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.

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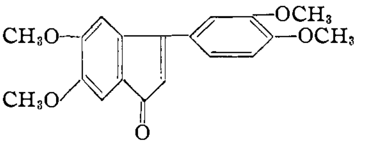
[4] Frear and Seiferle, *J. Econ. Entomol.*, **40**, 736 (1947).

[5] Kilgore, *Ind. Eng. Chem.*, **34**, 494 (1942).

[6] Murti, Rao and Seshadri, *Proc. Indian Acad. Sci.*, **25A**, 22 (1947).



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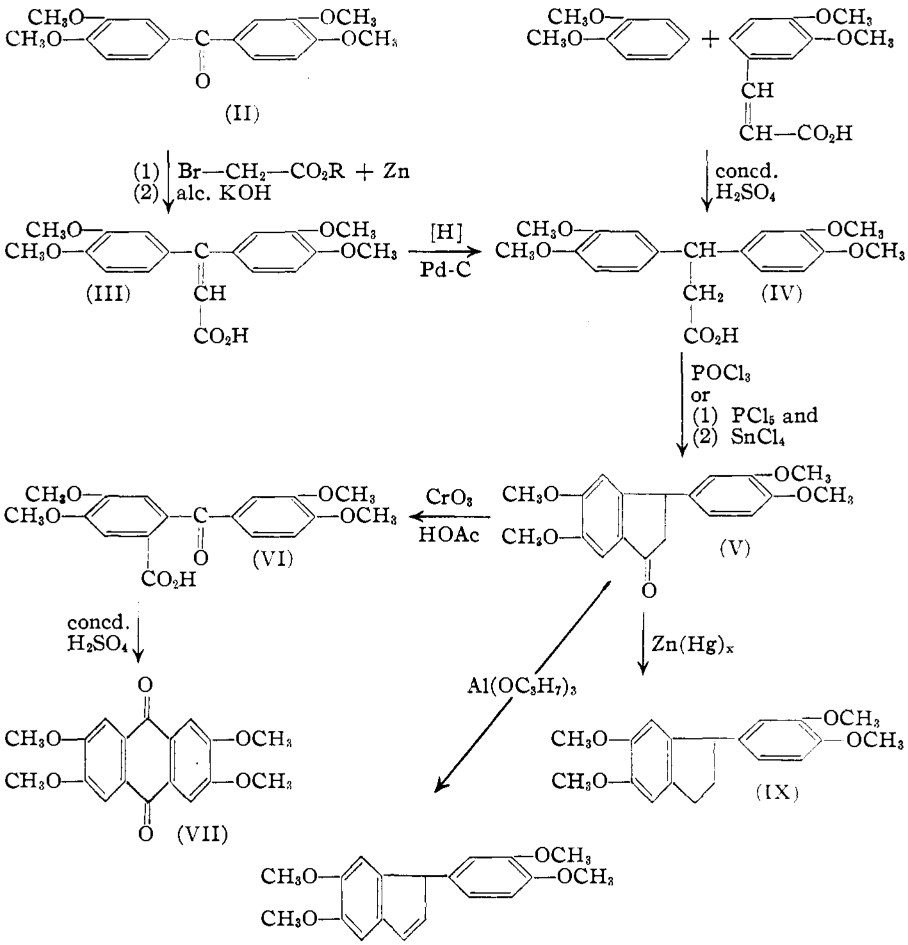
prepared in the process. The sequences of reactions employed have been outlined in the accompanying formula diagram.



(VIII)

The route to the desired indone (I) which was at first expected to be best, involved preparation of β,β-bis-(3,4-dimethoxyphenyl)-acrylic acid (III) followed by cyclization. The substituted-acrylic acid was prepared readily by means of a Reformatsky reaction of ethyl bromoacetate and 3,3′,4,4′-tetramethoxybenzophenone. A resinous mixture of products and starting material was obtained, which, upon saponification, gave 58.1% of the desired diveratryl-acrylic acid (III). Attempts to cyclize this compound, however, by means of thionyl chloride or by means of phosphorus pentachloride, followed by anhydrous stannic chloride, produced a monochloro derivative of the desired indone. Attempts to employ sulfuric acid gave either water soluble products or recovered starting material; phosphorus oxychloride likewise gave only recovered starting material when the reaction period was short, but caused formation of a purple-colored compound under more strenuous conditions (ten minutes at the boiling point).

