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NEW COMPOUNDS

Synthesis of New Multidentate Ligands. Carbonyl Addition Reactions of Di-2-pyridyl Ketone

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Ethylenediamine and 1,3-diaminopropane add slowly to the carbonyl group of di-2-pyridyl ketone (dpk) to form the compounds $(py)_2C(OH)NHCH_2CH_2NHC(OH)(py)_2$ and $(py)_2C(OH)NHCH_2CH_2CH_2NHC(OH)(py)_2$, respectively (py = 2-pyridyl). Under reflux conditions in benzene, using boron trifluoride etherate as a catalyst, dpk adds to ethylenediamine, 1,3-diaminopropane, and 1,2-diaminopropane (with loss of H_2O) to form the Schiff bases $(py)_2C{=}NCH_2CH_2N{=}C(py)_2$, $(py)_2C{=}NCH_2CH_2CH_2N{=}C(py)_2$, and $(py)_2C{=}NCH_2CH(CH_3)N{=}C(py)_2$, respectively. These new multidentate ligands were characterized by elemental analysis and infrared, NMR, and thermogravimetric techniques.

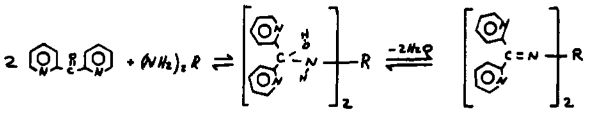
Introduction

In our continuing studies of the coordination chemistry of di-2-pyridyl ketone (dpk), we wish to report the synthesis of several new multidentate ligands formed when dpk condenses with various diamines. It is well established that aldehydes and aliphatic ketones readily undergo addition to primary amines to produce Schiff bases, as shown below (reaction 1) (*1-3*).

$$RR'C{=}O + {:}NH_2R'' \rightleftharpoons RR'C{=}NR'' + H_2O \qquad (1)$$

However, when R and R′ are aromatic groups, as in di-2-pyridyl ketone, the reactions require much more vigorous conditions. To shift the equilibrium to the product side, higher temperatures, increased reaction times, and the use of a catalyst are generally required. Also, removal of water during the reaction greatly enhances product formation (*4,5*). (See ref *6-11* for related dpk information.)

In our investigations, reactions were carried out (in benzene) between di-2-pyridyl ketone and ethylenediamine, 1,2-diaminopropane, and 1,3-diaminopropane. To produce the desired Schiff bases, it was found necessary to use a catalyst (BF_3·etherate), extended reaction times (2-15 h at reflux temperatures) and a Dean-Stark apparatus to remove water as it formed during the reaction. By using diamines and a 2:1 molar ratio of dpk to amine we were able to synthesize compounds containing six nitrogen atoms per molecule. In addition to the Schiff bases, isolation of the "intermediate" hydroxy compounds was also accomplished (reaction 2 where R = $(CH_2)_2$ and $(CH_2)_3$). These hydroxy compounds precipitate slowly from benzene solution after being warmed (no catalyst) and allowed to stand at room temperature for 24-48 h. The coordination behavior of these new ligands with various transition metals is presently under investigation.



(2)

Experimental Section

Spectral Studies. NMR spectra were recorded on a Varian EM 90-MHz unit using deuterated chloroform as a solvent with Me_4Si as an internal standard. Infrared data were obtained in the 4000-600-cm^{-1} region using a Perkin-Elmer 710B instrument. Samples were prepared as Nujol mulls between KBr plates.

Thermal Studies. The thermal decomposition of the compounds was recorded on a Perkin-Elmer TGS-2 system. Finely powdered samples of ~5 mg were heated at 10°/min in a 5-mm platinum crucible under an argon atmosphere at a flow rate of 15 cm^3/min.

Preparation of Compounds. Elemental analyses were obtained from a commercial laboratory.

