409. *Studies on Indene Derivatives. Part VII. New Reactions of Triketoindane and Experiments with Hydrindantin and Related Compounds.*

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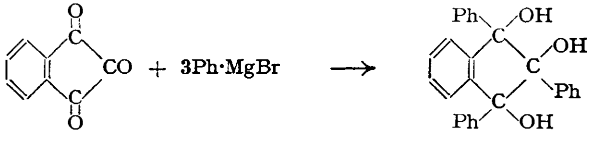
and Abdel Mogid Othman.

New derivatives of triketoindane have been prepared. The thermal decomposition of bis-(2-hydroxy-1 : 3-diketoindan-2-yl) (V) yields bis-(3-hydroxy-1-ketoinden-2-yl) (VI) and phthalic anhydride. The nature of the deep blue colour obtained from (I) $+H_2O$, (V) $+2H_2O$, and 2 : 2-dihydroxyperinaphthane-1 : 3-dione by strong alkali is discussed; in the last case, after acidification, 2-hydroxyperinaphthane-1 : 3-dione is obtained in good yield.

Continuing the work of one of us (R. M.) on the properties of indane-1 : 2 : 3-trione (I), we have investigated its reaction with phenylmagnesium bromide [*] and isolated 1 : 2 : 3-trihydroxy-1 : 2 : 3-triphenylindane (II), which is oxidised to *o*-dibenzoylbenzene by boiling nitric acid.

(I.)



(II.)

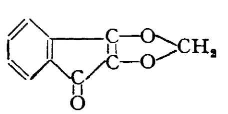
As with diphenyl triketone (Schönberg and Moubasher, *J.*, 1941, 348), a five-membered ring is formed when the indanetrione [†] (I) or the analogous perinaphthindanetrione (VII $-$ H_2O) is treated with diazomethane, giving 2 : 3-methylenedioxyindan-1-one (III) and 2 : 3-methylenedioxyperinaphthinden-1-one respectively, which with boiling alcoholic hydrochloric acid yield bis-(3-hydroxy-1-ketoinden-2-yl) (VI) and 2 : 3-dihydroxyperinaphthinden-2-one (the enolic form of VIII) respectively.

Thionaphthan-3-one and (I) give the violet red 2-(3-ketothionaphthen-2-ylidene)indane-1 : 3-dione (IV), but attempted condensation with indane-1 : 3-dione gave only (VI).

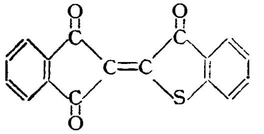
[*] These experiments were performed by Moustafa Ibrahim.

[†] These experiments were performed by William Awad.

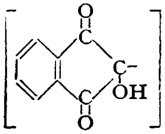
The anhydrous substance (V) (Schönberg *et al.*, *J.*, **1950**, 376), when heated at 270° in a vacuum or in carbon dioxide, gives (VI) and phthalic anhydride. When (V) is exposed to sunlight with benzoquinone in benzene solution, dehydrogenation takes place, followed by fission, with the formation of the trione (I); this behaviour is frequently met with in pinacols (Schönberg and Mustafa, *J.*, 1944, 67).



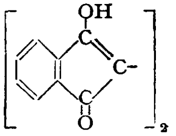
(III.)



(IV.)



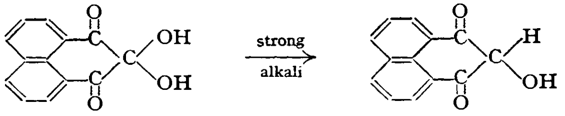
(V.)



(VI.)

The action of strong alkali on hydrindantin or (V) leads to the formation of a blue colour owing to formation of the alkali salt of the enolic form of 2-hydroxyindane-1 : 3-dione (Ruhemann, *J.*, 1911, **99**, 1306). Its formation is easily explained on the basis of the formula (V + $2H_2O$) for hydrindantin (cf. the formation of benzhydrol and fluorenol by the action of the alkali on tetraphenylethylene glycol and the acetate of fluorenone-pinacol, respectively; Thörner and Zinke, *Ber.*, 1877, **10**, 1473; Klinger and Lonnes, *ibid.*, 1896, **29**, 2157). The intense blue colour which is produced when ninhydrin is treated with concentrated alkali is, according to Errera (*Chem. Centr.*, 1913, **11**, 774), also caused by formation of a salt similar in structure to (VIII). In favour of this opinion are the facts that perinaphthindane-1 : 2 : 3-trione hydrate (VII) gives with strong alkali a deep-blue solution which when acidified yields 2 : 3-dihydroxyperinaphthinden-1-one (the enolic form of VIII), and that (VIII) and benzoyl chloride yield the corresponding dibenzoate.

