50. *Studies on Indene Derivatives. Part IV. Synthesis of Bis-1 : 3-diketoindanylidene, and Experiments with "Ninhydrin" (Triketoindane Hydrate).*

By ALEXANDER SCHÖNBERG and RADWAN MOUBASHER.

Bis-1 : 3-*diketoindanylidene* (II) has been prepared and its properties compared with those of indigo. Bisindane-1 : 3-dione (bis-1 : 3-diketoindanyl) (III) can be prepared from "ninhydrin" (triketoindane hydrate) (IV) by the action of hydrogen sulphide. Hydrindantin is shown to be, not (VI) as hitherto supposed, but (VII).

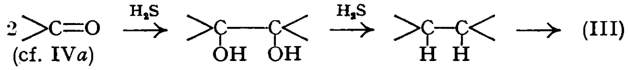
BIS-1 : 3-DIKETOINDANYLIDENE (II) had not hitherto been synthesised, earlier claims to that effect (Kaufmann, *Ber.*, 1897, **30**, 382) having been found to be erroneous (Gabriel and Leupold, *Ber.*, 1898, **31**, 1159). We obtained (II) by treating 2 : 2-dichloro-1 : 3-diketoindane (I) in xylene with copper bronze; it is red and is oxidised at 200° by atmospheric oxygen in the presence of selenium to phthalic anhydride.

The reduction products of (II) may be divided into two groups depending on whether they are derivatives of indane or of naphthacene. For instance, when (II) in amyl alcohol is treated with hydrogen sulphide at about 100°, bisindane-1 : 3-dione (III) is formed. On the other hand, the action of sodium hydrosulphite (dithionite) on (II) yields 6 : 11-dihydroxynaphthacene-5 : 12-quinone (V), and when (II) in acetic acid is treated with zinc powder (V*a*) is obtained. We believe that when derivatives of naphthacene are obtained, reduction proceeds *via* bisindane-1 : 3-dione (III), for we have found that (*a*) (V) is obtained when (III) is treated with sodium hydrosulphite, and (*b*) (V*a*) is produced when (III) in acetic acid is treated with zinc acetate. It is already known that (III) may be converted into (V), *inter alia*, by the action of pyridine (Wanag, *Ber.*, 1937, **70**, 276).

Bis-1 : 3-diketoindanylidene (II) degrades α-amino-acids in aqueous medium; *e.g.*, benzaldehyde is obtained from phenylglycine. This reaction is in agreement with the proposed constitution, as only substances containing the group $O{:}C{\cdot}[C{:}C]_n{\cdot}C{:}O$ (where *n* may be zero) bring about the Strecker degradation [Schönberg, Moubasher, and Mostafa (Mrs. A. Said), *J.*, 1948, 176].

*Comparison between Bis-*1 : 3-*diketoindanylidene* (II) *and Indigo.*—The ketone (II), which may be named carbonylindigo (compare the term thioindigo), has many properties in common with indigo; both are coloured and difficultly soluble in organic solvents, and both may be sublimed in a vacuum and can bring about the Strecker degradation of α-amino-acids; on the other hand, the reduction product of indigo (indigo-white) is colourless and can easily be oxidised to indigo, whereas the corresponding reduction product of (II), *i.e.*, (III), is deep violet and has not yet been oxidised to (II).

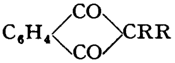
New Synthesis of Bisindane-1 : 3-*dione* (III).*—This substance has not been readily accessible, but it has now been found that it may be obtained in excellent yield from ninhydrin (IV) by the prolonged action of hydrogen sulphide. As an intermediate, hydrindantin is formed; according to Ruhemann (*J.*, 1911, **99**, 797) this is (VI), but the pinacolic formula (VII) is more probable as the formation of (III) is then easily explicable :



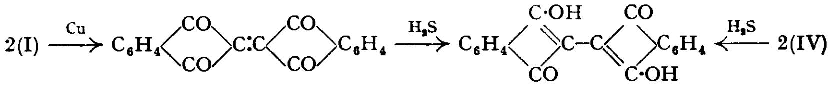
$$2{>}C{=}O \xrightarrow{H_2S} {>}\underset{OH}{C}{-}\underset{OH}{C}{<} \xrightarrow{H_2S} {>}\underset{H}{C}{-}\underset{H}{C}{<} \longrightarrow (III)$$