Following these unsuccessful attempts to prepare the indone, synthesis of this compound was attempted by dehydrogenation of the corresponding indanone (V). The latter product was prepared by cyclization of β,β-bis-(3,4-dimethoxyphenyl)-propionic acid by means of phosphorus pentachloride to prepare the acid chloride, followed by stannic chloride in the cold; the cyclization has also been carried out by means of boiling for three minutes in solution in phosphorus oxychloride. These successful methods of cyclization were found only after many unsuccessful attempts with various concentrations of sulfuric acid, with phosphoric anhydride, and with thionyl chloride followed by aluminum chloride.

The cyclized product, 5,6-dimethoxy-3-(3,4-dimethoxyphenyl)-1-indanone (V), was a colorless solid, m. p. 124.2–125.0°, which was characterized by means of its 2,4-dinitrophenylhydrazone, m. p. 220.5–222.0° dec.

Several attempts have been made to dehydrogenate the indanone both by means of palladium–charcoal at high temperatures, and by some bromination–dehydrobromination reactions. These methods also have failed to produce the indone (I). With palladium–charcoal, the indanone was recovered almost quantitatively, while in the brominations it was found that nuclear bromination occurred in preference to bromination in the α position to the carbonyl group. This produced a monobromoindanone of unknown constitution, in which the bromine was unreactive to usual basic dehydrohalogenation reagents. Similar results were obtained both with bromine in acetic acid and with N-bromosuccinimide in carbon tetrachloride. When an excess of N-bromosuccinimide was employed, it was found that some monobromoindenone was formed, presumably by occurrence of both nuclear and side chain bromination, followed by dehydrobromination.

Preparation of β,β-bis-(3,4-dimethoxyphenyl)-propionic acid (IV) has been accomplished by two distinct methods. Catalytic hydrogenation (5% palladium–charcoal catalyst) of diveratrylacrylic acid (III) has been carried out with excellent results. For the preparation of larger quantities, the sulfuric acid catalyzed addition of veratrole to 3,4-dimethoxycinnamic acid gave diveratrylpropionic acid in 64.3% yield. This method was used by Muller and Gal to prepare the corresponding α-methyl acid in their synthesis of diisohomogenol[7] and is based on the work of Liebermann and Hartmann.[8]

In cyclizations of this type of compound, where ring closure both *ortho* and *para* to the *meta* methoxyl group might be expected, it has been found generally that the reaction occurs predominantly at the *para* position.[9]

That similar orientation occurs in the cyclization of diveratrylpropionic acid has been proved by oxidation in the cold of the tetramethoxyindanone (V) by means of chromium trioxide in glacial acetic acid to 4,5-dimethoxy-2-(3,4-di-methoxybenzoyl)-benzoic acid, (VI), m. p. 223.6–225.2°, and subsequent conversion of the latter to 2,3,6,7-tetramethoxyanthraquinone (VII). Both of these compounds have been reported previously.[10,11]

Meerwein–Ponndorf reduction (aluminum isopropoxide) of the indanone (V) has been carried out, producing the dehydrated product, 5,6-dimethoxy - 1 - (3,4 - dimethoxyphenyl) - indene (VIII), m. p. 126.0–127.5°, in 34.1% yield. Reduction of the indanone (V) by means of amalgamated zinc and hydrochloric acid (Clemmensen), employing toluene as the immiscible solvent, gave 5,6-dimethoxy-1-(3,4-dimethoxyphenyl)-indan (IX), m. p. 85–86.8°, a colorless solid, in 86% yield.

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

Experimental[12]

Preparation of Starting Materials

Veratrole was prepared by methylation of guaiacol or catechol in 75–85% yield by direct adaptation of the method of Buck[13] for the methylation of vanillin. Veratraldehyde was prepared according to the literature[13] by the methylation of vanillin. Veratric acid was prepared in 68–74% yield by oxidation of veratraldehyde by the method of Lintner and Parks.[14]

3,3′,4,4′-Tetramethoxybenzophenone (II) was prepared principally by the Friedel–Crafts reaction of veratrole and veratroyl chloride in the presence of aluminum chloride according to the literature[15,16] in 40% yield. Various other methods given in the literature [17,18,19] for the preparation of this compound were found to be less convenient or inferior in over-all yield.

