2-(*N*-Pyrrolidyl)indene; An Enamine of Unusual Stability

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As earlier reported,[1-2] the enamines of 2-indanone have easily been synthesized by mixing ketone and secondary amine in methanol at room temperature without water separation. Moreover, the sterically more hindered enamine of 1-methyl-2-indanone can be prepared in a similar way [3] in good yield using different solvents. This shows an unique stability of these enamines of 2-indanones. These experimental results led us to investigate the equilibrium of the following condensation at 24°C.

Equimolar amounts of 2-indanone and pyrrolidine (0.3 mol/l) were dissolved in diglyme – DMSO (3:1). An appreciable amount of water (4.7 mol/l) was added at the beginning. The PMR-spectra of this mixture showed, after 6 h at the temperature mentioned above, that no 2-indanone could be detected as determined by integration of the peaks from the aromatic protons and the 3-proton. In a control experiment 2-(*N*-pyrrolidyl)indene (0.3 mol/l) and water (5 mol/l) were heated at 80°C for 2 h. Even in this case no ketone could be observed in the spectrum. This spectroscopic evidence clearly proves that the equilibrium is strongly in favour of the product.

Synthetic application of this experiment, using the comparable fast protonation-deprotonation reaction, is a very simple and cheap method of obtaining the fully deuterated enamine.

Experimental. The PMR-spectra were recorded on a JEOL C-60 HL NMR-spectrometer and mass spectra on a LKB Model 9000 Mass spectrometer.

*2-(*N*-Pyrrolidyl)indene-*d_3. 7.0 g 2-(*N*-pyrrolidyl)indene were dissolved in 40 ml of DMSO and 25 ml of dioxane at 80°C under nitrogen. 10 ml of D_2O were added in one portion with stirring and the mixture was heated for another 15 min. After cooling, 6.43 g (92 %) partially deuterated enamine were collected after washing with cold methanol. The whole procedure was repeated twice giving 2-(*N*-pyrrolidyl)indene-d_3 which was deuterated to 98 % as determined from PMR and mass spectra, m.p. 107 – 109°C.

Acknowledgement. The author is indebted to Professor Göran Bergson for valuable discussions.

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Received August 17, 1972.

Reaction of Molecular Oxygen with Mixed Cobalt(II) Complexes Containing (S)-Alanine and Heterocyclic Nitrogen Bases

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Among the reversible oxygen-carrying cobalt(II) complexes, bis(histidinato)-cobalt(II) is remarkable because the dinuclear oxygenated species is relatively stable against irreversible oxidation.[1,2] Apparently histidine, with its imidazole, amino, and carboxyl groups provides ligating atoms in a combination that favours the oxygen-carrying ability of cobalt(II). In this study we have examined complexes with mixed ligand systems which should produce surroundings for the cobalt atom comparable to the ligand sphere in the histidine complexes. The ligands used were (*S*)-alanine in combination

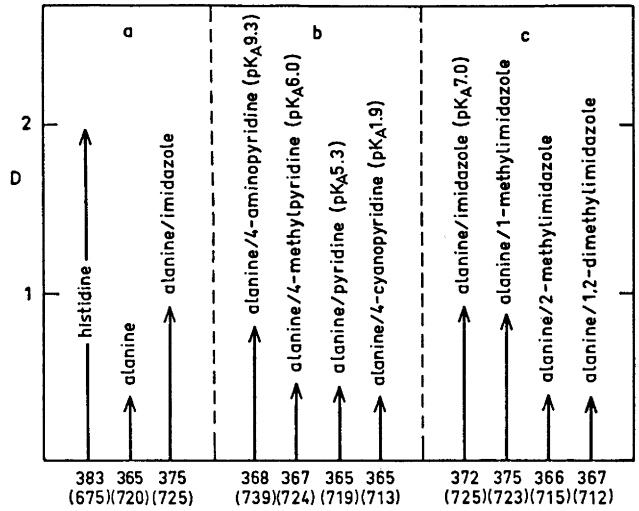

Fig. 1. Details of μ-peroxo absorption maxima. Optical densities given by height of arrows and wavelengths given in nm below each arrow. Pathlength 0.050 cm. a: comparison of histidine and alanine/imidazole systems. b: effect of pK_A of pyridines. c: steric effect of methyl substituted imidazoles. (The wavelengths of the μ-superoxo absorption maxima are given in parentheses.)

