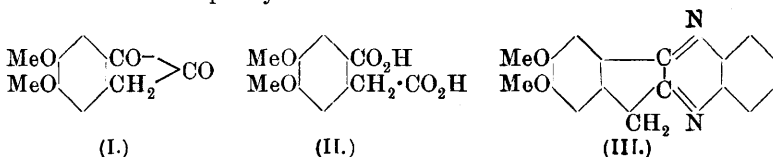


CCXXIV.—1:2-Diketo-5:6-dimethoxyhydrindene.

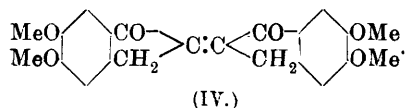
By WILLIAM HENRY PERKIN, jun., WALTER MORRELL ROBERTS, and
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IN a former communication the authors (T., 1912, 101, 232) have described a convenient method of producing 1:2-diketohydrindene, namely, the hydrolysis of *isonitroso*-1-hydrindone, by means of formaldehyde and hydrochloric acid. This process has now been applied with even better results to the preparation of 1:2-diketo-5:6-dimethoxyhydrindene (I) and of 1:2-diketo-5:6-methylene-dioxyhydrindene, substances which may very probably find an application in solving the difficult problem of the synthesis of brazilin and its derivatives.

The properties of the dimethoxy-diketone are similar to those of the parent substance; thus the 2-monoxime is produced by reaction with one molecule of hydroxylamine; oxidation with hydrogen peroxide yields 2-carboxy-4:5-dimethoxyphenylacetic acid (II), whilst 5:6-dimethoxyindenoquininoxaline (III) is formed by condensation with *o*-phenylenediamine:

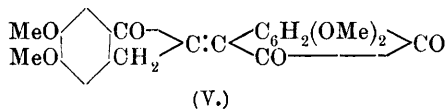


1:2-diketohydrindenes are reactive ketones which enter with ease into various condensations, and we investigated especially the condensation of 1:2-diketo-5:6-dimethoxyhydrindene with 5:6-dimethoxy-1-hydrindone, which should produce the indigotin-like substance (IV):



Equimolecular proportions of the components were dissolved in just sufficient acetic acid and warmed on the steam-bath with hydrochloric acid (half the volume of the mixture). The condensation product separated, and the liquid became filled with black, microscopic crystals, which were collected. This substance appeared to be a hydrochloride, and was changed to a dark brownish-red compound by aqueous sodium acetate. It dissolved in concentrated sulphuric acid to an intense indigo-blue solution. The compound was very sparingly soluble, and separated from pyridine solution in microscopic crystals, but no analysis that was made of it gave

satisfactory figures. Our failure to obtain this compound in a pure condition may be due to its admixture with *anhydrobis*-1:2-diketo-5:6-dimethoxyhydrindene (V), which was easily obtained by the action of piperidine on 1:2-diketo-5:6-dimethoxyhydrindene (see p. 2408):



EXPERIMENTAL.

1:2-Diketo-5:6-dimethoxyhydrindene (I).

*iso*Nitroso-5:6-dimethoxy-1-hydrindone (10 grams) (Perkin and Robinson, T., 1907, **91**, 1081) is mixed with formaldehyde (20 c.c. of 40 per cent. aqueous solution) and concentrated hydrochloric acid (5 c.c.), and the liquid heated to incipient boiling while being continually stirred. The *isonitroso*-compound passes into complete solution, and almost immediately the diketone begins to separate as a brownish-yellow, crystalline powder. After gently heating during half an hour the mixture is cooled, diluted with water, and the solid collected, washed with water, and dried at 100°. The yield is practically quantitative. The substance is best crystallised from benzene, and is obtained in golden-yellow plates melting at 187°, with previous softening at 160—165°. It is readily soluble in chloroform, but sparingly so in most organic solvents. Unlike 1:2-diketohydrindene, it may be crystallised unchanged from methyl or ethyl alcohols:

0.1271 gave 0.2984 CO₂ and 0.0579 H₂O. C=64.0; H=5.1.

C₁₁H₁₀O₄ requires C=64.1; H=4.9 per cent.

Cold sodium carbonate solution does not affect the substance, but on boiling it is gradually dissolved to a greenish-brown solution, from which, if concentrated, a green solid separates, and the unchanged diketone is obtained on acidification. With alkali hydroxide the above reaction is obtained in the cold, whilst, on boiling, the solution which is first green becomes brown and then green again. It is only from the cold solution in potassium hydroxide that the diketone can be regenerated on acidification.

Oxime (isoNitroso-5:6-dimethoxy-1-hydrindone).—This derivative is obtained when the diketone is heated with hydroxylamine hydrochloride (1½ mols.) and sodium acetate in alcoholic solution. The crystalline precipitate obtained on cooling the solution was collected and recrystallised from alcohol. The substance melted and decomposed at 235°, and its melting point was not lowered by admixture

with an equal quantity of pure *isonitroso*-5:6-dimethoxy-1-hydrindone (T., 1907, **91**, 1081). From this result we conclude that of the two carbonyl groups in 1:2-diketo-5:6-dimethoxyhydrindene, that in the β -position is the more reactive, and the more likely to enter into all kinds of condensation reactions.

5:6-Dimethoxyindenoquinoxaline (III).