β,β-Bis-(3,4-dimethoxyphenyl)-acrylic Acid (III).—To a solution of 30.2 g. (0.10 mole) of 3,3′,4,4′-tetramethoxybenzophenone (II) and 50.1 g. (0.30 mole) of ethyl bromoacetate in 200 ml. of 50% anhydrous benzene–toluene were added 20 g. (0.303 mole) of 30-mesh zinc (activated according to Fieser and Johnson[20]) and a crystal of iodine. After the mixture was refluxed for about twenty minutes, a vigorous reaction set in, which was controlled by cooling with a cold water-bath. After about fifteen minutes, heat was again applied to reflux the mixture, and this was continued for an hour. The solution was decanted into a mixture of 50 ml. of concentrated sulfuric acid and 250 g. of cracked ice. The organic layer, after decomposition of the complex, was separated, washed with water, dried over magnesium sulfate, and the solvents removed under reduced pressure leaving 47 g. of a dark oil. The latter was dissolved in 150 ml. of ethanol and refluxed for one hour with a solution of 20.0 g. (0.357 mole) of potassium hydroxide in 40 ml. of ethanol and 10 ml. of water. The reaction mixture was poured into 500 ml. of cold water, the insoluble unreacted ketone removed by filtration, and the filtrate acidified with cold 20% sulfuric acid. The oily precipitate solidified on standing and was separated and dried giving 31 g. of brown solid, m. p. 145–160°. Recrystallization from benzene–petroleum ether with decolorization afforded 20.0 g. (58.1%) of colorless solid, m. p. 160.5–162°.

Anal. Calcd. for $C_{19}H_{20}O_6$: C, 66.27; H, 5.86. Found: C, 66.07; H, 5.70.

Hydrogenation of β,β-Bis-(3,4-dimethoxyphenyl)-acrylic Acid

β,β-Bis-(3,4-dimethoxyphenyl)-propionic Acid (IV).—A solution of 10.0 g. (0.029 mole) of diveratrylacrylic acid (III) in 150 ml. of ethanol was hydrogenated at two atmospheres pressure and room temperature in the presence of 1.0 g. of 5% palladium–charcoal catalyst. After ten minutes the pressure had dropped 2.8 pounds per sq. in. After thirty minutes no further drop was noticed, so the catalyst was filtered off, the solution concentrated to 50 ml. and cooled, giving 7.8 g. (77.7%) of colorless needles, m. p. 161.4–162.4°. A mixed melting point determination with a sample of the starting material showed depression of the melting point to 145–153°, and the product gave a negative unsaturation test with bromine while the starting material reacted readily.

Anal. Calcd. for $C_{19}H_{22}O_6$: C, 65.88; H, 6.40. Found: C, 65.59; H, 6.19.

3,4-Dimethoxycinnamic Acid.—This compound was prepared according to the literature[21] in 78.4% yield.

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[7] Muller and Gal, *Ber.*, **77B**, 343 (1944).

[8] Liebermann and Hartmann, *ibid.*, **25**, 960, 2124 (1892).

[9] See, for example, Bachmann and Thomas, THIS JOURNAL, **64**, 94 (1942), and Ingold and Piggott, *J. Chem. Soc.*, 1469 (1923).

[10] Haworth and Mavin, *ibid.*, 1363 (1931).

[11] Vanzetti and Dreyfuss, *Gazz. chim. ital.*, **64**, 381 (1934); *C. A.*, **28**, 6432-6437 (1934).

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

[13] Buck, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 619.

[14] Lintner and Parks, *J. Am. Pharm. Assoc., Sci. Ed.*, **37**, 39 (1948).

[15] Perkin and Weizmann, *J. Chem. Soc.*, **89**, 1661 (1906).

[16] Kostanecki and Tambor, *Ber.*, **39**, 4027 (1906).

[17] Ford-Moore, *J. Chem. Soc.*, 952 (1947).

[18] Oliverio, *Boll. sedute accad. gioenia sci. nat. Catania* (3), (1937), No. 4. 4 pp. (separate); *C. A.*, **34**, 7885-7889 (1940).

[19] Oliverio, *ibid.*, No. 5. 4 pp. (separate); *C. A.*, **34**, 7886-7892 (1940).

[20] Fieser and Johnson, THIS JOURNAL, **62**, 575 (1940).

[21] Robinson and Shinoda, *J. Chem. Soc.*, **127**, 1977 (1925).

