

mate (4.5 ml) under reflux for 3 hr on water-bath and worked up following the procedure of Biltz and Jeltsch³. Crystallization from light petrol afforded ethyl-*N*-methylallophanate (0.5 g), m.p. 134°, $[\alpha]_D^{20}$ exactly identical (m.p., m.m.p., IR) with the compound A¹. (Found: C, 41.14; H, 6.92; N, 19.15. C₈H₁₀N₂O₃ requires C, 41.09; H, 6.89; N, 19.17%). *m/e* (rel intensity%) 145(100), 131(1), 117(5), 100(6), 90(3), 89(3), 88(4), 74(4), 70(4), 62(50), 58(78) and 45(32).

(ii) *From ethylallophanate* :

Ethylallophanate (0.2 g) prepared⁸ from urea and ethyl chloroformate was dissolved in abs. EtOH (175 ml) and CH₂N₂ liberated from nitrosomethylurea² (1 g) in ether was added to it. The reaction mixture was left for 2 hr at room temperature, solvent distilled and boiled with light petrol. The residue (0.17 g) was unconverted ethylallophanate while the desired product, m.p. 134° was obtained (12%) from the solvent phase on chromatography through neutral alumina.

References

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3-(2-Naphthyl)-1-phenyltriazene 1-oxide as Gravimetric Reagent for Palladium(II)

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SOGANI et al.^{1,2,3} have recommended 3-hydroxy-1, 3-diphenyltriazene (compound I) for the gravimetric determination of palladium. We have now examined 3-(2-naphthyl)-1-phenyltriazene 1-oxide (compound II) and 3-(2-naphthyl)-1-methyltriazene 1-oxide (compound III) as gravimetric reagents for the same purpose. Metal chelates formed by these reagents are granular, insoluble in water, intensely coloured, thermally stable, of definite composition and suitable for direct weighing. Palladium complexes obtained from these reagents are more stable than that from reagent I. In addition, reagent II has more favourable conversion

factor and thus offers a distinct advantage over reagents I and III. Hence, it is considered as a superior reagent for palladium estimation.

Preparation of the reagent :

The reagent is prepared by coupling in molar proportion 2-naphthalene diazonium chloride with phenylhydroxylamine in acetate buffered medium at 0°. The crude product is crystallised from benzene, m.p. 180°.

Reagent solution :

One gram of the reagent is dissolved in 100 ml of 0.5% alcoholic KOH.

Procedure for determination :

An aliquot of the solution, containing 10 to 25 mg of the metal, is diluted to 100 ml with distilled water. 5.0 ml of 10% w/v sodium acetate is added to it. Requisite amount of 1*N* HCl is then added to bring the pH between 2.5 and 3.5. To this solution, which may also contain varying quantities of foreign ions, reagent solution (20 to 25% in excess to that required by stoichiometry; metal to ligand, 12) is added. Palladium complex separates out as a green precipitate. The suspension is heated on a boiling water bath with occasional stirring for 30-35 min. The complex becomes granular and its colour changes to greenish-yellow. It is filtered using a G3 sintered crucible, washed with 25% hot aqueous-alcohol, until the washing gives no colour with 1% NaOH solution. Triazines develop an intense yellow colour with dil. NaOH solution. The precipitate is finally washed with 95% alcohol and dried to a constant weight at 120-125° for an hour. Conversion factor, 0.1687.

Adopting the above procedure, 10 to 25 mg of palladium has been gravimetrically determined in presence of 0.1 g of cobalt (II), nickel (II), zinc (II), manganese (II), cadmium (II), mercury (II), beryllium (II), magnesium (II), lead (II), aluminium (III), arsenic (III), chromium (III), thorium (IV), rhodium (IV), ruthenium (III), uranyl (II), tungstate, phosphate, fluoride, alkali and alkaline earth metals. The interference of zirconium (IV), tin (IV), titanium (IV) and molybdate is masked with sodium fluoride, and that of bismuth (III) and antimony (III) with sodium potassium tartrate. Hydrolysis of cerium (IV) is prevented by adding a small amount of solid ammonium sulphate. To separate palladium from platinum upto ten times its own weight, the method of Sogani et al.¹ has been successfully employed. Gold (III), silver (I), tin (II), vanadium (IV) and vanadate interfere in palladium estimations. Cyanide, more or less, completely masks the precipitation.

References

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