Contribution from the New University of Ulster COLERAINE, N. Ireland.

Schiff Base Formation and Activation at a Ferrous Center

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Received, December 13, 1971

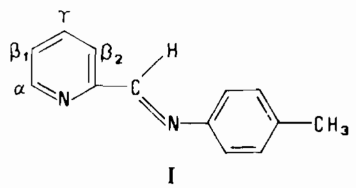
Decomposition of the ferrous complex of N(2-pyridyl-methylene) 4-methyl-aniline with E.D.T.A. gives a convenient route to the parent Schiff base. In acetone/water mixtures this decomposition gives an acetone adduct of the Schiff base, pointing to activation of the -C=N bond by complexation.

Introduction

Template syntheses[1] have most often involved nickel (II) or cobalt (II) centres - rarely Iron (II). We wish to report a simple Schiff base perparation by ferrous iron promoted condensation and subsequent removal of iron by the disodium salt of ethylenediaminetetracetic acid. The orthodox method[2] involves strongly basic conditions and often results in a tarry mess.

Experimental Section

The purple diamagnetic tris di-immine complex of ferrous iron and the Schiff base I was prepared from chloride, pyridine-2-aldehyde and *p*-toluidine and precipitated as the perchlorate.[3] A portion of the purple salt (3.0 gm) was suspended in 200 ml of 50% aqueous methanol and 5 gm of the disodium salt of ethylenediaminetetracetic acid were added. The mixture was stirred on a hot water bath for half an hour, at the end of which time the purple colour of the complex had disappeared. The reaction mixture was extracted with chloroform to give a yellow solution which was decolourized with charcoal, dried over sodium sulphate, and reduced to a yellow oil by evaporating the chloroform. The oil crystallised. The product re-crystallised from petrol (1.5 gm, 74% yield) as colourless needles mp. 57.5-58°C, analysis C, 79.9; H, 6.3; N, 14.0%. The literature mp. of the Schiff base I is 58.5-59°C[2] and the analysis required for $C_{13}H_{12}N_2$ is C, 79.6; H, 6.2; N, 14.3%.



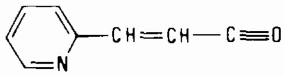
I

When de-metallation of the complex was carried out in 50% acetone/water mixture the product was a white crystalline solid mp. 99°C, with analysis C, 75.8; H, 7.1; N, 11.2%. This corresponds closely to the analysis required for $C_{16}H_{18}N_2O$ (C, 75.6; H, 7.1; N, 11.1%).

Results and Discussion

The fact that de-metallation of the ferrous complex yielded the Schiff base I was confirmed by n.m.r. and mass spectrometry. The n.m.r. spectrum in carbon tetrachloride was assigned as follows (peak intensities in brackets). Pyridine ring: α, doublet, 1.4τ, (1); γ, triplet, 2.25τ, (1); β_1, triplet, 2.75τ, (1); β_2, doublet, 1.75τ, (1); aldimino hydrogen, singlet, 1.45τ (1); aromatic hydrogens, singlet, 2.85τ (4); methyl hydrogens, singlet, 7.65τ (3). The mass spectrum showed a parent ion at m/e = 196 and a slightly stronger peak at m/e = 195 (parent ion –H), corresponding to loss of the aldimino hydrogen forming the stable $-C\equiv N-$ system. Other prominent peaks in the mass spectrum are at m/e = 181 (parent ion $-CH_3$), m/e 169 and 168 (parent ion –HCN, ion m/e 195 –HCN), m/e 91 (tropylium ion), m/e 79 (phenonium ion) and m/e 65 (m/e 91 $-C_2H_2$).

In acetone/water mixtures a different product was obtained, and the simplest formula from the analytical figures corresponded to the Schiff base I plus acetone, giving a molecular weight of 254, which corresponded to the highest m/e value in the mass spectrum. Other prominent peaks in the mass spectrum were at m/e 211 (parent - acetyl) m/e 197 (parent - acetonyl, m/e 147 (parent - toluidine), m/e 132 (possibly II),



II

106 (large) (possibly the methyl-aza-tropylium ion), m/e = 105 (m/e 132 –HCN) and m/e = 43 for the acetylium ion, $CH_3-C\equiv O^+$. In connection with a determination of the actual structure the n.m.r. spectrum in $CDCl_3$ was most helpful, and gave the structure as (III) below.

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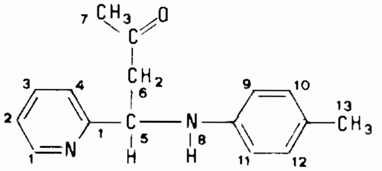
(1) E. g. vide "Transition Metal Complexes of the new Synthetic Macrocyclic Ligands" by D. M. Busch, p. 174 in *Helv. Chim. Acta.* Alfred Werner Commemoration volume (1966). A. E. Martell, *Pure and Applied Chem.*, *17*, 129-178 (1968).

(2) G. Bahr and M. Thamlitz, *Z. anorg. allgem. Chem.*, 282, 3 (1955).

(3) J Burgess and R.H. Prince, *J. Chem. Soc.* (*A*), 434 (1967).



III

The protons 1-13 apeared in the n.m.r. spectrum as follows (intensities in brackets): 1, doublet, 1.45τ, (1); 2,3,4, multiplet, 2.25-2.9τ, (3); 9,10,11, and 12 appear as an A_2X_2 type spectrum characteristic of p-disubstituted benzenes, 10,12, 3.08τ, 9,11, 3.42τ, $J_{9,10}$ = 8.5 cps (4); 5, triplet, 5.05τ, (1); 8, broad, 5.45τ, (1); 6, doublet, 6.95τ, (2); 13, singlet, 7.8τ, (3); 7, singlet, 7.9τ, (3). The latter two peaks were as in acetone and p-toluidine. The infrared spectrum of III gave some further confirmation; peaks at 3260 cm^{-1} (N–H) and 1715 cm^{-1} (C=O) agreed with III and were not present in the spectrum of I.

The compound III can be considered as formed by the attack of acetone on the –C=N– bond of the Schiff base, activated by complexation to ferrous iron. This attack seems also responsible for the "fading" of the ferrous complex in acetone/water mixtures in the absence of E.D.T.A., as we have detected III in the product mixture. This fading could be followed by conventional means and the rate maximum was observed with a 50 mole per cent acetone/water mixture. This points to a hydrate of acetone or possibly a minute amount of acetonyl anion being the reactive species.

Acknowledgments. We thank Drs. A. W. Addison, R. E. E. Hill, and M. V. Twigg for discussions and Mr. D. A. Gallagher for mass spectra, and the S.R.C. for a Postgraduate Studentship (D. J. Farrington).