Summary

1. 3,3′-Dichlorodiphenic acid (believed to be the first 3,3′-disubstituted diphenic acid) has been prepared by a short synthesis from commercial intermediates.

2. On heating at 360° this acid loses one mole of carbon dioxide and yields approximately equal amounts of 1,8- and 1,6-dichlorofluorenones.

3. However, on heating 3,3′-dichlorodiphenic *anhydride* at 310° a quantitative yield of 1,8-dichlorofluorenone is obtained; on heating 1,6-dichlorofluorenone-5-carboxylic acid (from the action of concentrated sulfuric acid at 125° upon 3,3′-dichlorodiphenic acid) at 350° there is obtained less smoothly only 1,6-dichlorofluorenone.

4. 3,6-Dichlorofluorenone is obtained by heating 5,5′-dichlorodiphenic anhydride at 400°.

5. In the course of this work the following new compounds have been prepared and characterized: 3,3′-dichlorodiphenic acid and its anhydride; 1,6-dichlorofluorenone-5-carboxylic acid and its acid chloride and amide; 3,3′-dichlorobiphenyl-2-carboxylic acid; 1,8-dichlorofluorenone and its oxime; 1,6-dichlorofluorenone and its oxime; 3,6-dichlorofluorenone and its oxime.

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The Action of Phosphorus Pentachloride on 1,3-Dioxoindane[1]

BY W. H. HUNTER AND ROSCOE E. JACKMAN

This paper describes the separation and characterization of 1,1,3-trichloroindene, and the previously unreported 1,1,3,3-tetrachloroindane, and 1,1-dichloro-3-oxoindane isolated from the products of the reaction between phosphorus pentachloride and 1,3-dioxoindane. 1,1,3,3-Tetrachloroindane (II) results in moderate yields from the normal interaction of the 1,3 diketone (I) with phosphorus pentachloride.[2] In addition, 1,1,3-trichloroindene (III) is formed in only slightly smaller amounts, together with a small proportion of 1,1-dichloro-3-oxoindane (IV). At least two other chlorine containing condensation products and a lachrymatory oil also result, but these were not identified.

The 1,1,3-trichloroindene (III) may result from either (a) the action of phosphorus pentachloride on the enol form of (I) or (IV) or (b) by the loss of hydrogen chloride from (II). The formation of 1,1-dichloro-3-oxoindane

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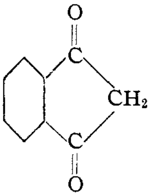
[1] This paper was prepared from a portion of the thesis of Roscoe E. Jackman presented to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July, 1929. The manuscript was written by the junior author after the death of Dr. Hunter in 1931.—L. I. SMITH.

[2] Wislicenus, *Ann.*, **252**, 72 (1889).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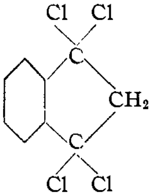
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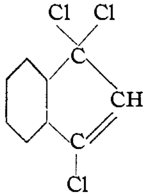
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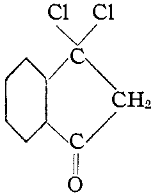
IV

(IV) very probably takes place in the expected manner, but hydrolysis of (III) during the separations employed must also be considered as a possible mode of formation since 1-oxo-2,3-dichloroindene[3] and 1-oxo-3-bromoindene[4] are by no means difficult to hydrolyze to 1,3-dioxo-2-chloroindane and 1,3-dioxoindane (I).

Experimental Part

1,3-Dioxoindane.—1,3-Dioxoindane was prepared according to the procedure of Kauffmann.[5] Improved quality and yields were obtained by the following modification of the sulfuric acid treatment and subsequent purification.

Eighteen grams of sodium derivative of 2-carbethoxy-1,3-dioxoindane was dissolved in 900 cc. of water and brought to 70°; 100 cc. of 20% sulfuric acid, also at 70°, was then stirred in with *vigorous* agitation, keeping the liberated yellow oil in fine suspension until decomposition was complete, as indicated by the fading of the bright yellow color.

The mixture was then quickly chilled in an ice–salt bath, the 1,3-dioxoindane filtered and washed with ice water. It was then dissolved in 15 cc. of chloroform, dried with anhydrous sodium sulfate and decolorized with norite. Pure white needles were then obtained by adding 150 cc. of low-boiling gasoline. After chilling and filtering, the crystals were placed in a desiccator over paraffin; yield 7–8 g., 80–90%; m. p. 129–131° with decomposition.[6]

Reaction between 1,3-Dioxoindane and Phosphorus Pentachloride.—Ten grams of 1,3-dioxoindane and 43 g. (3 moles) of pulverized phosphorus pentachloride were intimately mixed in a 250-cc. wide-mouthed flask with a stopper bearing an 8 mm. × 15 cm. length of glass tubing. The flask was then immersed in a water-bath at 60° and continuously shaken for one-half hour.

