171. Synthesis of 1,2,4,5-Tetrazino[1,6-*a*: 4,3-*a*′]diquinoxaline

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Summary

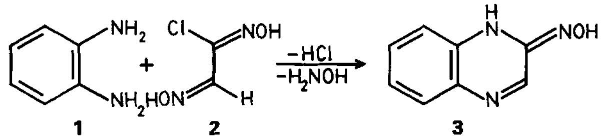
A new one-step synthesis of 2(1*H*)-quinoxalinone oxime (3) from (1,2-benzenediamine (1) and s-*trans*-chloroethanedial dioxime (2) is described. This oxime is converted into a new heterocyclic compound, 1,2,4,5,-tetrazino[1,6-*a*:4,3-*a*′]diquinoxaline (4), by the template effect of Co(II) and Ni(II) ions.

Introduction. – The aid of metal ions as templates to direct the steric course of condensations for heterocyclic compounds has been reported [1–3]. A metal ion brings together the reactants by coordination and the reaction takes place in a series of stereochemically controlled steps. The template effect also enables the synthesis of some compounds which are not otherwise accessible. We have investigated the structures and transition metal complexes of diaminoglyoxime and its substituted derivatives [5–12]. A completely conjugated 12-membered macrocycle, dibenzo[b,h]-1,4,7,10-tetraazacyclododecyne, has been obtained by refluxing its octahydrodioxime derivative in dimethyl sulfoxide [13].

A one-step preparation of 2(1*H*)-quinoxalinone oxime (3) is described, and a new heterocyclic ring system, 1,2,4,5-tetrazino[1,6-*a*:4,3-*a*′]diquinoxaline, obtained a template reaction was introduced.

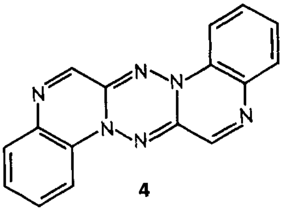
Results and Discussion. – The synthesis of 2(1*H*)-quinoxalinone oxime (3) from 2-(hydroxyimino)-1,2,3,4-tetrahydroquinoxaline has been reported [14] *via* the tetrahydro derivative obtained from *N*-(cyanomethyl)-1,2-benzenediamine and hydroxylamine by elimination of NH_3 [15]. After dehydrogenation with diethyl azodicarboxylate ($C_2H_5CO_2-N=N-CO_2-C_2H_5$), 3 was prepared [14].

In this work, 3 was synthesized in one-step by reaction of s-*trans*-chloroethanedial dioxime (2) with 1,2-benzenediamine (1) and elimination of H_2N-OH *(Scheme)*. The formation of a quinoxaline ring probably directed this cyclization. Similar reactions of



oxime and amine groups have been reported; *e.g.* the synthesis of quinoxaline derivatives from 1,2-benzenediamine (**1**) and α-oximino ketones [16].

In the IR spectrum of **3**, O–H stretching vibration is observed at 3220 cm^{-1}. Bands due to C=N and N–O stretching appear at 1628 and 982 cm^{-1} in agreement with previously reported amidoximes [17]. In the ^1H-NMR spectrum of **3**, the chemical shifts for the OH and NH protons are observed at 10.80 and 8.10 ppm, respectively, disappearing on deuterium exchange. In addition to these two absorptions a singlet at 7.80 ppm and a multiplet at 7.6–6.7 ppm correspond to N=CH and aromatic protons.



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1,2,4,5-Tetrazino[1,6-*a*:4,3-*a'*]diquinoxaline (**4**) was obtained as the product of a template reaction when a solution of $CoCl_2 \cdot 6H_2O$ in EtOH is added to a solution of **3** in EtOH. The color of the solution gradually turns to dark red, and bright crystalline organic compound precipitates. In the case of Co(II), these crystals are the pure **4**. When $NiCl_2 \cdot 6H_2O$ is used as the template ion, a black Ni(II) complex precipitates alongside with **4** as obtained in the case of $CoCl_2$. The elemental analysis correspond to $C_{16}H_{10}N_6$. In the IR spectrum, N–H and OH stretching bands disappeared, while C–H stretching vibrations appear at 3050 cm^{-1}. ^1H-NMR spectrum of $C_{16}H_{10}N_6$ in CF_3COOH showed two types of proton. The multiplet at 8.5–7.7 ppm is due to aromatic protons and the singlet at 9.5 ppm to protons on azomethine bonds. The ratio of HC=N/aromatic protons is 1:4. The chemical shifts are in agreement with the values reported for a similar compound (1,2,4,5-tetrazino[1,6-*c*:3,2-*c'*]- or -[1,6-*c*:4,3-*c'*]-diquinazoline [18].

The mass spectrum of $C_{16}H_{10}N_6$ shows a relatively intense $M^+ + 2$ peak (4.5%) instead of the M^+ peak. This behavior is characteristic for 1,2,4,5-tetrazines [19].

In the spectra of some esters, ethers, amines, aminoesters and nitriles a fragment at $M^+ + 1$ is observed which is due to the abstraction of a proton from a neutral molecule by the molecular ion [20]. The presence of four N-atoms in the tetrazine ring probably causes the abstraction of two protons. Important fragment-ion peaks are found at $m/z = 258$ ($M^+ - N_2$; 56%), 231 (5%), 156 (21%), 129 (100%), 102 (71%). The latter peaks can be derived from further fragmentations of the peak at $m/z = 258$ [21].

