

The residue, insoluble in ether and hot water was recrystallised from alcohol. It was identified as 3-nitro-4-methoxycinnamic acid. m. p. 244°-45° (Found : C, 53.99; H, 4.04; N, 6.03 per cent. Calc. for  $C_{10}H_9O_5N$ : C, 53.81; H, 4.03; N, 6.28 per cent).

The above procedure was repeated under various conditions (Table 1).

The 3-nitro-4-methoxycinnamic acid obtained was reduced by the method of Pettit and Neill<sup>3</sup> using ethanol as the solvent. m. p. 222-4°. Yield 33% (Found : C, 61.97; H, 5.67; N, 7.11 per cent. Calc. for  $C_{10}H_{11}O_3N$ : C, 62.18; H, 5.7; N, 7.25 per cent).

The amine was characterised by preparing the acetyl, benzoyl and sulphamido derivatives (Table 2).

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### Use of 2-Hydroxy-4-*n*-Propoxy Acetophenone Oxime (HPaox) as Analytical Reagent Gravimetric Determination of Nickel

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2-Hydroxy-4-*n*-propoxy acetophenone oxime (HPAOX) has been found to be a suitable chelating agent for gravimetric determination of nickel. The reagent reacts quantitatively with Ni(II) in the pH range 5.0 to 9.0 giving insoluble metal complex. The green nickel complex can be directly weighed as  $Ni(C_{11}H_{14}O_3N)_2$  after drying at 110°-120°. The Ni(II) has been determined gravimetrically at pH 5.5, the error being less than  $\pm 0.4\%$ . The interference due to several ions such as Ca(II), Ba(II), Zn(II), Mg(II), Co(II), Fe(III) have been avoided by working at controlled pH and by using suitable masking agent. The reagent was prepared from 2-hydroxy-4-*n*-propoxy acetophenone and crystallised from petroleum ether, colourless needles, m.p. 84° (Found N, 6.6 and calculated N, 6.7%).

The nickel bischelate (Ni calculated 12.37%, found 12.33%) with the reagent precipitated at pH 5.5 is green coloured and is insoluble in water, ethanol, ether and dil. acetic acid but it is soluble in chloroform.

*Procedure for the determination of Ni(II)* : An aliquot standard solution of Ni(II) was diluted to 200 ml and pH was adjusted using acetate buffer. The solution was warmed to 60°-70° and 1% ethanolic solution (10% excess) of the reagent was added with constant stirring. The precipitate was heated at 60°-70° and allowed to stand for about 30 min. It was filtered through a sintered glass crucible (G 4); washed with ethanol to remove excess reagent, dried at 110°-120° to constant weight. The conversion factor of nickel/nickel complex is 0.1237. The results of some of the estimations are given below

#### Determination of nickel

Ni(II) (taken) in mg	Ni(II) (found) in mg	% error
8.91	8.90	-0.11
14.85	14.84	-0.07
29.70	29.69	+0.34
44.55	44.53	-0.04
59.40	59.37	-0.05

*Determination of nickel in Presence of other ions* : Nickel(II) was determined in presence of Ca(II), Ba(II), Zn(II), Mg(II), at pH 5.5 as these ions were found to give no colour formation or insoluble chelate.

Co(II) gives orange yellow precipitate at pH 6.5 but cobalt chelate is soluble in ethanol. It was therefore possible to determine Ni(II), at pH 5.5 in the presence of Co(II). The maximum error is  $\pm 0.2\%$ .

The presence of Fe(III) interferes during the determination of Ni(II). However, the determination was carried out by sequestering the Fe(III) by potassium tartrate. (maximum error is  $\pm 0.3\%$ ).

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### Studies in Terpenes. Part XLI : Synthesis of Terpinolene

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THIS paper describes a simple synthesis of terpinolene (I) from the readily available d-limonene (II). d-Limonene dihydrobromide (III) obtained by hydrobromination<sup>1</sup> of (II), upon bromination under ultraviolet irradiation<sup>2</sup> provided 1,4,8-tribromo-*p*-menthane