1,1,6,6-Tetra(2-pyridyl)-2,5-diaza-1,5-hexadiene (I). Di-2-pyridyl ketone (5.53 g, 0.03 mol) was dissolved in 75 mL of dry benzene in a 250-mL boiling flask fitted with a Dean-Stark apparatus. To this solution were added 0.90 g of ethylenediamine (0.015 mol) and 1 mL of 40% BF_3·etherate. After approximately 15 h of relux the orange-brown solution was allowed to cool to room temperature. The solution was reduced to one-half of its original volume under vacuum and allowed to stand in the refrigerator. A white solid was later filtered from the solution under argon and dried under vacuum. An IR spectrum of this product indicated the presence of unreacted dpk (ν(C=O) at 1675 cm^{-1}). Recrystallization from dry benzene yielded the desired product with a yield of about 20%. The compound has a melting point of 174-177 °C. Infrared spectra show the disappearance of the carbonyl band of dpk (1675 cm^{-1}) and the appearance of a new band at 1635 cm^{-1} (ν(C=N). Other diagnostic absorptions occur at 1590 and 1565 cm^{-1} (pyridyl ring stretchings) and 1002 cm^{-1} (pyridyl ring breathing). The Schiff bases III and V produced similar results.

1,1,6,6-Tetra(2-pyridyl)-2,5-diaza-1,6-dihydroxyhexane (II). Di-2-pyridyl ketone and ethylenediamine were dissolved in benzene as described above with the exclusion of BF_3. The solution was warmed in a 65 °C water bath for 15 min with occasional stirring and then allowed to remain at room temperature for 48 h. A white precipitate which formed was filtered and washed with cold benzene. The yield was 47% and the compound melted at 97-101 °C. IR bands located at 3300 and 3050 cm^{-1} were assigned to the N-H and O-H stretching modes, respectively. Similar bands were found for IV, described below.

1,1,7,7-Tetra(2-pyridyl)-2,6-diaza-1,6-heptadiene (III). A 2:1 mole ratio of dpk (5.53 g) and 1,3-diaminopropane (1.11 g) was refluxed (with 1 mL BF_3 catalyst) for 3 h as previously described. After the solution was cooled and reduced the volume under vacuum, it was placed in the refrigerator. An orange solid precipitated which was washed with dry, cold

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Table I. NMR Spectral Data[a] (ppm Relative to Me_4Si)

compound	
$[(py)_2C(OH)NHCH_2]_2$	7.2–8.8 (py), m; 2.7 (CH_2), s; 1.4 (NH, OH), s
$[(py)_2C{=}NCH_2]_2$	7.2–8.8 (py), m; 3.9 (CH_2), s
$[(py)_2C{=}NCH_2]_2CH_2$	7.2–8.8 (py), m; 3.55 (CH_2), t; 2.1 (CH_2), p
$[(py)_2C(OH)NHCH_2]_2CH_2$	7.2–8.8 (py), m; 2.75 (CH_2), m; 1.6 (NH, OH), m
$[(py)_2C{=}NCH_2CH(CH_3)N{=}C(py)_2]$	7.2–8.8 (py), m; 1.3 (CH_3), d; 3.63(CH_2), d, 3.73 (CH_2), d; 4.05 (CH), m

[a] s = singlet; d = doublet; t = triplet; p = pentet; m = multiplet.

benzene to yield a white solid which proved to be the desired Schiff base. The extreme solubility of this compound in benzene renders recrystallization ineffective. The melting point was found to be 96–97 °C.

