

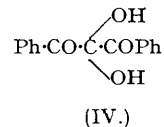
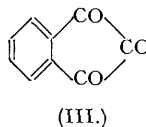
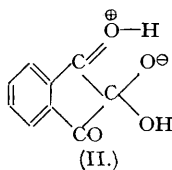
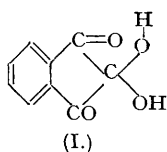
24. *Studies on Indene Derivatives. Part II. Triketohydrindene.*

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Triketohydrindene has been prepared by the action of thionyl chloride on triketohydrindene hydrate (ninhydrin). An inner-salt formula (II) for ninhydrin is advanced and some new reactions are mentioned.

TRIKETOHYDRINDENE (III) has not hitherto been described. It can be prepared by heating its hydrate (I) (ninhydrin) with thionyl chloride (yield, quantitative) or in a vacuum, but is obtained pure with difficulty by the latter method. When the hydrate is heated in the presence of oxygen, phthalic anhydride is formed. Triketohydrindene forms dark red needles, which melt to a bluish-green liquid; on cooling, the red crystals are re-formed. The colour of solutions of triketohydrindene depends on the solvent. When the blue-green solution of triketohydrindene in benzene is shaken with water, decoloration occurs almost instantly, owing to the formation of the colourless hydrate (I). This hydrate is readily soluble in cold water, whereas the hydrate

of diphenyl triketone (IV) is only very sparingly soluble. In order to explain the ready solubility of ninhydrin in water and its remarkable thermal stability we allocate to it the inner-salt formula (II). The possibility of resonance between the structures (I) and (II) should be stressed.



EXPERIMENTAL.

Preparation of Triketohydrindene.—(1) *By the action of thionyl chloride on ninhydrin.* Freshly distilled thionyl chloride (50 c.c.) was heated for about 40 minutes with ninhydrin (0.5 g.) recently crystallised from water. The reaction vessel was connected by means of a ground glass joint to a condenser fitted with a receiver connected to a filter-pump. The apparatus was exhausted, and the vessel heated in a bath at 60–70°. The ninhydrin dissolved, forming a solution having the colour of malachite-green; as the solution became more concentrated (owing to evaporation of the thionyl chloride), reddish-violet crystals of triketohydrindene separated. After about 45 minutes, all the thionyl chloride had distilled off and the vessel was placed in a vacuum desiccator containing sodium hydroxide in order to remove the last traces of thionyl chloride. The triketohydrindene (yield, quantitative) melted at 255°, forming a green liquid (Found : C, 67.7; H, 2.5. Calc. for $C_9H_4O_3$: C, 67.5; H, 2.5%).

(2) *By the thermal decomposition of ninhydrin.* Ninhydrin was heated in a vacuum in a bath at about 190°. It turned red and a sublimate was formed consisting of red needles and colourless material. The red crystals were separated by hand and washed with benzene; they melted at 255°, forming a green liquid, and were identical with the crystals obtained in (1).

Physical Properties of Triketohydrindene.—Triketohydrindene sublimes in a vacuum, forming violet-red crystals. It dissolves readily in benzonitrile, forming a violet-red solution, but only with difficulty in cold acetic anhydride, hot benzene, and nitrobenzene at 100°, bluish-green solutions being formed. It is practically insoluble in carbon tetrachloride and light petroleum (b. p. 50–60°). The solution of triketohydrindene in glacial acetic acid is blue-green when hot and practically colourless when cold, probably owing to the formation of a dissociable addition compound of acetic acid with the second carbonyl group of triketohydrindene. Triketohydrindene dissolves in concentrated sulphuric acid, forming a violet solution. Fused triketohydrindene (glass, quartz, or platinum vessel) has a very intense green colour. This occurs even when the substance is heated in a vacuum, showing that the production of the green colour is not due to atmospheric oxidation.

Action of Water on Triketohydrindene.—Triketohydrindene was heated for about 1 minute with a small quantity of water in the absence of direct sunlight. When the hot solution was filtered, evaporated somewhat, and allowed to cool, colourless crystals of ninhydrin, m. p. 139°, undepressed by an authentic specimen, separated in practically quantitative yield (Found : C, 60.2; H, 3.5. Calc. for $C_9H_6O_4$: C, 60.7; H, 3.3%).

Physical and Chemical Properties of Ninhydrin.—When ninhydrin is heated in benzene, a bluish-green solution is gradually produced owing to the formation of triketohydrindene. A colourless aqueous solution of ninhydrin, freshly prepared from a pure sample and protected from light, does not liberate iodine from aqueous potassium iodide, even after acidification. The colourless crystals of ninhydrin turn reddish when exposed to sunlight. Where these crystals are treated with hot water, and aqueous potassium iodide added to the filtrate, iodine is liberated after acidification.

Action of Oxygen on Ninhydrin.—Ninhydrin was heated in a vessel at 190° (bath temperature) in a current of oxygen. A sublimate of phthalic anhydride was obtained; after purification this had m. p. 129°, undepressed by an authentic specimen. The fluorescein test for phthalic anhydride was positive.