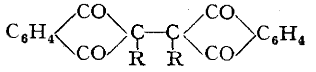
97. *Studies on Indene Derivatives. Part III. The Constitution and Some Reactions of Bishydroxyindone. The Photochemical Reduction of Triketohydrindene.*

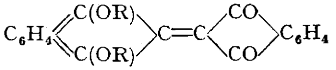
By Alexander Schönberg and Radwan Moubasher.

The structures of bis-1 : 3-indanedione (I) and 9 : 10-dihydroxynaphthacene-11 : 12-quinone (VII) are discussed. The photochemical reduction of triketohydrindene (XI) by *iso*propyl alcohol yields hydrindantin (XII).

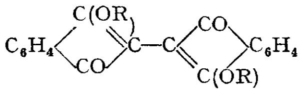
(A) A dark violet compound usually known as bis-1 : 3-indanedione (bisdiketohydrindene) (I) has frequently been described (Gabriel and Leupold, *Ber.*, 1898, **31**, 1160; Voswinkel, *Ber.*, 1909, **42**, 467; Dan Radulescu, *Centr.*, 1923, III, 140; Wanag, *Ber.*, 1937, **70**, 274; 1939, **72**, 973), but Hantzsch and Lister (*Annalen*, 1912, **392**, 319) expressed doubt about its ketonic nature and Eok and Marvel (*J. Amer. Chem. Soc.*, 1935, **57**, 1898) have stated that, since only two phenyl groups can be introduced into the molecule by the action of phenylmagnesium bromide, it must exist largely in the dienolic form. We now show that bis-1 : 3-indanedione is the corresponding dienol (IV, R = H) in the solid state, and, as all its reactions in neutral solvents may be explained on the basis of this formula, we propose to replace that name by bishydroxyindone.



(I; R = H.) (II; R = Me)
(IIa; R = OH.)

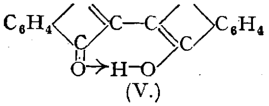


(III.)



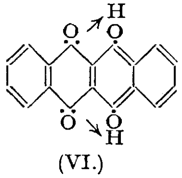
(IV.)

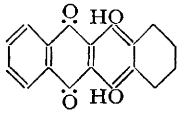
Dimethylbisindanedione (II) is colourless. Its constitution is established beyond doubt by its preparation from 2-methylindanedione (Gabriel and Leupold, *loc. cit.*, p. 1163). According to modern views a compound of constitution (I) should be colourless if (II) is colourless. On the other hand, (IV, R = H) would explain not only the violet colour of the compound but also the facts that it dissolves readily in cold aqueous sodium hydroxide with formation of a brown solution and reacts with diazomethane, giving an orange *dimethyl* ether (III or IV, R = Me). This is easily converted into (IV, R = H) by the action of sulphuric acid. Bishydroxyindone sublimes without decomposition in a vacuum at 340° : it is stable to oxygen at room temperature, but is readily oxidised by oxygen to phthalic anhydride at about 340° in the presence of selenium We failed to obtain the two forms (III and IV, R = H) of bishydroxyindone possible according to classical theory. It seems probable that (III and IV, R = H) and also (V) represent extreme forms of the same resonance state.

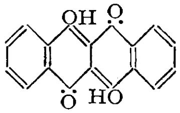


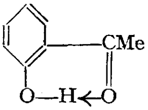
(V.)

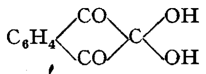
(B) *Comparison of the Reactions of Bishydroxyindone and* 9 : 10-*Dihydroxynaphthacene*-11 : 12-*quinone*.—There is a close relationship between bishydroxyindone (IV, R = H) and 9 : 10-dihydroxynaphthacene-11 : 12-quinone (VII), not only because the former can be very simply converted into the latter by the action of ammonia (Wanag, *Ber.*, **1937**, **70**, 274), but also because the corresponding resonance structures of the two substances show close similarities with one another (comp. III, R = H, with VII; IV, R = H, with VIII; V with VI). We have therefore compared the chemical reactivities of the two substances : bishydroxyindone proved to be much the more reactive, possibly owing to the presence of a seven-membered chelate ring (comparatively unstable) (V), whereas in 9 : 10-dihydroxynaphthacene-11 : 12-quinone, which does not react with diazomethane, there is a six-membered chelate ring (comparatively stable) (VI) [comp. also *o*-hydroxyacetophenone (IX), which does not react with diazomethane (private communication by A. Schönberg and Mrs. Abdel Fattah Ismail)]. The same explanation may be given to account for the slight solubility in aqueous alkali at 25° of (VII), in contrast to bishydroxyindone.