Addition of Veratrole to 3,4-Dimethoxycinnamic Acid

β,β-Bis-(3,4-dimethoxyphenyl)-propionic Acid (IV).—Forty grams (0.192 mole) of 3,4-dimethoxycinnamic acid and 100 g. of veratrole were heated with stirring on the water-bath, and 40 ml. of concentrated sulfuric acid was dropped in during one hour.[7,8] Stirring and heating were continued for five additional hours, and then the mixture was poured with stirring into a mixture of 500 g. each of ice and water. The solution was made basic with cold 25% sodium hydroxide solution, and the excess veratrole extracted with ether. The basic solution was filtered and acidified with hydrochloric acid. The crude acid weighed 54.1 g., m. p. 152–158°. Recrystallization from ethanol afforded 42.7 g. (64.3%) of colorless needles, m. p. 156–159°. Further recrystallization raised the melting point to 159–161°. A mixed melting point with a sample of the diveratrylpropionic acid prepared by hydrogenation of diveratryl-acrylic acid (III) showed no depression.

Cyclization of β,β-Bis-(3,4-dimethoxyphenyl)-propionic Acid (IV)

5,6-Dimethoxy-3-(3,4-dimethoxyphenyl)-1-indanone (V).—Twenty-three grams (0.0664 mole) of β,β-bis-(3,4-dimethoxyphenyl)-propionic acid was boiled in 60 ml. of phosphorus oxychloride for exactly three minutes. The dark red solution was then poured over ice and the green resinous mass washed with water several times. Then it was allowed to stand, with occasional stirring, in 300 ml. of 5% potassium hydroxide solution overnight. The solid was filtered off and washed well with water, giving 19.0 g. of yellow solid, m. p. 68–100°. Recrystallization from acetone gave 10.9 g. (45.8%) of nearly colorless solid, m. p. 120.0–123.0°. Recrystallization of 6.8 g. from acetone (cooling in ice-salt-bath) gave 5.0 g. of colorless solid, m. p. 124.2–125.0°.

Anal. Calcd. for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.10; H, 6.13.

The **2,4-dinitrophenylhydrazone** was dark red, m. p. 220.5–222.0° dec.

Anal. Calcd. for $C_{25}H_{24}N_4O_8$: C, 59.04; H, 4.76. Found: C, 59.20; H, 5.03.

This compound was also prepared by the following method in somewhat better yield. To a suspension of 10.4 g. (0.03 mole) of diveratryl-propionic acid (IV) in 30 ml. of anhydrous benzene were added 7.3 g. (0.035 mole) of phosphorus pentachloride in small portions with swirling cooling in an ice bath. The flask was fitted with a calcium chloride drying tube which was removed only during the addition of reagents. The mixture was warmed on the steam-bath for a few minutes to complete the reaction, and then the solution was cooled in an ice-bath until the benzene showed signs of beginning to crystallize. A solution of 8.2 ml. (18.3 g., 0.07 mole) of anhydrous stannic chloride in 8 ml. of anhydrous benzene was added at once with swirling, giving a deep green colored complex.

After five minutes, the complex was decomposed with cracked ice followed by 25 ml. of concentrated hydrochloric acid, and the product was extracted with benzene. Working up the benzene extracts in the usual manner left 9.7 g. of oil which solidified on seeding and cooling. Recrystallization from acetone (20 ml.) afforded 6.9 g. (70%) of colorless product, m. p. 122.5–127°. Recrystallization again gave 4.7 g., m. p. 124.2–126.8°, which was identical to the compound prepared by means of phosphorus oxychloride.

Degradation Reactions. Oxidation of 5,6-Dimethoxy-3-(3,4-dimethoxyphenyl)-1-indanone

4,5-Dimethoxy-2-(3,4-dimethoxybenzoyl)-benzoic Acid (VI).—A solution of 2.85 g. of the indanone (V) in 40 ml. of glacial acetic acid, cooled in an ice-bath, was treated with 3.5 g. of chromium trioxide and a drop of sulfuric acid. The mixture was allowed to come to room temperature gradually and allowed to stand a total of 24 hours. The mixture was poured over ice, the insoluble material filtered off, extracted with 50 ml. of 10% sodium carbonate solution, and filtered. Acidification of the filtrate gave 0.45 g. of tan solid, m. p. 210–219°. Recrystallization from ethanol with decolorization yielded 0.13 g. of colorless prisms, m. p. 223.6–225.2° (reported in the literature,[10] m. p. 222–223°).

Anal. Calcd. for $C_{18}H_{18}O_7$: C, 62.43; H, 5.24; neut. equiv., 346.3. Found: C, 62.28; H, 5.41; neut. equiv., 353.3.