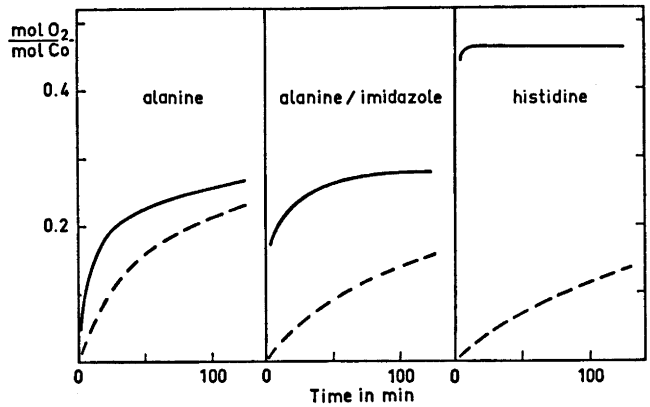

Fig. 2. Total (———) and irreversible (— — —) oxygen uptake as a function of time.

with imidazoles and pyridines. (Histidine is alanine with an imidazole group at the β position.) The solvent was water.

Experimental. The oxygenation reactions were followed by manometric and spectrophotometric methods using the following conditions: Temperature 20.0°C, oxygen pressure 1 atm, pH 9; concentrations: cobalt 1.25×10^{-2} M, (*S*)-alanine *or* (*S*)-histidine 1.25×10^{-1} M, N-base 1.25×10^{-1} M *or* absent. These ligand concentrations were those found to give highest concentrations of the oxygenated species in the cobalt/alanine/imidazole system.

The total oxygen consumed by solutions containing 2.50×10^{-5} mol of cobalt was measured directly by the Warburg technique.[1] The irreversible reduced oxygen was considered

to be that not released on addition of excess EDTA.[2]

The Ce(IV) oxidations were carried out by mixing the brown oxygenated solutions with excess $(NH_4)_2Ce(NO_3)_6$ dissolved in 1 M HNO_3 at 0°C.

Results and discussion. Whereas no reaction could be detected between cobalt(II)/imidazole and oxygen, solutions of cobalt(II)/alanine, with and without addition of N-base, changed from pink to brown on exposure to oxygen. Vigorous bubbling of N_2 through the solution caused the brown colour to disappear and another oxygenation was then possible. The brown colour of the oxygenated solutions was found to be due to broad absorption bands centered around 370 nm, typical of μ-peroxo-dicobalt(III) complexes.[3] The optical density, D, and wavelength of these band maxima, measured after 15 min oxygenation, are shown in Fig. 1. Prolonged exposure to oxygen led to decrease of D and eventual formation of red-violet solutions. No pH change greater than 0.1 unit was observed during the oxidations.

Fig. 2 shows the total and the irreversible oxygen uptake as a function of time for the systems of central interest. The difference between the two curves represents the reversibly bound oxygen.

Evidence for the presence of the μ-peroxo-dicobalt(III) type of oxygenated species was obtained by reaction with Ce(IV). The absorption spectra of the products showed maxima at *ca.* 700 nm; the wavelengths are included in Fig. 1. Such absorptions are characteristic of μ-superoxo-dicobalt(III) complexes which are formed by one-electron oxidation of the brown μ-peroxo species.[3]

The results suggest that under the conditions used cobalt(II)/alanine is oxidised by oxygen to cobalt(III) species and that μ-peroxo-dicobalt(III) complexes are intermediates in this process. When imidazole is also present a higher concentration of μ-peroxo complex is obtained and the rate of irreversible oxidation decreases. Imidazole therefore is coordinated to and is stabilizing the μ-peroxo species. Judging from Fig. 1, the ability of added pyridines to increase the degree of oxygenation increases with increasing pK_A (σ donor strength), but none of the pyridines investigated had as large an effect as imidazole. However, pK_A values are not adequate when comparing pyridines with imidazoles, due to the more pronounced π acceptor properties of the former. The pyridines with low pK_A values and the 2-substituted imidazoles have little influence on the oxygenation reaction, the probable explanation being that they are not coordinating in significant amounts; in the latter case this may be explained by steric hindrance. We note that the wavelength of the superoxo band in the pyridine series (Fig. 1b) decreases with decreasing σ donor strength of the base.

While this work was in progress Jezowska-Trzebiatowska *et al.* reported on the oxygenation of the related cobalt/glycine/imidazole system.[4,5] Addition of alcohol to their oxygenated mixtures precipitated a solid which was found to contain a *mononuclear* cobalt-O_2 complex. However, we interpret our present results in terms of predominant formation in solution of *dinuclear* μ-peroxo complexes

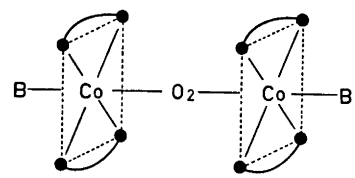

Fig. 3. Possible structure of the oxygenated species.
B ≡ N-base, ●——● ≡ alanine.

such as sketched in Fig. 3. Attempts to determine the composition and structure of these complexes are being made.

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Received August 21, 1972.