1,1,7,7-Tetra(2-pyridyl)-2,6-diaza-1,7-dihydroxyheptane (IV). Dpk (0.03 mol) and 1,3-diaminopropane (0.015 mol) were refluxed in 80 mL of benzene for 2 h. After approximately 50 mL of benzene was removed under vacuum, the solution was allowed to cool for several hours in the refrigerator. A white precipitate formed which was filtered, washed with dry benzene, and dried under vacuum. The NMR spectrum of this compound showed the characteristic band due to benzene protons at 7.2 ppm. Mild heating under vacuum failed to remove the benzene. Attempts to prepare this compound in a manner similar to that described earlier for the hydroxy addition product were unsuccessful due to our inability to purify the product by recrystallization. The solubility of dpk and the product are apparently identical in benzene. Even after repeated recrystallizations there was no decrease in the unreacted dpk content (as judged from the carbonyl band in the IR). We therefore used the more vigorous reflux conditions.

1,1,6,6-Tetra(2-pyridyl)-2,5-diaza-3-methyl-1,5-hexadiene (V). This white solid was prepared in a manner similar to that described above for the other Schiff bases using dpk and 1,2-diaminopropane. The NMR spectrum indicates the presence of benzene in the product which could not be removed by recrystallization or warming under vacuum.

Results and Discussion

The compounds prepared in this study are white solids when pure, but darken slowly when exposed to the atmosphere. Even when stored under dry argon, they become brown after 2–3 weeks at ambient temperatures.

NMR data summarized in Table I clearly indicate the various structural features expected of these compounds. The integrated areas for the different proton environments were all consistent with the theoretical values. The four pyridyl rings present in all compounds yield a complicated multiplet between 7.2 and 8.8 ppm. A noticeable difference is apparent, however, between the Schiff bases and the hydroxy compounds. Specifically, the proton adjacent to the nitrogen of the pyridyl ring shows two doublets centered at 8.8 ppm in the Schiff base and a broad unresolved multiplet in the addition products. For a more detailed discussion of NMR data pertaining to dpk complexes, see ref *7* and *12*.

An interesting structural feature of compound V is the presence of a chiral carbon which renders the adjacent CH_2 protons nonequivalent. These two proton resonances should be split into doublets due to the neighbor C–H proton. As expected, the NMR spectrum contains two very sharp doublets separated by only 0.1 ppm (3.63 and 3.73 with $J = 3$ Hz).

Protons on oxygen and nitrogen are subject to hydrogen bonding and are exchangeable, which may result in partial or complete spin decoupling. In deuterated chloroform both II and IV exhibit a broad unresolved band centered near 1.5 ppm. Due to exchange and H bonding the NH and OH protons are apparently magnetically equivalent in this solvent.

Compound II, when subjected to thermogravimetric analysis, shows a weight loss of nearly 10% at 50 °C. This compares quite closely with the theoretical water content of 8.4%. This was not, however, a satisfactory method to form the Schiff base. Analysis of the hydroxy compound after the 10% weight loss showed it to be an unresolvable mixture of decomposition products. Above 50 °C the compound continually loses weight, the loss becoming extremely rapid above 90 °C. No well-defined plateaus were discernible on the thermograms for the other ligands, but all continually lost weight above 40 °C while heated under an argon atmosphere. The relatively low thermal stability of these compounds was again demonstrated when I was subjected to GC-MS analysis (Hewlett-Packard 5970B). At an injection port temperature of 240 °C and oven temperature programmed from 70 to 210 °C, this Schiff base breaks up into four major neutral fragments. The atomic masses of these fragments, with tentative formulas are as follows: mass 170, $(py)_2CH_2$; mass 185, $(py)_2CHNH_2$; mass 196, $(py)_2CNCH_2$; and mass 247, $(py)_3CH$. It is interesting to note that the atomic mass of 196 is exactly one-half of the original molecule. Compounds II, III, and IV decompose under the same conditions to produce a common neutral fragment of *m/e* 170, similar to I. The mass 196 fragment was also prominent in III.

Registry No. I, 102285-13-2; II, 102285-14-3; III, 102285-15-4; IV, 102285-16-5; V, 102306-09-2; di-2-pyridyl ketone, 19437-26-4; ethylenediamine, 107-15-3; 1,3-diaminopropane, 109-76-2; 1,2-diaminopropane, 78-90-0.

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