2,3,6,7-Tetramethoxyanthraquinone (VII).—A solution of 0.4 g. of veratroyl-veratric acid (VI) in 20 ml. of concentrated sulfuric acid was warmed for thirty minutes in a boiling water-bath giving a dark green solution. Then the solution was poured into 500 ml. of ice-cold water and the yellow precipitate filtered off, dried and recrystallized from 200 ml. of glacial acetic acid. The fine yellow needles, 0.25 g., m. p. 330–340°, sublimed without decomposition (uncor.) gave an orange vat with sodium hydrosulfite. This compound has been reported previously, m. p. 346°,[11] subliming without dec.

5,6-Dimethoxy-1-(3,4-dimethoxyphenyl)-indene (VIII).—Four grams (0.0122 mole) of indanone derivative (V) was placed in a 100-ml. flask with 10 g. of aluminum isopropoxide and 50 ml. of anhydrous isopropyl alcohol, and the flask attached to a special condenser which allows slow distillation of isopropyl alcohol. Slow distillation was continued for seven hours with losses of alcohol being replaced. At the end of six hours no acetone could be detected. The solution was poured over ice, acidified to congo-red paper with hydrochloric acid, and extracted with three 50-ml. portions of ether. The ether extracts gave 3.7 g. of yellow oil. Crystallization from 5 ml. of methanol afforded 1.3 g. (34.1%) of a crystalline product, m. p. 122–126°, which depressed the melting point of the starting material to 105–113°. Repeated recrystallization from methanol yielded colorless leaflets, m. p. 126.0–127.5°.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.05; H, 6.46. Found: C, 72.76; H, 6.48.

5,6-Dimethoxy-1-(3,4-dimethoxyphenyl)-indan (IX).—Twelve grams of 30-mesh zinc was cleaned with concentrated sulfuric acid at 100° for fifteen minutes. The zinc was washed with water and then amalgamated with 1.2 g. of mercuric chloride in 20 ml. of water and 0.5 ml. of concentrated hydrochloric acid. The liquid was decanted after shaking for five minutes, and to the zinc were added 7.5 ml. of water and 17.5 ml. of concentrated hydrochloric acid. Then 10 ml. of toluene and 4.0 g. (0.0122 mole) of the indanone (V) were added and the mixture was refluxed for twenty-eight hours, 5-ml. portions of concentrated hydrochloric acid being added after four, eight, twelve and twenty-four hours.

The toluene layer was separated and the aqueous layer extracted with ether. The ether extracts and toluene layer combined were washed with water, and dried. Removal of the solvents left a yellow oil which solidified on cooling and scratching to 3.3 g. (86%) of a colorless solid, m. p. 79–83°. Repeated recrystallization from methanol and ethanol gave clusters of colorless needles, m. p. 85.0–86.8°.

Anal. Calcd. for $C_{19}H_{22}O_4$: C, 72.58; H, 7.04. Found: C, 71.92; H, 6.95.

Attempted Syntheses of 5,6-Dimethoxy-3-(3,4-dimethoxyphenyl)-1-indenone (I)

(A) Attempted Cyclizations of Diveratryl-acrylic Acid (III).—(1) Treatment of 3.44 g. of β,β-bis-(3,4-dimethoxyphenyl)-acrylic acid with 3 ml. of thionyl chloride at room temperature for several minutes and then gentle warming for five minutes and pouring on ice, followed by extraction with 10% sodium carbonate solution, gave 1.3 g. of red solid, m. p. 198–202°. Recrystallization from glacial acetic acid and toluene yielded deep red prisms, m. p. 220.6–221.4°. This compound gave positive tests for halogen and for unsaturation. It analyzed as a monochloro derivative of the indone (I).

Anal. Calcd. for $C_{19}H_{17}ClO_5$: C, 63.25; H, 4.75; Cl, 9.83. Found: C, 63.22; H, 4.84 (average of four analyses all within 0.2 of calculated values); Cl, 9.90.

The red-brown 2,4-dinitrophenylhydrazone was recrystallized from glacial acetic acid, m. p. 273.2–273.8°, dec.

Anal. Calcd. for $C_{25}H_{21}ClN_4O_8$: C, 55.51; H, 3.91. Found: C, 55.80; H, 4.14.

(2) A solution of 2.7 g. of diveratryl-acrylic acid (III) in 8 g. of phosphorus oxychloride was allowed to stand at room temperature for five minutes. The red solution, upon working up in the usual manner, gave 2.5 g. of starting material.

