

CONVENIENT SYNTHESSES OF 4-AMINOPENT-3-EN-2-ONE AND ITS COPPER AND NICKEL COMPLEXES

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4-Aminopent-3-en-2-one is generally prepared by the method of Combes,¹ namely, the reaction of warm acetylacetone with dry, gaseous ammonia. However, during the course of a mass spectrometric study of metal complexes of β -amino ketones,² it was found that acetylacetone could react with *aqueous* ammonia to give a practically quantitative yield of the β -amino ketone. These results are reported in the light of a recent paper³ describing the rapid preparation of bis(4-aminopent-3-en-2-onato)nickel(II).

Experimental

Slow addition of concentrated ammonia (3 ml, d 0.880) to acetylacetone (2.0 g, 20 mmole) gave a white precipitate of the ammonium salt with the evolution of heat. The reaction mixture was allowed to stand in a closed flask at room temperature for 24 hr, whereupon a yellow solution (A) was obtained. A similar solution (B) was obtained, more rapidly, by heating a mixture of acetylacetone (2.0 g) and concentrated ammonia (20 ml, d 0.880) on a steam-bath for 15 min in an open flask. Extraction of A or B with ether after saturating with NaCl, followed by drying and removal of the solvent, gave crystalline 4-aminopent-3-en-2-one in 85–90% yield. It had m.p. 42–43° (lit.¹ 43°) on recrystallization from cold ether (Found: C, 60.9; H, 9.0; N, 13.9. C_5H_9NO requires C, 60.6; H, 9.15; N, 14.1%).

Metal complexes were prepared from the isolated β -amino ketone by established methods⁴ but simpler procedures were devised for the copper and nickel complexes. Thus if A or B was added at room temperature, with stirring, to a solution of tetramminecopper(II) ions formed from copper acetate (2.0 g, 10 mmole) in dilute ammonia (50 ml, 1*N*), rapid precipitation of bis(4-aminopent-3-en-2-onato)copper(II) resulted. Similarly, if an aqueous solution of nickel nitrate (2.9 g, 10 mmole) was added to A or B, diluted with water, a precipitate of bis(4-aminopent-3-en-2-onato)nickel(II) was obtained. More product was formed by slowly adding KOH solution to the mother liquors and leaving to stir overnight. The recrystallized products were identical to those prepared from the isolated β -amino ketone by established procedures, and mass spectrometry and elementary analyses confirmed the absence of any β -diketone complex.

Discussion

The aqueous methods of preparation of 4-aminopent-3-en-2-one are much more convenient than the standard procedure.¹ Also, the published preparations of bis-

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¹ Combes, A., and Combes, C., *Bull. Soc. chim. Fr.*, 1892, [3] 7, 778.

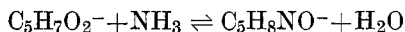
² Lacey, M. J., Macdonald, C. G., and Shannon, J. S., unpublished data.

³ Jameson, R. F., and Peacock, R. D., *J. chem. Soc. (A)*, 1969, 2453.

⁴ Holm, R. H., Everett, G. W., Jr., and Chakravorty, A., *Prog. inorg. Chem.*, 1966, 7, 83.

(4-aminopent-3-en-2-onato)copper(II)⁵ and bis(4-aminopent-3-en-2-onato)nickel(II)⁶ are laborious, insofar as they necessitate the synthesis and isolation of the ligand molecule under anhydrous conditions, and are therefore less attractive than the above methods where the ligand molecule is prepared *in situ*. These complexes are potentially useful as starting materials for the syntheses of other complexes by ligand-exchange reactions.^{7,8}

The method of Jameson and Peacock³ for the facile preparation of bis(4-aminopent-3-en-2-onato)nickel(II) involves the heating of acetylacetone with excess concentrated ammonia until there is no smell of NH₃, then adding aqueous nickel nitrate (sulphate, chloride) solution and basifying to precipitate the complex. However, copper(II) gives bis(acetylacetonato)copper(II) under these conditions. Although these authors postulated a mechanism to account for the difference in behaviour of nickel(II) and copper(II) in their procedure, namely, that only nickel(II) has the ability to displace the equilibrium:



to the right, their results can be rationalized quite simply in terms of the strikingly different rates of hydrolysis of the *pre-formed* 4-aminopent-3-en-2-one (see Experimental) in the presence of nickel(II) and copper(II). Thus, bis(acetylacetonato)copper(II) precipitates from an aqueous solution of the β -amino ketone and copper nitrate after less than a minute's standing, whereas several hours are required before precipitation of bis(acetylacetonato)nickel(II) commences from an aqueous solution of the β -amino ketone and nickel nitrate (though more rapidly on warming⁶). Hydrolysis of the β -amino ketone in the presence of copper(II) is effectively prevented by working in basic solution.

In view of the ease of formation of 4-aminopent-3-en-2-one in aqueous, ammoniacal solution, it is recommended that extra caution be taken in the use of aqueous ammonia as buffer and solvent in the preparation of metal complexes of acetylacetone. Microanalyses of the complexes, if based solely on the carbon, hydrogen, and metal content, may not be sufficiently precise to preclude the possibility that β -amino ketone or mixed-ligand complexes have been formed. Thus, it has been recently found⁹ that the Stites method¹⁰ for the preparation of lanthanon acetylacetonates, using an ammoniacal solution of acetylacetone, results in the formation of ytterbium and lutetium complexes containing an adduct molecule of 4-aminopent-3-en-2-one. Also, bis(4-aminopent-3-en-2-onato)nickel(II) has been found to contaminate bis(acetylacetonato)nickel(II), prepared from an aqueous, ammoniacal solution of acetylacetone and nickel(II).³

⁵ Holtzclaw, H. F., Jr., Collman, J. P., and Alire, R. M., *J. Am. chem. Soc.*, 1958, **80**, 1100.

⁶ Archer, R. D., *Inorg. Chem.*, 1963, **2**, 292.

⁷ Hseu, T.-M., Martin, D. F., and Moeller, T., *Inorg. Chem.*, 1963, **2**, 587.

⁸ Struss, A. W., and Martin, D. F., *J. inorg. nucl. Chem.*, 1963, **25**, 1409.

⁹ Richardson, M. F., Wagner, W. F., and Sands, D. E., *J. inorg. nucl. Chem.*, 1969, **31**, 1417.

¹⁰ Stites, J. G., McCarty, C. N., and Quill, L. L., *J. Am. chem. Soc.*, 1948, **70**, 3142.