(VI.)

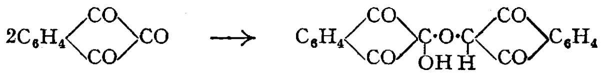

(VII.)


(VIII.)


(IX.)


(X.)

(C) The photochemical reduction of benzophenones by *iso*propyl alcohol in sunlight yields pinacols (Cohen, *Rec. Trav. chim.*, **1920**, **39**, 243; Bachmann, *Org. Synth.*, **14**, 8; Schönberg and Mostafa, this vol., p. 67). Very little is known about the photochemical reduction of polyketones under the above conditions. We have found that the red triketohydrindene (XI) (Schönberg and Moubasher, J., 1943, 71) is converted into the colourless hydrindantin (XII), previously prepared in the dark by the action of hydrogen sulphide on

(XI.)


$$2C_6H_4{<}^{CO}_{CO}{>}CO \longrightarrow C_6H_4{<}^{CO}_{CO}{>}\underset{OH}{C}\cdot O\cdot \underset{H}{C}{<}^{CO}_{CO}{>}C_6H_4$$

(XII.)

ninhydrin (X) (Ruhemann, J., 1911, **99**, 797). Thus, in this case, the photo-reduction product is not a pinacol, but an ether. The pinacol (II*a*), prepared by Gabriel and Leupold (*loc. cit.*, p. 1164) in the dark, is very different in properties from the photo-product obtained from triketohydrindene.

EXPERIMENTAL.

Action of Diazomethane on Bishydroxyindone (IV, R = H).—The powdered substance reacted vigorously with an ethereal solution of diazomethane, dissolving in the cold after 24 hours; the ether was then driven off, and the residue crystallised from methyl alcohol. The first crystals did not appear uniform under the microscope; after seven recrystallisations, the first crop being used each time, uniform orange crystals of the *dimethyl* ether, m. p. about 112° (decomp.) (depending on the rate of heating), were obtained, easily soluble in methyl alcohol and ether and insoluble in sodium hydroxide solution (Found : C, 75·2; H, 4·8. $C_{20}H_{14}O_4$ requires C, 75·4; H, 4·4%).

The ether was treated with cold concentrated sulphuric acid and then left for several minutes in a water-bath at 50°. The violet solution obtained, when cold, was poured on ice, giving a violet deposit, which, dried and crystallised from nitrobenzene, gave bishydroxyindone, m. p. 297°, undepressed by an authentic specimen.

Action of Oxygen on Bishydroxyindone in Presence of Selenium.—Bishydroxyindone (0·5 g.) was powdered with red selenium (1 g.) and heated at 340° (bath temperature) in a current of air. A sublimate of colourless crystals of phthalic anhydride, m. p. 130°, was obtained. The same reaction, carried out with the dimethyl ether (III or IV, R = Me), also gave phthalic anhydride.

Diazomethane and 9 : 10-*Dihydroxynaphthacene*-11 : 12-*quinone*.—The quinone, after prolonged treatment with diazomethane as described above, was recovered unchanged. It crystallised easily from dioxan.

Diazomethane and o-*Hydroxyacetophenone* (A. Schönberg and Mrs. A. F. Ismail).—*o*-Hydroxyacetophenone, after treatment with diazomethane during 3 days in the cold, was recovered unchanged and identified by its acetyl derivative and by the violet colour reaction with ferric chloride solution.

Photochemical Reaction between Triketohydrindene and iso*Propyl Alcohol.*—Freshly prepared triketohydrindene (XI) (2 g.), suspended in freshly distilled *iso*propyl alcohol (10 g., dried with calcium carbide) in a closed tube, was exposed to sunlight for 10 days. The red substance gradually disappeared and a colourless solid was formed. The excess of *iso*propyl alcohol was then removed in a vacuum, and the residue crystallised from acetone. The photo-product showed the properties of hydrindantin (XII); it turned red at about 200° and, decomposed at higher temperatures with evolution of gas, and formed a blue solution with sodium hydroxide (formation of a sodium salt after enolisation). It was crystallised from acetone and air-dried (under these conditions it forms a dihydrate; comp. Ruhemann, *loc. cit.*) (Found : C, 60·0; H, 4·2. Calc. for $C_{18}H_{10}O_6,2H_2O$: C, 60·3; H, 3·9%).

FOUAD I UNIVERSITY, CAIRO, EGYPT.

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