A solution of 2.5 g. of diveratryl-acrylic acid (III) in 8 g. of phosphorus oxychloride was boiled for ten minutes, giving a deep purple solution, which when poured over ice gave a brilliant purple solid, m. p. 163–180° dec., with prior sintering. This product was found to be soluble in glacial acetic acid, alcohol, benzene, acetone, dioxane in the cold, but only partially soluble in ether, and insoluble in petroleum ether. The purple product, after washing well with water and drying, when treated with warm 2% aqueous-alcoholic potassium hydroxide, lost its purple color, giving a red-brown solid. The latter was filtered off, and the filtrate found to give a positive test for chloride ion with aqueous silver nitrate, after acidification with nitric acid. The red-brown product was slightly purified by solution in benzene, filtration and precipitation with petroleum ether, giving a light tan product. The latter reformed the purple material upon treatment with dilute or concentrated hydrochloric acid. The tan material with acetyl chloride or bromine in carbon tetrachloride solution gave a deep purple solution. These products have not been identified further, but attempts are being made to obtain them pure for analysis.

Three grams of diveratryl-acrylic acid in 9 ml. of phosphorus oxychloride at the boiling point for one minute gave a purple solution, which, when poured over ice and filtered, gave a yellow precipitate, 2.9 g., insoluble in 5% sodium hydroxide solution, which did not give a 2,4-dinitrophenylhydrazone.

(3) To a suspension of 10.3 g. (0.03 mole) of diveratryl-acrylic acid in 100 ml. of anhydrous benzene was added 7.3 g. (0.035 mole) of phosphorus pentachloride with external cooling in an ice-bath. No reaction occurred so the mixture was warmed on the steam-bath for a few minutes. The solution then was cooled in the ice bath and 18.3 g. (0.07 mole) of anhydrous stannic chloride in 8 ml. of benzene was added at once. After five minutes, the deep blue complex was decomposed with cracked ice and 25 ml. of concentrated hydrochloric acid. An emulsion formed, and more benzene was required to extract the product; however, a large amount of colorless solid was insoluble, and was found to be partially inorganic, probably undecomposed complex. The benzene layer, upon separation, drying, and evaporation of the solvent, left 6.5 g. of orange colored solid. Methanol extracted the colored fraction leaving 3.8 g. of tan solid. This was insoluble in base, m. p. 186–216°. Recrystallization of 1.0 g. of the latter material from glacial acetic acid three times gave red prisms, m. p. 218–220° dec., which were identical (mixed melting point) with the product obtained by the action of thionyl chloride on diveratrylacrylic acid.

(B) **Attempted Dehydrogenations of 5,6-Dimethoxy-3-(3,4-dimethoxyphenyl)-1-indanone (V).**—A mixture of 2.0 g. of the indanone (V), 1.0 g. of 5% palladium–charcoal catalyst and 10 ml. of butyl cellosolve was heated for three hours at 135°; then the temperature was raised gradually to 155° during three hours; and, finally, the temperature was raised to 165° for an hour. The catalyst was filtered off, and the solution was diluted with water. Overnight standing gave fine, colorless needles, 1.6 g., which proved to be starting material.

A second attempt was made using α-methylnaphthalene (b. p. 241°) as the solvent. Five grams of indanone in 15 ml. of solvent was refluxed vigorously with 2.0 g. of 5% palladium–charcoal catalyst for five hours. The catalyst then was filtered off and washed with ether, giving a red solution. Removal of the solvents under diminished pressure gave 14 g. of recovered solvent (methylnaphthalene) and 4.8 g. of red viscous material. Methanol dissolved the red material, which apparently was present in small amount, leaving a nearly colorless solid, m. p. 110–120°, which gave a dark red 2,4-dinitrophenylhydrazone, m. p. 210–220°. The methanol solution gave a dark red solid which gave a 2,4-dinitrophenylhydrazone identical with that above.

(C) **Attempted Synthesis of 5,6-Dimethoxy-3-(3,4-dimethoxyphenyl)-1-indenone (I) by Bromination–Dehydrobromination Reactions.**—(1) To a solution of 6.57 g. (0.02 mole) of 5,6-dimethoxy-3-(3,4-dimethoxyphenyl)-1-indanone (V) in 25 ml. of glacial acetic acid were added 1.66 g. of fused sodium acetate, followed by 3.2 g. (0.02 mole) of bromine in 25 ml. of acetic acid dropwise during thirty minutes. After ten minutes longer under strong illumination, the mixture was poured into 500 ml. of cold water, giving a tan precipitate, 8.2 g., m. p. 184–193°. Boiling 0.1 g. in pyridine for fifteen minutes gave an orange colored solution, which on pouring into water gave a tan solid, m. p. 190–194°, which contained bromine. Eight grams of the product recrystallized from 75 ml. of acetic acid and 150 ml. of ethanol gave 6.4 g. of colorless prisms, m. p. 188–194.6°. A second recrystallization from ethanol gave colorless prisms, m. p. 192.6–195.6°. This compound gave a red 2,4-dinitrophenylhydrazone.

