



SYNTHESIS OF SOME SCHIFF BASES

Six new Schiff bases having — ONNO — donor system have been synthesized from the condensation of biacetyl monoxime, benzil, *o*-vanillin, 9,10-phenanthrene quinone and ethanolamine, 1,3-diaminopropan-2-ol, ethylenediamine. Their characterization has been based on their physical, analytical and spectral data.

1 — INTRODUCTION

Throughout the years Schiff bases have played an important role as chelating ligands for a large variety of metal ions. Recently, more emphasis has been put in the Schiff base complexes of metals as it plays an important role in understanding complex biochemical reactions. Schiff base complex formation as intermediate in biochemical reactions have already been reported long time ago [1], even before the general preparation of the Schiff base ligands [2]. Large number of Schiff bases complexes of metal ions are prepared *in situ*. But the isolation of the free base before its reaction with a metal ion has many advantages. The major disadvantage in *in situ* reaction is that the reactants used to prepare Schiff bases are often good coordination agents themselves. Hence, a small excess of the one or the other of these reactants may give rise to other complexes of the metal ion and thus contaminate the product. Also characterization of the free ligand gives the chance of comparative study to be made of its physico-chemical properties with those of the corresponding metal complexes. Keeping this end in view, we have undertaken the synthesis of some multidentate Schiff bases, which are potential ligands for transition metal ions to study their physiological properties and to study the complex biochemical processes involving these metal ions and Schiff bases. The present paper describes the preparation and characterization of Schiff bases including α -diimines.

2 — EXPERIMENTAL

2.1 — MATERIALS

Biacetyl, benzil, biacetyl monoxime, *o*-vanillin, 9,10-phenanthrenequinone, ethanolamine, ethylene diamine, 1,3-diaminopropan-2-ol were obtained commercially and were used without further purification.

2.2 — IR, NMR AND UV SPECTRA

I.r. spectra were recorded by using a PERKIN-ELMER 580 Spectrometer (4000–400 cm^{-1}) in nujol mull.

N.m.r. spectra were recorded on a PERKIN-ELMER EM 360–60MHz Spectrometer using TMS as internal standard in CDCl_3 solvent.

U.v. spectra were measured by using a HEWLETT-PACKARD 8450A Spectrophotometer.

Molecular weights are quoted from the parent peak in mass spectra.

2.3 — SYNTHESIS OF SCHIFF BASES

2.3.1 — ATTEMPTED CONDENSATION OF BIACETYL AND ETHANOLAMINE, [BA-ENOL-H₂], C₈H₁₆N₂O₂

i) To a solution of biacetyl (0.1 mole; 8.61 g) in absolute ethanol (50 cm³) stirred at room temperature was added ethanolamine (0.2 mole; 12.02 g). Reaction took place immediately with the evolution of heat. The reaction mixture was then boiled under reflux for 1 h. Removal of ethanol left a tarry mass which resisted all attempts at purification and characterization.

ii) The reaction was repeated using dry benzene instead of ethanol as solvent. This also produced the tarry mass which seemed to be polymeric product.

2.3.2 — CONDENSATION OF BENZIL AND ETHANOLAMINE: [B-ENOL-H₂] C₁₈H₂₀N₂O₂

Ethanolamine (0.2 mole; 12.02 g) was added to a stirred solution of benzil (0.1 mole; 21.02 g) in dry benzene (50 cm³) at room temperature. The reaction mixture was then boiled under reflux for 1 h. The water formed in the reaction was then distilled off azeotropically with benzene. Evaporation of the solvent at reduced pressure gave a pale yellow oil. The oil was triturated with benzene and pet-ether (1:1) and was stored in the freezer for 48 h. The precipitated solids were filtered off and was found to be unreacted benzil. Solvents were then removed from the filtrate under vacuum at 40°C. The almost colourless heavy oil (23.71 g; 80%) was found to be the desired product. (Found C 72.81, H 6.76, N 9.39; C₁₈H₂₀N₂O₂ calcd. C 72.95, H 6.80, N 9.45%) M.W. 296 (calcd. 296.36); i.r. (nujol) ν OH 3390, ν C=N 1630, ν C-O 1066 cm⁻¹; nmr (CDCl₃) δ Ph 6.80-7.12 m, δ -N-CH₂-2.80 t, δ -CH₂-O 3.60 t, δ OH 7.20 s,b, ppm; u.v. (MeOH) 220, 260, 305 nm.