(cf. IV*a*)

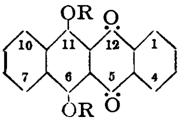
Moreover, (VII) is in agreement with the fact that hydrindantin is obtained when triketoindane (IV*a*) in *iso*propyl alcohol is exposed to sunlight, and the product is crystallised from a medium containing water (cf. Schönberg and Moubasher, *J.*, 1944, 366); it is well known that pinacols may be obtained from ketones under these conditions (Schönberg and Mustafa, *Chem. Reviews*, **1947**, **40**, 181).



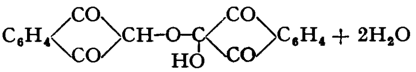
(I, R = Cl;
IV, R = OH;
IV*a*, RR = O.)



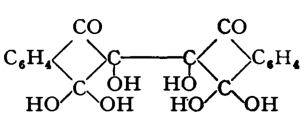
(II.) (III.)



(V, R = H;
V*a*, R = Ac.)



(VI.)

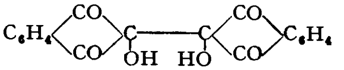


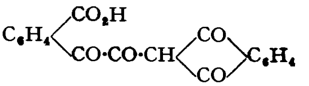
(VII.)

Further evidence for the correctness of (VII) for hydrindantin may be found in the fact that it is formed when triketoindane (IV*a*) is treated with the Gomberg–Bachmann reagent (magnesium iodide in ether in the presence of metallic magnesium), followed by the action of an acid. It is known that aromatic ketones, *e.g.*, benzophenone, yield pinacols under these conditions (Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1927, **49**, 236).

Gabriel and Leupold (*loc. cit.*), by the oxidation of (III) by alkaline hydrogen peroxide, obtained a deep yellow compound which they regarded as the anhydrous form of (VII), *viz.*, (VIII). This cannot be correct because the yellow substance is soluble in sodium hydrogen carbonate solution at room temperature with evolution of carbon dioxide; in a forthcoming publication it will be shown that the yellow compound is *o*-(1 : 3-diketo-2-indanylglyoxyloyl)-benzoic acid (IX).

(VIII.)





(IX.)

EXPERIMENTAL.

2 : 2-*Dichloro*-1 : 3-*diketoindane* (I).—Ninhydrin (IV) (1 g.) was dissolved at room temperature in phosphorus oxychloride, and phosphorus pentachloride (25 g.) added. The solution was heated on the water-bath (calcium chloride safety tube) for ½ hour, cooled, poured into ice-water, and left for an hour. The deposit was filtered off, washed with cold water, dried, and washed with light petroleum, and the residue, 2 : 2-dichloro-1 : 3-diketoindane (I) was crystallised from ethyl alcohol; it had the properties described by Zincke and Gerland (*Ber.*, 1888, **21**, 2379).

Bis-1 : 3-*diketoindanylidene* (II).—The foregoing diketone (2 g.) in dry benzene (100 c.c.) was refluxed (calcium chloride safety tube) for 6 hours in the presence of copper-bronze (5 g.). The solution was filtered while hot, and on concentration, red crystals formed which were recrystallised from toluene and then sublimed in vacuum (1·2 g.), m. p. 269—271° (not sharp) (Found : C, 75·1; H, 3·1. $C_{18}H_8O_4$ requires C, 75·0; H, 2·8%). The *tetraketone* forms red crystals difficultly soluble in the usual organic solvents, and giving a pink colour with concentrated sulphuric acid; it does not condense with *o*-phenylenediamine, and is insoluble in concentrated or dilute alkali at room temperature or on warming.

Oxidation. The tetraketone (0·2 g.) was mixed with red precipitated selenium (0·5 g.) and heated in a test-tube in a stream of oxygen at 200° (bath temp.); colourless crystals were formed on the cold parts of the tube. These were identified as phthalic anhydride (m. p. and mixed m. p. and properties).

