Huntress and Bornstein (1949) report that N-chloroacetylisatin is yellow, but crystallizes from methanol in a colourless form containing 1 mole of solvent. For the following reasons it is considered that the colourless compound is the methyl ester of N-chloroacetylisatin acid (I, $R = \text{CH}_3$) rather than a hemiketal type (II) analogous to ninhydrin:

(i) The methanol cannot be replaced by crystallization of the methanol adduct from other alcohols or from water, nor removed by prolonged distillation with toluene.

(ii) Whereas N-chloroacetylisatin dissolves in concentrated sulphuric acid to an orange solution, the methanol adduct gives a colourless solution from which it is precipitated unchanged by pouring into water. Ninhydrin dissolves in concentrated sulphuric acid giving a red solution, the colour of which is due to unhydrated triketohydrindene (MacFadyen 1950).

(iii) The addition of water to N-chloroacetylisatin is only achieved with difficulty and the product, which is acidic, is evidently N-chloroacetylisatin acid.

Methyl N-chloroacetylisatin ester is reconverted to N-chloroacetylisatin by heating with acetic anhydride. The ethyl ester (I, $R = \text{C}_2\text{H}_5$) has been prepared.

Experimental

Melting points are corrected. Microanalyses were carried out in the C.S.I.R.O. Microanalytical Laboratory.

(a) N-Chloroacetylisatin Acid.—N-Chloroacetylisatin (1 g) dissolved in cold 1% sodium hydroxide giving a red solution which changed rapidly to yellow. Acidification with cold 5% hydrochloric acid precipitated a pale yellow solid (0.54 g), which was filtered off immediately, and crystallized three times from ethyl acetate. N-Chloroacetylisatin acid separated as almost

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colourless needles, m.p. 167–168 °C (Found: C, 49·9; H, 3·3%). Calc. for C₁₃H₁₄O₃NCI: C, 49·7; H, 3·3%). Isatin (m.p. and mixed m.p. 203–204 °C) separated from the aqueous acid filtrate on standing. N-Chloroacetylisatin acid dissolves in aqueous sodium bicarbonate with evolution of carbon dioxide.

(b) Solvolysis of N-Chloroacetylisatin.—N-Chloroacetylisatin was recovered unchanged (yellow needles, m.p. and mixed m.p. 210–211 °C) after boiling with ethyl acetate or acetone, or on pouring a solution in concentrated sulphuric acid into water. Refluxing for 1 hr with 50% aqueous acetone (0·5 g N-chloroacetylisatin in 40 ml) and evaporating to 15 ml gave N-chloroacetylisatin acid (0·28 g), m.p. and mixed m.p. 167–168 °C after recrystallization from water. Isatin (0·12 g) was recovered from the filtrates. N-Chloroacetylisatin dissolved slowly in boiling water and after refluxing the solution for 3 hr the only product was isatin (0·13 g from 0·2 g chloroacetyl compound), m.p. and mixed m.p. 203–204 °C.

The methyl ester of N-chloroacetylisatin, obtained as colourless needles, m.p. 83–83·5 °C after boiling a solution of N-chloroacetylisatin in methanol, was unchanged by crystallization from water, ethanol, isopropanol, chloroform, ethyl acetate, benzene, or ether. It separated unchanged from a toluene solution which had been concentrated by slow distillation for 1½ hr, but was converted to N-chloroacetylisatin, m.p. and mixed m.p. 209–210 °C by refluxing for 1 hr with acetic anhydride. The methyl ester dissolved in concentrated sulphuric acid to a colourless solution from which it was precipitated unchanged on pouring into water.

The ethyl ester of N-chloroacetylisatin acid, prepared by boiling an ethanol solution of N-chloroacetylisatin, crystallized from light petroleum as cream plates, m.p. 64–64·5 °C (Found: C, 53·9; H, 4·6%). Calc. for C₁₂H₁₄O₄NCI: C, 53·4; H, 4·5%).

References