2.3.3 — CONDENSATION OF BIACETYL MONOXIME AND ETHANOLAMINE: [BAM-ENOL-H₂] C₆H₁₂N₂O₂

Ethanolamine (0.1 mole; 6.01 g) was reacted with biacetylmonoxime (0.1 mole; 10.11 g) in the same manner as in 2.3.2. After usual working up a white

crystalline solid (11.15 g; 77%) was obtained. M.p. 112°C [MeOH]; (Found C 49.89, H 8.23, N 19.29; C₆H₁₂N₂O₂ calcd. C 49.99, H 8.39, N 19.43%); M.W. 144 (calcd. 144.18); i.r. (nujol) ν OH 3410, ν N-OH 3360, ν C=N 1620, ν C-O 1082 cm⁻¹, nmr (CDCl₃) δ CH₃ 1.46 s, 1.90 s, δ N-CH₂ 2.86 t, δ -CH₂O 3.70 t, δ OH 7.60 s,b, δ N-OH 9.60 s,b ppm; u.v. [MeOH] 210, 240, 325 nm.

2.3.4 — CONDENSATION OF 9,10-PHENANTHRENE-QUINONE AND ETHANOLAMINE: [PQ-ENOL-H₂] C₁₈H₁₈N₂O₂

Ethanolamine (0.2 mole; 12.02 g) was reacted with 9,10-phenanthrene quinone (0.1 mole; 20.82 g) in benzene (100 cm³) in the same manner as in (2.3.2). Usual workup gave the desired product as dark-yellow powder (17.66; 60%); m.p. 250°C [MeOH-CHCl₃]; (Found C 73.30, H 6.11, N 9.40; C₁₈H₁₈N₂O₂ calcd. C 73.45, H 6.16, N 9.52%); M.W. 294 (calcd. 294.34); i.r. (nujol) ν OH 3410, ν C=N 1615, 1560, ν C-O 1065, cm⁻¹, nmr (CDCl₃) δ Ph 7.15-7.30 m, δ N-CH₂ 3.65 t, δ -CH₂O 3.33 t, δ OH 7.70 s,b; u.v. [CHCl₃] 211, 254, 301, 334, 400, 500 nm.

2.3.5 — CONDENSATION OF BENZIL AND ETHYLENEDIAMINE: [BB-EN] C₃₂H₂₈N₄

Benzil (0.1 mole; 21.02 g) and ethylenediamine (0.1 mole; 6.01 g) were reacted in benzene (50 cm³) in the same fashion as in (2.3.2). Usual work-up gave the desired product as yellow solid (19.68 g; 84%); m.p. 154°C [MeOH]; (Found C 82.10, H 5.88, N 11.90; C₃₂H₂₈N₄ calcd. C 82.02, H 6.02, N 11.96%); M.W. 468 (calcd. 468.57); i.r. (nujol) ν C=N 1650, 1550 cm⁻¹; nmr (CDCl₃) δ N=C-Ph 6.85-7.12 m, δ N-CH₂-CH₂-N 3.30-3.60 m; u.v. [CHCl₃] 215, 255, 310, 402 nm.

2.3.6 — CONDENSATION OF o-VANILLIN AND ETHYLENEDIAMINE: [o-VAN-EN-H₂] C₁₈H₂₆N₂O₄

o-Vanillin (0.1 mole; 15.21 g) and ethylenediamine (0.05 mole; 3.01 g) were reacted in benzene (50 cm³) as in (2.3.2). Usual work-up of the reaction mixture gave the desired product as yellow needles (13.13 g; 80%) m.p. 165°C [EtOH]; (Found C 65.69, H 6.08, N 8.49; C₁₈H₂₆N₂O₄ calcd. C 65.84, H 6.14, N 8.53%); M.W. 328 (calcd. 328.36); i.r. (nujol) ν OH 3400, ν C=N 1628, ν C-O 1370 cm⁻¹, nmr (CDCl₃) δ N=C-H 8.33 s, δ Ph 6.84 m.

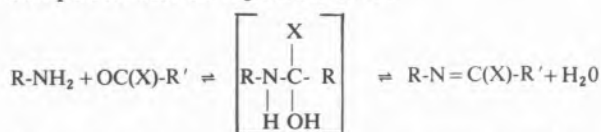
δ CH₃-O and -CH₂-3.70-3.87 m, δ OH 12.12 s,b ppm: u.v. [CHCl₃] 223, 263, 310, 368, 400, 420, 435 nm.

2.3.7 — CONDENSATION OF *o*-VANILLIN AND
1,3-DIAMINOPROPAN-2-OL:
[*o*-VAN-DAP-H₃] C₁₈H₂₂N₂O₅

o-Vanillin (0.1 mole; 15.21 g) and 1,3-diaminopropan-2-ol (0.05 mole; 4.51 g) were reacted in benzene (50 cm³) as described in (2.3.2). Usual workup of the reaction mixture gave the desired product as dull yellow solid (13.08 g; 73 %). M.p. 125°C [yellow needles from EtOH/CHCl₃]; (Found C 63.62, H 6.09, N 7.63; C₁₉H₂₂N₂O₅ calcd. C 63.88, H 6.19, N 7.81 %); M.W. 358 (calcd. 358.39); i.r. (nujol) ν -OH 3420, ν C=N 1632, ν C-O 1260 cm⁻¹; nmr (CDCl₃) δ N=CH 8.30 s, δ Ph 6.90 m, δ CH₃-O and -CH₂- 3.68-3.84 m, δ Ar-OH 12.90 s,b, δ C-OH 7.80 s,b, ppm: u.v. [MeOH] 216, 218, 226, 245, 248, 262, 274, 283, 294, 299, 369, 418 nm.