(VII.)



(VIII.)

Experimental.

*Action of Phenylmagnesium Bromide on Indane-*1 : 2 : 3*-trione.*—The trione (Schönberg and Moubasher, *J.*, 1943, 71) (1 g.) was added to ethereal phenylmagnesium bromide (from 1 g. of magnesium and 8 g. of bromobenzene in 50 c.c. of ether), a vigorous reaction taking place. Benzene (50 c.c.) was then added, and the whole refluxed for ½ hour and left overnight. The mixture was then treated with dilute hydrochloric acid and extracted with ether, the ethereal extract dried (Na_2SO_4), filtered, and evaporated up to dryness, and the residue (2 g.) crystallised from benzene–light petroleum (1 : 3 by vol.). 1 : 2 : 3*-Trihydroxy-*1 : 2 : 3*-triphenylindane* forms colourless needles, m. p. 124—130° (Found: C, 83·6; H, 6·0. $C_{27}H_{22}O_3,C_6H_6$ requires C, 83·8; H, 5·9%). When this substance is left for few days at room temperature or dried in a vacuum, benzene of crystallisation is lost, giving the colourless anhydrous *form*, m. p. 178° (Found: C, 82·3; H, 5·8; active, H, 0·7%; *M*, 388. $C_{27}H_{22}O_3$ requires C, 82·2; H, 5·6; active H, 0·7%; *M*, 394). It is soluble in benzene or ethyl alcohol, insoluble in sodium hydroxide, and gives with concentrated sulphuric acid a yellow-orange colour.

Oxidation of 1 : 2 : 3*-Trihydroxy-*1 : 2 : 3*-triphenylindane* (II).—The triol (0·5 g.), concentrated nitric acid (10 c.c., *d* 1·42), and water (20 c.c.) were refluxed for 2 hours. A yellow oil was formed which, after cooling, solidified (0·2 g.). This was recrystallised from benzene–light petroleum giving *o*-dibenzoylbenzene as yellow needles, m. p. 147° undepressed on admixture with authentic sample.

Action of Diazomethane.—(a) *On indane-*1 : 2 : 3*-trione.* The trione (0·5 g.) was added to an excess of ethereal diazomethane, a vigorous reaction taking place. The mixture was left overnight in an ice-chest. The ether was removed and the brown oily mass triturated with aqueous methyl alcohol, to give a yellowish solid (0·45 g.) which crystallised from methyl alcohol. 2 : 3*-Methylenedioxyinden-*1*-one* forms pale yellow crystals, m. p. 185° (Found: C, 69·4; H, 3·9%; *M*, 166. $C_{10}H_6O_3$ requires C, 68·9; H, 3·4%; *M*, 174).

The product (0·2 g.), hot methyl alcohol (15 c.c.), and concentrated hydrochloric acid (10 c.c.) were refluxed for 6 hours. A violet crystalline deposit (0·1 g.) formed which crystallised from benzene in violet needles, m. p. 298°, and was proved to be bis(3-hydroxy-1-ketoinden-2-yl) by mixed m. p. and general properties.

(b) *On perinaphthindane-*1 : 2 : 3*-trione* [Moubasher and (in part) Awad, *J.*, 1949, 1137)]. The trione (0·2 g.), treated with an excess of ethereal diazomethane as in (a), gave 2 : 3*-methylenedioxyperinaphthinden-*1*-one* as pale yellow crystals (from methyl alcohol), m. p. 200° (brownish-red melt) (0·18 g.) (Found: C, 74·9; H, 3·2. $C_{14}H_8O_3$ requires C, 75·0; H, 3·5%). This gives a persistent orange colour with concentrated sulphuric acid. It is insoluble in sodium hydroxide solution.

Hydrolysis, carried out as above, gave a reddish flocculent substance which crystallised from ethyl alcohol in red needles, m. p. 258°, undepressed with authentic 2 : 3-dihydroxyperinaphthinden-1-one prepared according to Errera (*loc. cit.*), and giving a blue colour with sodium hydroxide solution.

