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

Department of Organic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

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 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-d₃. 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 D₂O 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 $2 \cdot (N \cdot \text{pyrrolidyl}) \text{ inden} \cdot d_3$ which was deuterated to 98 % as determined from PMR and mass spectra, m.p. $107 - 109^{\circ}\text{C}$.

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

- Schroth, W. and Fischer, G. W. Chem. Ber. 102 (1969) 575.
- Blomquist, A. T. and Moriconi, E. J. J. Org. Chem. 26 (1961) 3761.
- Edlund, U. and Bergson, G. Acta Chem. Scand. 25 (1971) 3625.

Received August 17, 1972.

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

SVEN BAGGER and KEITH GIBSON

Chemistry Department A, Building 207, The Technical University of Denmark, DK-2800 Lyngby, Denmark

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. 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