Formation of Bisindane-1 : 3-*dione* (III).—(a) *From bis*-1 : 3-*diketoindanylidene* (II). The tetraketone (0·5 g.), partly dissolved and partly suspended in amyl alcohol (50 c.c.), was heated on the water-bath for

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* This experiment was carried out by Mohamed Zaki Barakat.

6 hours, during which a stream of dry hydrogen sulphide was passed through the mixture; after standing at room temperature (48 hours) the crystals formed were filtered off and proved to be (III) by m. p. and mixed m. p. and properties; yield *ca.* 90%.

(b) *From ninhydrin.* Ninhydrin (0·5 g.) in alcohol (90%; 150 c.c.) was refluxed for 3 hours, during which a stream of dry hydrogen sulphide was passed through the mixture; subsequent treatment as above afforded (III) in *ca.* 90% yield.

(c) *From hydrindantin* (VII). The procedure was as described under (*b*); yield *ca.* 90%.

6 : 11-*Diacetoxynaphthacene*-5 : 12-*quinone* (V*a*).—(a) *From the tetraketone* (II). To (II) (0·5 g.) in boiling acetic acid (25 c.c.), zinc dust (2 g.) was added in portions, and the product heated under reflux for 3 hours; the hot solution was then filtered and concentrated. To the cold filtrate water (100 c.c.) was added. After 2 hours the orange-yellow deposit was filtered off and recrystallised from acetic acid. It did not give a characteristic reaction with concentrated sulphuric acid, was insoluble in cold aqueous alkali, and was proved to be (V*a*) by m. p. and mixed m. p. (Gabriel and Leupold, *Ber.*, 1898, **31**, 1281).

(b) *From* (V). The dihydroxynaphthacenequinone (0·2 g.) in acetic acid (25 c.c.) containing zinc acetate (corresponding to 1·0 g. of zinc) was heated on the water-bath for 3 hours and then treated as above. The product proved to be the diacetoxy-compound.

(c) *From* (III). The compound (III) (0·2 g.) in acetic acid (25 c.c.) containing zinc acetate as above was heated, and the reaction product isolated as described; it proved to be the diacetoxy-compound (V*a*).

Action of Bis-1 : 3-*diketoindanylidene* (II) *on Phenylglycine.*—The tetraketone (0·2 g.) was added to phenylglycine (0·5 g.) in a mixture of glycerol (50 c.c.) and water (25 c.c.), and the mixture refluxed for 20 minutes at 150° (bath temp.). The product was distilled in an atmosphere of carbon dioxide, and the distillate (20 c.c.) treated with an alcoholic solution of phenylhydrazine; a crystalline colourless substance was obtained, which proved to be the benzaldehyde phenylhydrazone (m. p. and mixed m. p.); yield 0·3 g.

Action of Sodium Hydrosulphite (*Dithionite*).—(a) *On bis*-1 : 3-*diketoindanylidene* (II). Sodium hydroxide (10 g.) was dissolved in water (50 c.c.), and after addition of (II) (0·2 g.), sodium hydrosulphite (20 g.) was added. The mixture was heated on the water-bath for 10 minutes, kept at room temperature for 24 hours, and then poured into cold 18N-sulphuric acid. Red crystals were formed which, by m. p., mixed m. p., and properties, were shown to be the quinone (V).

(b) *On bisindane*-1 : 3-*dione* (III). This reaction was similarly carried out, and the same product was obtained (identified as above).

Action of Gomberg and Bachmann's Reagent on Triketoindane (IV*a*).—To powdered magnesium (4 g.) in a mixture of dry ether (50 c.c.) and dry benzene (thiophen-free) (50 c.c.), iodine was added until its colour persisted. Then dry magnesium powder (4 g.) and triketoindane (freshly prepared, 1 g.) were added, and the mixture shaken at room temperature for ½ hour. The product was added in portions to ice-cold dilute hydrochloric acid and left overnight in an open vessel; the deposit was filtered off and recrystallised from alcohol; colourless crystals (0·6 g.) were obtained which were proved by m. p., mixed m. p., and properties to be hydrindantin (VII).

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