Bromination of the indanone (V) in acetic acid in the absence of sodium acetate, and in direct sunlight, caused evolution of hydrogen bromide and formation of the same compound as obtained above, m. p. 191–194.6°. This compound analyzed as a monobromo derivative of the indanone, and showed absence of unsaturation. The bromine was not hydrolyzable by means of sodium methoxide, alcoholic silver nitrate or alcoholic potassium hydroxide, and, therefore, is believed to be located on the 3-phenyl nucleus.

Anal. Calcd. for $C_{19}H_{19}BrO_5$: Br, 19.62. Found: Br, 20.0.

Oxidation of 1.0 g. of the above compound by means of 4.0 g. of potassium permanganate in 80 ml. of water and 0.2 g. of sodium hydroxide, at the boiling point for four hours, gave a colorless filtrate upon removal of the manganese dioxide. The solution was extracted with ether giving a small amount of oil which was partially soluble in sodium bicarbonate solution. Upon filtration and acidification, 0.05 g. of acid was obtained, m. p. 90–125°, which on sodium fusion showed the presence of bromine. Oxidation of the monobromoindanone by means of chromium trioxide in the cold gave only a very small amount of acid, insufficient for purposes of identification.

(2) Four grams (0.0122 mole) of indanone (V) in 50 ml. of carbon tetrachloride and 2.17 g. (0.0122 mole) of N-bromosuccinimide were refluxed for thirty minutes, giving a dark red solution, and evolution of hydrogen bromide. The insoluble succinimide was filtered off, and the filtrate refluxed for fifteen minutes with 25 ml. of dry pyridine. There was no evident change. The solvents were removed giving 4.0 g. of solid, m. p. 125–175°. Extraction with hot methanol gave 2.8 g. of colorless solid, insoluble, m. p. 185–193°, identical with the compound obtained by direct bromination. The fraction soluble in methanol, 0.7 g., m. p. 78–105°, was largely impure starting material.

When a slight excess of N-bromosuccinimide was used, or with benzoyl peroxide added, another compound was isolated, m. p. 194–200° dec., in low yield. Recrystallization several times from glacial acetic acid gave dark red prisms, m. p. 222.5–224°, which analyzed as a monobromo derivative of the indene (I).

Anal. Calcd. for $C_{19}H_{17}BrO_5$: C, 56.32; H, 4.22. Found: C, 56.38; H, 4.48.

Summary

5,6-Dimethoxy-3-(3,4-dimethoxyphenyl)-1-indanone and two related compounds have been prepared for study as possible insecticidal agents. The attempted synthesis of 5,6-dimethoxy-3-(3,4-dimethoxyphenyl)-1-indenone by several methods has been described. This work has produced two

mono-halo derivatives of the indenone and a monobromo indanone of unknown structure.

Two new compounds of possible value as phytotoxic or insecticidal agents, β,β-bis-(3,4-dimethoxyphenyl)-acrylic acid and β,β-bis-(3,4-dimethoxyphenyl)-propionic acid, have also been prepared.

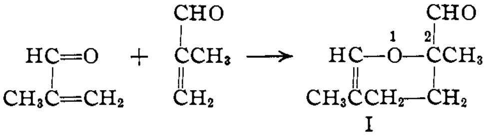
BETHLEHEM, PENNA. RECEIVED JUNE 29, 1949

[CONTRIBUTION FROM BATTELLE MEMORIAL INSTITUTE]

Methacrylaldehyde Dimer. Derivatives Obtained through the Cannizzaro Reaction[1]

BY GEORGE G. STONER[2] AND JUSTIN S. MCNULTY

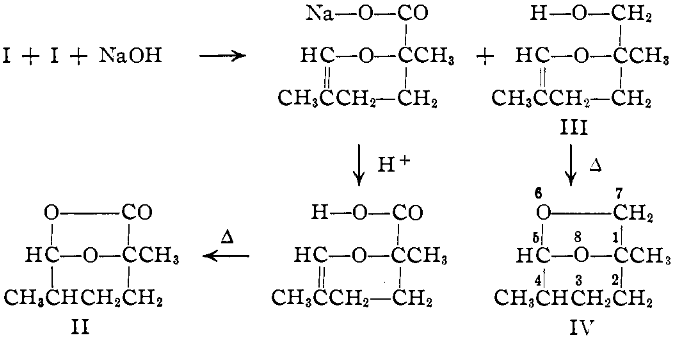
In common with other α,β-unsaturated aldehydes[3a,b,c] and ketones,[3b,d,e] methacrylaldehyde (methylpropenal, methacrolein) undergoes a Diels–Alder type[4] of reaction with itself to produce a dimer[5] (I), 3,4-dihydro-2,5-dimethyl-1,2H-pyran-2-carboxaldehyde.