3 — RESULTS AND DISCUSSION

The general reaction of an amine with a carbonyl compound can be represented as:



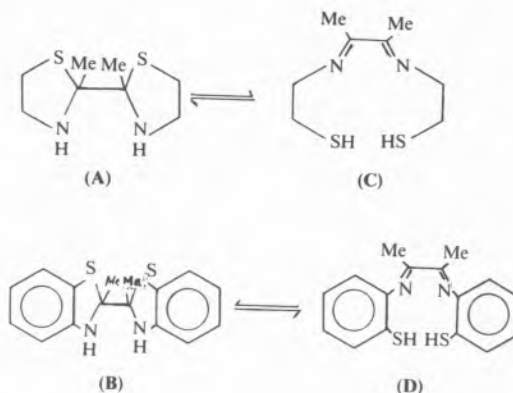
where R and R' are the organic moieties and X is an alkyl, aryl or hydrogen.

The reaction is often catalyzed by the presence of either an acid or a base. In some cases, unless the water formed in the reaction is removed, the formation of Schiff base does not proceed favourably. Our attempt to isolate the Schiff base, BA-ENOL-H₂, from the condensation of biacetyl and ethanolamine, in the absence or presence of H⁺ or OH⁻, always resulted in the formation of a polymeric material which we failed to identify.

Many 2-Hydroxy or 2-Thiol amines are known to react with aldehydes or ketones to give heterocyclic compounds instead of Schiff bases [3,4]. It has earlier been reported that an α -diimine system is very difficult to isolate and the system is stabilized only in the presence of a metal ion [5]. Reaction of biacetyl and β -mercaptoethanolamine, in the presence of Ni²⁺, has given the α -diimine complex in good yields [6]. On the other hand biacetyl and β -mercaptoethanolamine in 1:2 molar

ratio gave dithiazolidiene (A) [7,8]. Similarly, 2-thioaniline has given the corresponding dibenzothiazoline (B) [9].

Nevertheless, in solution, it has been shown that both the products exist in equilibrium with their respective tautomeric Schiff bases (C) and (D):



Addition of a number of metal ions to the solution of (A) and (B) has given rise to high yields of intensely coloured metal complexes of (C) and (D) [8-14]. It has been postulated that the metal ion sequesters the Schiff base form from the equilibrium and hence, thermodynamic template effect appears to operate in these reactions.

We successfully condensed biacetyl and ethanolamine in the presence of Fe²⁺, Fe³⁺, Co²⁺, Ni²⁺ and Cu²⁺ with a hope that the ligand exchange reaction with a strong coordinating ligand such as CN⁻ ion would help us in isolating the free base, BA-ENOL-H₂. Unfortunately, we failed to obtain the free Schiff base.

On the other hand, the reaction of benzil, also an α -diketone, with ethanolamine in anhydrous benzene, occurred smoothly and we isolated the Schiff base, B-ENOL-H₂, an α -diimine, in good yield. We also isolated the Schiff base, BAM-ENOL-H₂, from the condensation of biacetylmonoxime and ethanolamine.

Apart from the Schiff bases, B-ENOL-H₂ and BM-ENOL-H₂, which are colourless, all other Schiff bases are yellow powders or needles.

The i.r. data of the Schiff bases exhibit a strong absorption around 1615-1650 cm⁻¹, which can be attributed to C=N stretching vibration [15]. In some cases we have observed another band around 1550-1570 cm⁻¹, which may also be due to ν C=N.

The absorption around 1065-1080 cm^{-1} is due to ν alkyl-C-O and that of 1260-1370 cm^{-1} is due to ν aryl-C-O-. Two other bands in the region 880 cm^{-1} and 770 cm^{-1} may be assigned to -C=N-C bending.

Their n.m.r. spectra exhibit the peak for aryl-OH around 12 ppm and that of alkyl-OH around 7.70 ppm. Both the peaks are broad and disappear on addition of D_2O to the sample. A slight shift observed for the values of $\delta = \text{N-CH}_2\text{-}$, $\delta\text{CH}_2\text{-O-}$, is probably due to imine bond formation. In case of *o*-vanillin bases, $\delta = \text{N-CH}_2\text{-}$ is difficult to assign as it appears with $\delta \text{O-CH}_3$. A slight shift in the values for $\delta\text{-N=C-R}$ (where R-Me or Ph), in case of B-ENOL- -H_2 and BAM-ENOL- -H_2 , are also due to imine bond formation.

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