N-CHLOROACETYLISATIC ACID*

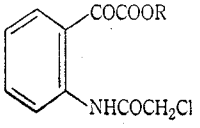
By R. JOHNSTONE† and J. R. PRICE†

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*-chloroacetylisatic acid (I, R$=CH_3$) rather than a hemiketal type (II) analogous to ninhydrin:

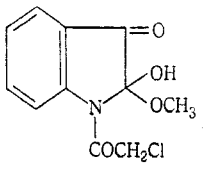
(i) The methanol cannot be replaced by crystallization of the methanol adduct from other alcohols or from water, nor removed by prolonged distillation with toluene.

(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*-chloroacetylisatic acid.



(I)



(II)

Methyl *N*-chloroacetylisatic ester is reconverted to *N*-chloroacetylisatin by heating with acetic anhydride. The ethyl ester (I, R$=C_2H_5$) has been prepared.

Experimental

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

(*a*) *N-Chloroacetylisatic 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*-Chloroacetylisatic acid separated as almost

* Manuscript received December 16, 1953.

† Division of Industrial Chemistry, C.S.I.R.O., Melbourne.

colourless needles, m.p. 167–168 °C (Found : C, 49·9 ; H, 3·3%. Calc. for $C_{10}H_8O_4NCl$: 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*-Chloroacetylisatic 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*-chloroacetylisatic acid (0·26 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, *iso*propanol, 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*-chloroacetylisatic 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 $C_{12}H_{12}O_4NCl$: C, 53·4 ; H, 4·5%).

References

HUNTRESS, E. H., and BORNSTEIN, J. (1949).—*J. Amer. Chem. Soc.* **71** : 745.
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