The velocity of the reaction was slow below 40°, but it went to completion within a few minutes at 60°. Above 60° the reaction was very vigorous, often approaching explosive violence. Since higher temperatures also result in excessive self-condensation of 1,3-dioxoindane due to phosphorus oxychloride, this reaction should only be carried out with small amounts of materials.

Separations of the Products of the Reaction.—After decomposing the excess phosphorus pentachloride by the cautious addition of ice, the mixture was gradually added with vigorous agitation to 500 cc. of ice water, and allowed to stand an hour.

The pasty red mass was then agitated with three successive portions of ice water, and transferred to a 50-cc. dropping funnel, the stem of which dipped below the water surface of an actively boiling steam distillation system. In this manner it was rapidly steam-distilled in small portions. The distillate contained 9–10 g. of a lachrymatory oil, which solidified on chilling.

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[3] Roser, *Ann.*, **247**, 129 (1888).

[4] Schlossberg, *Ber.*, **33**, 2425 (1900).

[5] Kauffmann, *ibid.*, **30**, 385 (1897); Wislicenus, *ibid.*, **20**, 593 (1887); *Ann.*, **246**, 349 (1888); Wislicenus and Kötzle, *ibid.*, **252**, 72 (1889); **252**, 80 (1889).

[6] Schmidt, *Ber.*, **33**, 546 (1900).

The direct separation of this mixture of substances was difficult. The components separated as oils from water soluble solvents, and were miscible in all proportions with the usual non-aqueous solvents. Vacuum distillation at 25 mm. resulted in extensive decomposition, although a partial separation could be effected by sublimation.

Steam distillation provided the most rapid separation of the chlorinated indanes from the other substances present, and the losses by hydrolysis are no greater than those resulting from other methods of separation.

A preliminary separation of the steam distillate into a mixture of 1,1,3,3-tetrachloroindane and 1,1,3-trichloroindene on one hand, and an impure fraction of 1,1-dichloro-3-oxoindane on the other, was made as described in the following typical experiment.

Ten grams of the mixture was dissolved in the minimum amount of glacial acetic acid at 100–110°, after which the flask was set aside to cool. The crystals were filtered, washed, first with 80% acetic acid and then water, and dried. The mother liquor was then brought to 70°, the washings added and sufficient hot water stirred in (5–25 cc.), to produce a faint turbidity at 70°. This turbidity was discharged by means of a few drops of glacial acetic acid, and the solution quickly chilled. The cold mixture was filtered when or if yellow material was deposited, and any yellow material was washed from the filtered precipitate with 50% acetic acid followed by water. This second crop of white plates and needles was combined with the first, while the yellow filtrates and washings were further diluted to one liter with water and cooled.

The yellow needles were filtered and washed with water and then dried in a desiccator. The combined filtrates and washings were cooled and further diluted by adding 100-cc. portions of water until an oil appeared. This oil later solidified, after which the yellow solid was filtered and washed as before, and combined with the first crop of yellow solid; yield, 5–6 g. of white fractions and 1–3 g. of yellow fractions.

Repeated fractional crystallization of the combined colorless fractions from acetic acid or alcohol yielded some pure 1,1,3,3-tetrachloroindane (usually present in larger amounts) and an equimolecular mixture of 1,1,3,3-tetrachloroindane and 1,1,3-trichloroindene, m. p. 58–59°, but a complete separation by recrystallization alone was impossible.

Mol. wt. in benzene. Calcd. 237. Found: 241, 244. *Anal.* Calcd.: Cl, 52.22. Found: Cl, 51.11. Melting point of synthetic equimolecular mixture, 56–59°.

The following procedure based on fractional solution and recrystallization from absolute alcohol effected the separation of this mixture into its components.

Large crystals were first produced by preliminary recrystallization of 5.0 g. of mixture from 25 cc. of hot glacial acetic acid. The large crystals were then transferred to a 500-cc. beaker, covered with cold absolute alcohol (5–10 cc.), and allowed to stand for a short time (one to three minutes) before decanting the extract. This operation was repeated until the plates were comparatively free from needles.

The plates remaining were then repeatedly recrystallized (two to five times) from a minimum volume of hot alcohol (about 50 cc.), until the melting point reached that of pure 1,1,3,3-tetrachloroindane, 104–105.5°; yield, 1–2 g.

