

EXPERIMENTAL.

Action of Hydrogen Peroxide.—(1) *On 1:3-diketo-2-acetylindane.* The triketone was prepared by Kilgore's, Ford, and Wolfe's modification (*loc. cit.*) of Schwerin's method (*Ber.*, 1894, **27**, 104). There was a small increase in yield when the sodium methoxide recommended was replaced by sodamide.

In alkaline solution. In a typical experiment the ketone (1.0 g.) was dissolved in a slight excess of 0.5*N*-sodium hydroxide, and after addition of excess of a solution of pure hydrogen peroxide (0.75 g. of 50% aqueous solution), it was left at 0° for 8 days. The reaction mixture yielded on acidification a precipitate of unchanged ketone (0.1 g.) and phthalic acid (0.75 g.), m. p. and mixed m. p. 203° (decomp.). Ether extraction gave a trace of phthalic acid and acetic acid (0.15 g.); *p*-phenylphenacyl ester, m. p. and mixed m. p. 115°.

In acid solution. 1:3-Diketo-2-acetylindane (1.0 g.), dissolved in sulphuric acid (10 c.c. of 80% solution), was treated at 0° with aqueous hydrogen peroxide (0.75 g. of 50% solution). After the initial reaction had subsided the mixture was left at room temperature for 24 hours, and then poured on ice. Phthalic and acetic acids were obtained in quantitative yield.

In neutral solution. The ketone was dissolved in the minimum of absolute ether, treated with excess of ethereal hydrogen peroxide [5 c.c. of 20% solution; prepared by concentrating a dried ethereal extract of freshly distilled and concentrated hydrogen peroxide (approximately 25%)], and left for 21 days at room temperature. The reaction mixture, on evaporation and treatment with water, yielded a light yellow solid, which was separated by extraction with chloroform into insoluble phthalic acid (0.02 g.) and a mixture of unchanged ketone (0.22 g.) and white leaflets (0.70 g.), m. p. 96°, which were separated by crystallisation from ethyl acetate–light petrol (b. p. 40–70°) [Found, for the leaflets: C, 64.5, 64.4; H, 4.1, 4.1; *M* (cryoscopic in benzene), 192. C₁₁H₈O₄ requires C, 64.7; H, 3.9%; *M*, 204]. In alcoholic solution this product, 1:3-diketo-2-acetoxyindane (IIIa), has no action on ferric chloride or acidified potassium iodide but gives a series of colour reactions. It dissolves very slightly in water to give a yellow solution, but gives colourless solutions in non-polar solvents. In 2*N*-sodium hydroxide it gives a yellow solution which rapidly changes to a deep ultramarine-blue. On acidification in the absence of oxygen this passes reversibly from blue (pH 11.0) through red (pH 6.0) to light yellow (pH 4.0). Both the red and the blue solution are rapidly decolorised through atmospheric oxidation. An alcoholic solution develops a strong purple stain on the human skin after several hours.

(2) *On 1:3-diketo-2-acetoxyindane.* The indane (0.10 g.), when dissolved in 2*N*-sodium hydroxide to give a blue solution or in the form of its yellow solution in 2*N*-sodium carbonate, reacted vigorously with excess of hydrogen peroxide. Acidification of the mixture gave phthalic acid in quantitative yield. Similarly in sulphuric acid solution (80%) quantitative oxidation to phthalic and acetic acids occurred.

Characterisation of 2-hydroxy-1:3-diketoindane. When air was blown through the acidified solution obtained on alkaline hydrolysis of 1:3-diketo-2-acetoxyindane (0.20 g.), a white solid (0.18 g.), m. p. 236° (decomp.), was precipitated. This was identified as hydrindantin hydrate (Ruhemann, *loc. cit.*) (Found: C, 60.5; H, 3.9. Calc. for C₁₈H₁₀O₆·2H₂O: C, 60.3; H, 3.9%) by m. p. and mixed m. p. The same product was formed on acidification of the alkaline hydrolysis solution of 1:3-diketo-2-acetoxyindane with an alcoholic solution of 1:2:3-triketointhane hydrate.