1:2-Diketo-5:6-dimethoxyhydrindene (2.1 grams) and *o*-phenylenediamine (1.1 grams) were together dissolved in hot ethyl alcohol (5 c.c.). The crystalline product, obtained on cooling the solution, was collected and recrystallised from ethyl alcohol. The slender, yellow needles melt at 177—178°:

0.1196 gave 0.3200 CO₂ and 0.0543 H₂O. C=73.0; H=5.0.

C₁₇H₁₄O₂N₂ requires C=73.4; H=5.0 per cent.

This substance is rather sparingly soluble, and can be crystallised from most solvents. It dissolves in sulphuric acid to a deep violet solution, from which a bright orange sulphate separates on the addition of water, and orange salts are also formed when the quinoxaline is treated with dilute mineral acids. The ferrichloride obtained in the usual way is a brown, microcrystalline powder. The base itself exhibits a strong bluish-violet fluorescence in alcoholic or benzene solution.

Oxidation of 1:2-Diketo-5:6-dimethoxyhydrindene.

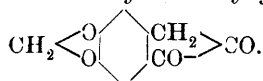
In common with other diketones, for example, benzil and phenanthraquinone, this diketohydrindene is readily attacked by hydrogen peroxide, and in this instance the oxidation is readily effected, when the substance is warmed on the steam-bath with dilute alkali and an excess of the reagent, until the yellow colour disappears. The solution was cooled, treated with hydrochloric acid, and the precipitate collected. The substance was crystallised from water, and was found to melt at 215°, and to be completely identical with 2-carboxy-4:5-dimethoxyphenylacetic acid (II), one of the oxidation products of trimethylbrazilin (Perkin, T., 1902, **81**, 1028). The substance obtained by the above oxidation of the diketone when mixed with a specimen which had been obtained by the action of phosphorous pentachloride on *isonitroso*-5:6-dimethoxy-1-hydrindone (Perkin and Robinson, T., 1907, **91**, 1082) melted at 215° (Found, C=55.1; H=5.2. C₁₁H₁₂O₆ requires C=55.0; H=5.0 per cent.).

Anhydrobis-1:2-diketo-5:6-dimethoxyhydrindene (V).

This condensation product is obtained by boiling 1:2-diketo-5:6-dimethoxyhydrindene with a few drops of piperidine in alcoholic solution or by passing hydrogen chloride into the alcoholic solution. In either case the brownish-red product was collected and purified by extraction with boiling alcohol, when a very sparingly soluble, red substance remained, which could not be crystallised, although it was distinctly crystalline to the touch and in appearance. Its solution in concentrated sulphuric acid is bright cherry red, and yields a clear yellow liquid on dilution with water:

0.1182 gave 0.2901 CO₂ and 0.0496 H₂O. C=66.9; H=4.7.

C₂₂H₁₈O₇ requires C=67.0; H=4.6 per cent.

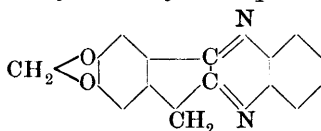
1:2-Diketo-5:6-methylenedioxyhydrindene,

This substance is prepared from *isonitroso-5:6-methylenedioxy-1-hydrindone* (Perkin and Robinson, T., 1907, **91**, 1085) by the method already described in the case of the corresponding dimethoxy-compound (p. 2406). It crystallises from benzene in golden-yellow needles, which soften at 140° and melt at 166°, and the yield obtained was more than 90 per cent. of the theoretical:

0.1379 gave 0.3175 CO₂ and 0.0384 H₂O. C=62.8; H=3.1.

C₁₀H₆O₄ requires C=63.2; H=3.2 per cent.

This substance is rather less soluble in organic solvents than the corresponding dimethoxy-derivative. Its behaviour with sodium carbonate and potassium hydroxide is similar to that described in the case of 1:2-diketodimethoxyhydrindene. With hydroxylamine hydrochloride and sodium acetate in alcoholic solution the β -monoxime was readily obtained, and melted and decomposed at 230°, either alone or mixed with a specimen of *isonitroso-5:6-methylenedioxy-1-hydrindone* which had been obtained from 5:6-methylenedioxy-1-hydrindone by the action of *isoamyl nitrite* and hydrochloric acid (*loc. cit.*, p. 1085).

5:6-Methylenedioxyindenoquinazoline,

When 1:2-diketo-5:6-methylenedioxyhydrindene (2 grams) was heated with *o*-phenylenediamine (1 gram) in alcoholic solution,

condensation occurred immediately, and 2·8 grams of the product was obtained on cooling the solution. The quinoxaline crystallises from alcohol in yellow needles melting at 204—205°, and is sparingly soluble in organic solvents in the cold:

0·1275 gave 0·3438 CO₂ and 0·0471 H₂O. C=73·5; H=4·1.

C₁₆H₁₀O₂N₂ requires C=73·3; H=3·8 per cent.

The concentrated alcoholic solution exhibits a green fluorescence, but the dilute solution in benzene shows an intense violet fluorescence. With dilute mineral acids, orange salts are produced, whilst in concentrated sulphuric and hydrochloric acids halochromism is exhibited, the solutions being bluish-violet and reddish-violet respectively, and yielding the orange salts on dilution with water. Concentrated ferric chloride acting on the solution of the base in acetic and hydrochloric acids produces the *ferrichloride*, which separates in slender, yellow needles.

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