The combined alcoholic extracts were now diluted with water until turbid, cleared up with a few drops of absolute alcohol, and chilled. The crystals, mostly needles with a few plates, were then recrystallized from absolute alcohol until the melting point reached that of pure 1,1,3-trichloroindene, 77–78°; yield, 0.5–1.5 g.

All of the mother liquors, washings and intermediate fractions were then united, diluted with water to precipitation, chilled and more water added from time to time until crystallization was complete. The above described resolution was then repeated with this material.

1,1,3,3-Tetrachloroindane.—1,1,3,3-Tetrachloroindane formed colorless irregular plates with mild camphor-like odor, subliming readily; m. p. 104–105.5°.

Anal. Calcd. for $C_9H_6Cl_4$: Cl, 55.44. Found: 55.52, 55.51.

It is slowly hydrolyzed in contact with water or moist solvents, producing first a yellow substance and finally a deep red substance containing halogen and melting at 182–183°. In cold glacial acetic acid solution the indane reacts slowly with bromine to produce a colorless solid melting above 251°. The reaction with aqueous alkalies leads to a deep red tar. However, it reacts smoothly in the cold with one mole of sodium ethylate or sodium hydroxide in absolute alcohol, to produce 1,1,3-trichloroindene.

1,1,3-Trichloroindene.[7]—This substance is best prepared directly from the mixture of the indene and indane. 5.0 g. of mixture was dissolved in 100 cc. of warm absolute alcohol, and treated with an alcoholic solution containing the theoretical quantity of sodium hydroxide (0.8 g.) assuming 100% 1,1,3,3-tetrachloroindane. After standing for about one-half hour (less if color developed in the solution), the solution was decanted from the sodium chloride, diluted with sufficient water to produce turbidity, and chilled. The colorless needles were recrystallized from hot alcohol, m. p. 77–78°; yield about 3.0 g.

1,1,3-Trichloroindene crystallizes from alcohol or acetic acid, in colorless sublimable needles of naphthalene-like odor, m. p. 77–78°. An equimolecular mixture of 1,1,3-trichloroindene and 1,1,3,3-tetrachloroindane melts sharply at 58–59°, and recrystallizes unchanged from the usual solvents. Other mixtures tend to separate as oils from hot concentrated solutions.

Anal. Calcd. for $C_9H_5Cl_3$: Cl, 48.48. Found: Cl, 48.34.

It is hydrolyzed under the same conditions as is 1,1,3,3-tetrachloroindane, and the products are very similar. It reacts with one mole of bromine in glacial acetic acid, forming a white leafy compound, m. p. 92–94°.

1,1-Dichloro-3-oxoindane.—Three grams of the yellow solid from the preliminary separations product was extracted with 30 cc. of 50% alcohol at room temperature; 30 cc. of water was then stirred into this extract and the mixture chilled. The yellow precipitate was then recrystallized from a minimum of hot alcohol (10–15 cc.), until the long silky needles melted at 85–86°; yield 0.5–1.0 g.

1,1-Dichloro-3-oxoindane is very soluble in organic liquids, with the exception of low-boiling petroleum fractions, in which the solubility is moderate. It is sparingly soluble in water, and crystallizes well by dilution of its alcoholic or acetic acid solutions with water. Its mixtures with 1,1,3,3-tetrachloroindane and 1,1,3-trichloroindene tend to separate as oils from hot concentrated solutions in alcohol or acetic acid. The substance has an odor very much like that of quinone.

Anal. Calcd. for $C_9H_6OCl_2$: Cl, 35.29. Found: Cl, 36.18, 35.49%.

It reacted very slowly with bromine in light, producing a white compound decomposing at 110–114°. It forms a yellow oxime, which after recrystallization from 50% alcohol sintered at 178–182° and melted with decomposition at 190–191°. This oxime dissolves in dilute alkali with a yellow green color, and is apparently precipitated unchanged by dilute acid.

Anal. Calcd. for $C_9H_7ONCl_2$: Cl, 32.84. Found: Cl, 33.03.

Summary

1,1,3,3-Tetrachloroindane, 1,1,3-trichloroindene, and 1,1-dichloro-3-oxoindane have been isolated from the mixture produced when phosphorus pentachloride and 1,3-dioxoindane react, and have been characterized. A qualitative procedure has been devised for isolating them from their ternary mixtures.

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[7] Straus, Kollek and Heyn, *Ber.*, **63B**, 1885 (1930).