(3) *On 1:3-diketo-2-benzoylindane.* The indane (prepared after the manner of Schwerin, *loc. cit.*) in 2*N*-sodium hydroxide solution reacted with excess of hydrogen peroxide more slowly than did the acetyl derivative to give, together with a trace of unchanged ketone, phthalic and benzoic acids, which were separated and identified by mixed m. p. determination. In sulphuric acid quantitative yields of these acids were also obtained.

A solution of 1:3-diketo-2-benzoylindane (1.0 g.) in the minimum of absolute ether, on treatment with a large excess of ethereal hydrogen peroxide (7 g. of 20% solution) during 20 days, gave on evaporation a light yellow solid from which phthalic acid (0.1 g.), benzoic acid (0.05 g.), and a white solid (0.70 g.), m. p. 136.5–137°, were obtained. This solid crystallised as prisms from ethyl acetate–light petrol (b. p. 40–60°) [Found: C, 72.2; H, 3.9; *M* (cryoscopic in benzene), 258. C₁₆H₁₀O₄ requires C, 72.2; H, 3.8%; *M*, 266]. This product, 1:3-diketo-2-benzoyloxyindane (IIIb), gives similar colour reactions to the acetyl analogue. In 2*N*-sodium hydroxide the first-formed yellow solution changes more slowly than (IIIa) to deep ultramarine-blue. Alkaline hydrolysis of (IIIb) under hydrogen gave benzoic acid and 2-hydroxy-1:3-diketoindane, characterised, as previously, through conversion into hydrindantin.

(4) *On tribenzoylmethane.* Tribenzoylmethane (0.50 g.), prepared from dibenzoylmethane (*Org. Synth.*, Coll. Vol. I, 1941, 205) by the procedure of Birckenbach *et al.* (*Ber.*, 1932, **65**, 1071), was dissolved in 2*N*-sodium hydroxide solution and treated with excess of hydrogen peroxide (1.0 g. of 50% solution) overnight at room temperature. Concentration and acidification of the colourless solution yielded benzoic acid (0.47 g.), m. p. 122°. In sulphuric acid (10 c.c.) at 0°, hydrogen peroxide (1 c.c. of 50% solution) also converted the triketone (0.5 g.) into benzoic acid. Under neutral conditions (nitrobenzene solution or ethereal suspension) hydrogen peroxide had no action on the ketone over a period of 28 days.

(5) *On dibenzoylacetylmethane.* The methane (Claisen and Falk, *Annalen*, 1896, **291**, 25) in alkaline solution was degraded completely by hydrogen peroxide at room temperature in 3 days. Benzoic acid was isolated from the acidified solution in quantitative yield. In sulphuric acid solution (15 c.c.) at 0°, dibenzoylacetylmethane (0.5 g.) was hydrolysed to dibenzoylmethane (0.40 g.), m. p. and mixed m. p. 77°, in the absence of hydrogen peroxide.

Treatment of the keto-form of dibenzoylacetylmethane (1.0 g.) in ether with ethereal hydrogen peroxide (2 c.c. of 10% solution) at room temperature for 7 days yielded, besides unchanged material (0.3 g.), benzoic acid (0.2 g.) and a crude peroxide (m. p. 80–90°) which sublimed at 70–80°/0.01–0.02 mm. and readily liberated iodine from acidified potassium iodide. No pure material was isolated from the crude product.

The enolic form of dibenzoylacetylmethane (0.5 g.), m. p. 85° (107°; Claisen and Falk, *loc. cit.*), on

standing in ethereal hydrogen peroxide for 30 days, yielded unchanged product (0.45 g.) and a trace (0.02 g.) of an amorphous peroxide.

The analyses were by Messrs. C. L. Carter and J. A. Mills.

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