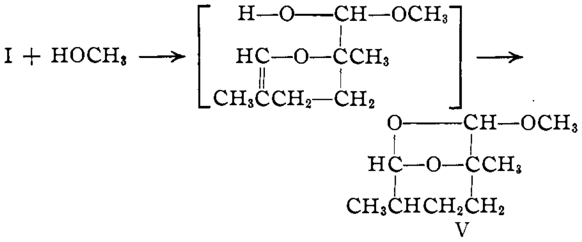


In storage, methacrylaldehyde containing hydroquinone dimerized 29% in one year at 26–27°. After freshly distilled methacrylaldehyde had been refluxed (68–72°) for two days with 1% of its weight of hydroquinone, the conversion into dimer was about 10%. Under autogenous pressure at 140–150°, 89% of the methacrylaldehyde dimerized in forty-four hours. The dimer had a tendency to retard macropolymerization, possibly because of allylically activated hydrogen atoms in the 4-position and in the 5-methyl group, thus terminating chains. Practically no tendency was shown by the dimer to form a trimer of methacrylaldehyde by participating as a "dienophile" (more strictly, as an enalophile). Substitution in the 5-position presumably suppressed such a tendency. (Acrolein dimer readily reacted with acrolein to form a series of low polymers.[3a,c]) Furthermore, dimerization of methacrylaldehyde probably was enhanced by a favorable polarizing influence of its methyl group.[6]

Methacrylaldehyde dimer is an aldehyde which has no α-hydrogen. Accordingly, the Cannizzaro reaction was clean-cut.[5b] The expected unsaturated acid[5b] and alcohol[5a,b] (III) isomerized readily into a saturated lactone (II) and acetal (IV), respectively. Such reactions are characteristic of substituted vinyl-type ethers such as 3,4-dihydro-1,2H-pyrans.

A saturated methyl acetal (V), stable to hot, 20% sodium hydroxide solution, was formed at room temperature from a solution of the dimer, methanol and calcium chloride. It did not represent reaction solely of the aldehyde function, nor solely of the vinyl-type ether grouping (as did acetals formed in the presence of more acidic catalysts from dihydropyran[7] and from butenone dimer).[3d] Moreover, it was not the simple combination of both of these types (see data in Table I), although both functional groups were involved. Probably the intermediate was an unsaturated hemiacetal.





Experimental Details

Methacrylaldehyde Dimer (I).—The following conditions were the best found in a series of such dimerizations

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(1) This work was sponsored by the Minnesota Mining & Manufacturing Company, St. Paul 6, Minn.

(2) Mailing address: 129 Grant Street, Easton, Pa.

(3) (a) K. Alder and E. Rüden, *Ber.*, **74B**, 920–926 (1941); (b) K. Alder, H. Offermanns and E. Rüden, *ibid.*, **74B**, 926–929 (1941); (c) S. M. Sherlin, A. Ya. Berlin, T. A. Serebrennikova and F. E. Rabinovich, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 22–34 (1938); (d) K. Alder, H. Offermanns and E. Rüden, *Ber.*, **74B**, 905–920 (1941); and (e) C. Mannich, *ibid.*, **74B**, 554–570 (1941).

(4) (a) J. A. Norton, *Chem. Revs.*, **31**, 494 (1942); and (b) compare E. C. Coyner and W. S. Hillman, THIS JOURNAL, **71**, 324–326 (1949).

(5) (a) N. M. Bortnick, U. S. Patent 2,473,497 (1949); (b) R. R. Whetstone, U. S. Patent 2,479,283 (1949); and (c) also compare R. R. Whetstone, U. S. Patent 2,479,284 (1949).

(6) For instance, T. L. Gresham and T. R. Steadman, THIS JOURNAL, **71**, 737–738 (1949), reported that 2-methyl-1,3-pentadiene underwent a Diels–Alder type of reaction with formaldehyde, whereas 1,3-butadiene did not react in that way with formaldehyde.

(7) G. F. Woods and D. N. Kramer, *ibid.*, **69**, 2246 (1947).