

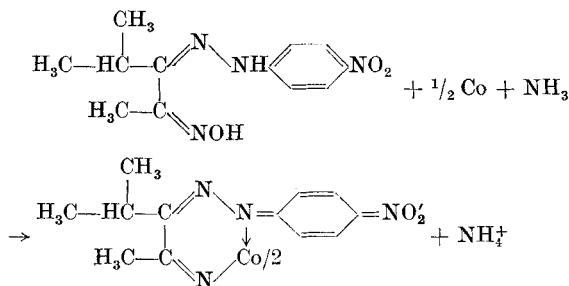
## New Reagents for Cobalt

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### Abstract

Two new selective reagents in the series of nitrophenylhydrazones of vicinal diketomoximes, p-nitro- and 2:4, dinitro-phenylhydrazones of 2-methyl-3 oximo-pentanone-4 are repeated. Both show high sensitivity and selectivity for cobalt. Limits of identification and dilution limits for the reagents have been determined as 0.2 microgram and 1:500,000 respectively.

The usefulness of nitrosubstituted phenylhydrazones of vicinal diketomoximes as sensitive and selective reagents for cobalt has been fairly well established<sup>2-6</sup>. The reagents do not, however, lend well to spectrophotometric determination of cobalt because of the instability of their complexes with cobalt. The search for new reagents in the series therefore continues. p-Nitro-(i) and 2:4 Dinitro-(ii) phenylhydrazones of 2, methyl-3 oximo-pentanone-4 have been investigated and found to be very sensitive reagents for the detection of cobalt in ammoniacal solutions. Both form violet chelates having the nitro group in the aci form; which may be represented for (i) as:



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<sup>3)</sup> V. D. ANAND and G. S. DESHMUKH, *Naturwissenschaften* **46**, 648 (1959).

<sup>4)</sup> G. S. DESHMUKH, V. D. ANAND and K. N. MEHROTRA, *Zhur. anal. Khim.*, **XVI**, 313 (1961).

<sup>5)</sup> V. D. ANAND, *Mikrochim. Acta* 1961 (4), 650.

<sup>6)</sup> V. D. ANAND, *Chemist Analyst* **50**, 44 (1961).

Preparation of 2, Methyl-3 oximo-pentanone-4: Mix 120 gms. of 2-methyl pentanone-4 with 3 ml. conc. HCl in a three necked pyrex flask. Add 100 ml. of amyl nitrite in the course of 2 hours with continuous stirring and cooling, so that the temperature does not exceed  $50^{\circ}$  throughout the course of reaction. Treat with 80 gms of 33 percent sodium hydroxide and extract the released amyl alcohol with a large excess of ether. Acidify the alkaline aqueous phase with dilute sulphuric acid, maintaining the temperature below  $10^{\circ}\text{C}$ . The semisolid mass separating out is removed and purified by repeated crystallization (m. p. in a capillary —  $59-60^{\circ}\text{C}$ )

(i) Preparation of p-Nitro phenylhydrazone of 2 Methyl-3 oximopentanone-4: Suspend 1.5 gms. of p-nitro phenylhydrazone in 50 ml. of hot water acidified with a few drops of acetic acid and add a solution of 1.3 gms. of the oxime dissolved in the minimum quantity of alcohol. Keep on a steam bath for 30 minutes. Cool, extract the hydrazone with ether and recover the solid by ether removal. The hydrazone is recrystallized from dilute alcohol as brownish yellow crystals and has a m. p. of  $154-55^{\circ}\text{C}$  in a capillary.

(ii) Preparation of 2:4Dinitrophenylhydrazone of 2, Methyl-3, oximo pentanone-4: Reflux equimolar proportions of the oxime and 2:4 dinitrophenylhydrazone for 5 hours. Cool, dilute with water and extract the hydrazone with ether. Recrystallize from ethylacetate. The orange yellow product has a m. p. of  $196^{\circ}\text{C}$  in a capillary.

### Test for Cobalt

Place a drop of the test solution basified with two drops of ammonia liquor in a micro test tube and treat with two drops of 0.1 percent of the reagent solution. Shake with two 1 ml. portions of ether to extract the excess reagent. A positive test consists of a pink to violet colour in the aqueous phase, colour intensity depending on cobalt concentration.

The limits of identification and the dilution limits were 0.2 microgram and 1:500,000 respectively for both the p-nitro-(i) and the 2:4 dinitro-(ii) phenylhydrazones. Under the conditions of test, colour of the cobalt complex was stable for 2 hours.

There was no interference from  $\text{Zn}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Pb}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Te}^{+4}$ ,  $\text{Se}^{+4}$ ,  $\text{Cr}^{+3}$ ,  $\text{Al}^{+3}$ ,  $\text{Ce}^{+6}$ ,  $\text{W}^{+6}$ ,  $\text{UO}_2^{+2}$ ,  $\text{Bi}^{+3}$ ,  $\text{Sb}^{+3}$ ,  $\text{Tl}^{+}$ ,  $\text{Th}^{+4}$ ,  $\text{V}^{+5}$ ,  $\text{Au}^{+3}$ ,  $\text{Zr}^{+4}$ ,  $\text{Fe}^{+3}$ ,  $\text{As}^{+3}$ ,  $\text{Li}^{+}$ ,  $\text{Na}^{+}$ ,  $\text{K}^{+}$ ,  $\text{Ca}^{+2}$ ,  $\text{Sr}^{+2}$ , and  $\text{Ba}^{+2}$ . At lower concentrations  $\text{Ni}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Ag}^{+}$  and  $\text{Pd}^{++}$  also do not interfere but at higher concentrations  $\text{Ag}^{+}$ ,  $\text{Ni}^{++}$  and  $\text{Cu}^{++}$  give coloured reactions with the reagent. The interference from these and that due to the coloured amines of  $\text{Ni}^{++}$  and  $\text{Cu}^{++}$  is overcome by addition of KCN. Centrifugation is necessary if metals forming insoluble hydroxides are present. The tolerance limits for  $\text{Ni}^{++}$ ,  $\text{Cu}^{++}$  and  $\text{Ag}^{+}$  were determined to be 500, 2600 and 12000 micrograms respectively.

Ammonia may be replaced with ethylenediammine, triethanolammine, magnesium oxide or calcium oxide but the sensitivity of the test is considerably impaired.

With alkali hydroxides the reagent gives a deep colouration probably due to the formation of the quinnoidal aci — form of the reagent. With

ammonia, this conversion is incomplete and only a light pink colour is formed. The formation of the cobalt chelate which obviously contains this quinoidal form of the reagent seems to complete the rearrangement initiated by ammonia.

Large amounts of ammonium salts and cyanides inhibit the reaction and should be absent. In presence of a large excess of the former, evaporation to dryness, ignition of the residue and dissolution in  $\text{HNO}_3$  are recommended.

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