Action of Thionaphthan-3-one on Indane-1 : 2 : 3-trione.—The trione (0·5 g.) and freshly crystallised thionaphthan-3-one (0·5 g.) in dry benzene (50 c.c.) were refluxed for ½ hour. After cooling a violet deposit (0·7 g.) was filtered off and crystallised from benzene. 2-(3-*Ketothionaphthan-2-ylidene*)*indane-1 : 3-dione* forms violet needles, m. p. 275° (decomp.) (Found : C, 69·3; H, 2·9; S, 11·4. $C_{17}H_8O_3S$ requires C, 69·8; H, 2·7; S, 11·1%). It gives an orange-red fluorescence in xylene and an intense blue-green colour with concentrated sulphuric acid.

Action of Indane-1 : 3-dione on Indane-1 : 2 : 3-trione.—The trione (0·5 g.) and the dione (0·5 g.) in glacial acetic acid (25 c.c.) were refluxed for 2 hours, and then cooled and filtered. The solid residue was extracted several times with benzene. From the benzene extract only violet crystals of (VI) were obtained (0·5 g.), m. p. 298° alone or mixed with an authentic sample.

Thermal Decomposition of Bis-(2-hydroxy-1 : 3-diketoindan-2-yl).—The substance (1 g.) was heated for 5 minutes at 270° (bath-temp.) in a vacuum or in a stream of carbon dioxide. On the cold part of the tube, colourless crystals of phthalic anhydride were formed (0·08 g.) (m. p. 130° alone or mixed with an authentic sample; fluorescein test positive). A residue of (VI) (0·5 g.) remained which, crystallised from benzene, had m. p. 298°, undepressed on admixture with an authentic sample (colours with concentrated sulphuric acid and with sodium hydroxide solution).

Photo-reaction of p-*Benzoquinone and Bis-(2-hydroxy-1 : 3-diketoindan-2-yl).*—The bisindanyl compound (1 g.), suspended in dry benzene (30 c.c.) containing *p*-benzoquinone (5 g.), in a Monax tube filled with carbon dioxide, was exposed to sunlight for 7 days (May). The black solid quinone separated out. The mixture was filtered and the solid treated with hot water and collected. The aqueous filtrate was extracted several times with ether (5-c.c. portions). The dried ethereal extracts were evaporated, to give ninhydrin as colourless crystals (0·1 g.), becoming red at 139° and melting at 260° to a green melt, undepressed by admixture with an authentic specimen. It gave the characteristic blue colour with concentrated sodium hydroxide solution.

Action of Alkali.—(a) *Perinaphthindane-1 : 2 : 3-trione hydrate.* The substance (0·1 g.) was suspended in distilled water (5 c.c.), and sodium hydroxide (10%; 1 c.c.) was added, an intense blue colour developing; benzoyl chloride (10 c.c.) was added immediately and the reaction mixture shaken vigorously with cooling for 1 minute, thereupon becoming yellow. The whole was added to cold water; a yellow precipitate was filtered off (0·1 g.) and recrystallised from benzene or dilute acetic acid in yellow green prisms, m. p. 215°, undepressed on admixture with an authentic sample of 2 : 3-dibenzoyloxyperinaphthinden-1-one (Errera, *loc. cit.*).

When the experiment was carried out without the addition of benzoyl chloride, acidification with hydrochloric acid after the formation of the blue colour gave 2 : 3-dihydroxyperinaphthinden-1-one (70%) which crystallised from ethyl alcohol in red needles, m. p. 258° undepressed on admixture with authentic sample.

(b) *Ninhydrin.* To ninhydrin (0·1 g.) in the minimum amount of water were added a few c.c. of aqueous sodium hydroxide. A blue colour was formed. The mixture was acidified with concentrated hydrochloric acid and kept for 24 hours, whereupon hydrindantin (0·02 gr.) crystallised, having m. p. 220° (decomp.) alone or mixed with an authentic sample.

(c) *Hydrindantin.* Hydrindantin (0·1 g.) was triturated with aqueous sodium hydroxide (10%; 10 c.c.). A violet colour developed. The mixture was acidified and kept for 24 hours, hydrindantin (0·15 g.), identified as above, separating.

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