas was passed through for thirty minutes. The indone dissolved rapidly forming a light yellow solution. Evaporation of the solvent on the steam-bath left an orange colored oil, which solidified on cooling. Recrystallization from 50% ethanol–glacial acetic acid gave 0.7 g. (62.9%) of brilliant orange needles, m. p. 196.5–197.6°.

Anal. Calcd. for $C_{15}H_7Cl_3O$: C, 58.19; H, 2.28. Found: C, 57.93; H, 2.05.

The **2,4-dinitrophenylhydrazone** was a red solid, m. p. 270–273°.

In a repetition of the above experiment, 3.0 g. (0.0109 mole) of the indenone (IX) in 50 ml. of chloroform were treated with chlorine gas with cooling in an ice-bath. The compound absorbed chlorine and formed a yellow solution as before. The excess chlorine and solvent were removed under reduced pressure in the cold, but even under these conditions the solution gradually became orange colored. No further attempt was made to isolate the addition product. The dehydrohalogenation was completed on the steam-bath, leaving 3.4 g. (quantitative) of orange colored oil which solidified on cooling.

2,2,3,6-Tetrachloro-3-(*p*-chlorophenyl)-1-indanone (XV).—The crude product from the above reaction was dissolved in 25 ml. of dry chloroform, and dry chlorine gas was again passed through for ten minutes. The dark orange solution gradually became nearly colorless. The chloroform was removed on the steam-bath, leaving a yellow oil which solidified giving 4.1 g. of yellow material. Fractional crystallization from 50% ethanol–acetic acid gave 0.4 g. of orange needles, m. p. 196–198°, which showed no depression of the melting point in a mixed melting point determination with the starting material (XIII). Also obtained were 1.6 g. of yellow–orange prisms, m. p. 135–149°, which upon repeated recrystallization from ethanol gave 0.75 g. of yellow prisms, m. p. 150.6–152°.

Anal. Calcd. for $C_{15}H_7Cl_5O$: C, 47.36; H, 1.85. Found: C, 47.43; H, 2.31.

Summary

6-Chloro-3-(*p*-chlorophenyl)-1-indenone, 6-chloro-3-(*p*-chlorophenyl)-1-indanone, and five related compounds have been synthesized and characterized for study as possible new insecticidal agents.

In the course of these investigations, seven intermediates have been prepared for study as insecticidal or phytotoxic materials. Three of the latter had not been prepared previously, including β,β-bis-(*p*-chlorophenyl)-hydracrylic acid and its methyl ester, and ethyl β,β-bis-(*p*-chlorophenyl)-propionate. In addition, alternate methods of synthesis have been described for several of the intermediates which had been prepared previously.

BETHLEHEM, PENNA. RECEIVED JUNE 29, 1949

[CONTRIBUTION FROM THE WM. H. CHANDLER CHEMISTRY LABORATORY, LEHIGH UNIVERSITY]

3-Phenylindones. II. The Synthesis of 5,6-Dimethoxy-3-(3,4-dimethoxyphenyl)-1-indanone and Some Related Compounds[1,2]

BY JAMES F. FEEMAN[3] AND E. D. AMSTUTZ

In view of the possibility of harmful effects attending the use of chlorinated materials for the control of insect pests where human food sources are involved, it seemed desirable to attempt the preparation of non-halogenated organic compounds of possible insecticidal value.

From a consideration of the results obtained by Frear and Seiferle[4] in their correlation of insecticidal efficiency with definite chemical groupings, it may be seen that the indene ring system ranks high because of the high toxicity of chlordane and of the 1,3-indandiones of Kilgore.[5] Also, among the various functional groups which have a high rating in the Frear, Seiferle study, based upon a large number of tested compounds, are polyether groups. Although this survey included compounds showing as low as 10% toxicity, a study of most of the naturally occurring fish and insect poisons of relatively high toxicity reveals that poly-ether groupings are present in most. Murti, Rao and Seshadri[6] have reported recently that methylation of free hydroxyl groups in various coumarins and flavones converts the inactive parent compounds into strong fish poisons, and, therefore, insecticides, since the two properties are usually concomitant.

These considerations, together with the fact that the $-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O$ conjugated system is found frequently in natural and synthetic insecticides (see paper I of this series[1]), led us to attempt the synthesis of 5,6-dimethoxy-3-(3,4-dimethoxyphenyl)-1-indenone (I) and some related compounds.

Thus, far, methods of synthesis of the indone (I) attempted have failed to give this product, but a number of related compounds have been

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[1] For the preceding paper of this series see THIS JOURNAL, **72**, 1522 (1950).

[2] Abstracted from the dissertation of James F. Feeman, presented to the faculty of the Graduate School of Lehigh University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1949.

[3] Lehigh Institute of Research Fellow in Organic Chemistry, 1947–1949; present address: Chemistry Department, The Ohio State University, Columbus 10, Ohio.

[4] Frear and Seiferle, *J. Econ. Entomol.*, **40**, 736 (1947).

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