Experimental. – The UV/VIS spectra (λ_{max}nm(ε)) were obtained in a *Varian-Techtron* Model *635*. IR spectra (cm^{-1}) were recorded on a *Perkin-Elmer 598* spectrophotometer in KBr pellets. ^1H-NMR spectra were determined on a *Varian-EM-360* 60-MHz spectrometer. Mass spectra were measured on a *Varian Mat 711* spectrometer.

*2(1*H*)-Quinoxalinone Oxime* (**3**). A solution of 1,2-benzenediamine (**1**) (3.24 g, 30 mmol) in abs. EtOH (60 ml) was slowly added with stirring to a solution of s-*trans*-chloroethanedial dioxime (**2**) (2.45 g, 20 mmol) in abs. EtOH (40 ml) at r.t. After 5 min a yellow product started to precipitate and the reaction was complete in 3 h. After filtration, the solid was washed with hot H_2O, then with cold EtOH and extracted with Et_2O; yield 2,29 g (71%); m.p. 186–8°(dec.). After recrystallization in EtOH, the m.p. of the bright yellow crystals became

190°. This compound was soluble in acetone, pyridine, DMSO, DMF and slightly soluble in EtOH, dioxane and AcOEt. UV(EtOH): 243 (1780), 264 (1780), 372 (946). IR: 3220, 3045, 1628, 1610, 1560, 1440, 1323, 1110, 982, 960, 775, 737 cm^{-1}. ^{1}H-NMR ((D_6)DMSO): 10.8 (*s*, 1H); 8.1 (*s*, 1H); 7.8 (*s*, 1H); 7.6–7.35 (*m*, 4H). Anal. calc. for $C_8H_7N_3O$ (161.16): C 59.63, H 4.35, N 26,09; found: C 59.57, H 4.32, N 26.10.

*1,2,4,5-Tetrazino[1,6-*a*:4,3-*a'*]diquinoxaline* (**4**). To a solution of **3** (0.322 g, 2.0 mmol) in 50 ml of EtOH was added $CoCl_2 \cdot 6H_2O$ (0.238 g, 1.0 mmol) in 20 ml of EtOH. The solution became green and turned into dark red by heating on a water-bath. The heating was continued for 1 h and then the solution was evaporated to half of its volume. The precipitated bright dark-red crystals were filtered, washed with H_2O and then with EtOH and extracted with Et_2O; 0.214 g (74.0%); m.p. 250–2°. Compound **4** was soluble in $CHCl_3$, DMF, CF_3COOH and slightly soluble in EtOH, acetone, benzene, pyridine, AcOEt, and DMSO. UV($CHCl_3$): 270 (20920), 360 (31320), 460 (420). IR: 3050, 1605, 1560, 1488, 1350, 1210, 1185, 985, 928, 912, 806, 780, 620, 562, 415. ^{1}H-NMR (CF_3COOH) 9.5 (*s*, 2H); 8.5–7.7 (*m*, 8H). Anal. calc. for $C_{16}H_{10}N_6$ (286.28): C 67.13, H 3.50, N 29.37; found: C 66.43, H 3.50, N 29.04.

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REFERENCES

[1] *J.P. Candlin, K.A. Taylor & D.T. Thompson,* 'Reactions of Transition-Metal Complexes', Elsevier, Amsterdam, 1968, p. 87.

[2] *S. Peng, G.C. Gordon & V.L. Goedken,* Inorg. Chem. *17,* 119 (1978).

[3] *V.L. Goedken & S. Peng,* J. Chem. Soc., Chem. Commun. *1973,* 62.

[4] *N. Bıçak & Ö. Bekâroğlu,* Boğaziçi Universitesi Dergisi-Chem. Eng. *8–9,* 15 (1980); Chem. Abstr. *99,* 15417 g.

[5] *Ö. Bekâroğlu, S. Sarısaban, A.R. Koray & M.L. Ziegler,* Z. Naturforsch., B *32,* 387 (1977).

[6] *S. Sarısaban, H. Wyden & Ö. Bekâroğlu,* Thermochim. Acta *25,* 349 (1977).

[7] *Ö. Bekâroğlu, S. Sarısaban, A.R. Koray, B. Nuber, K. Weidenhammer, J. Weiss & M.L. Ziegler,* Acta Crystallogr., Sect. B *34,* 3591 (1978).

[8] *Y. Gök & Ö. Bekâroğlu,* Synth. React. Inorg. Metal-Org. Chem. *11,* 621 (1981).

[9] *S. Serin & Ö. Bekâroğlu,* Z. Anorg. Allg. Chem. *496,* 197 (1983).

[10] *G. İrez & Ö. Bekâroğlu,* Synth. React. Inorg. Metal-Org. Chem. *13,* 781 (1983).

[11] *A. Gül & Ö. Bekâroğlu,* J. Chem. Soc., Dalton Trans. 2537 (1983); *K. Karadeniz & Ö. Bekâroğlu,* Synth. React. Inorg. Metal-Org. Chem. *13,* 1029 (1983); *C. Bank & Ö. Bekâroğlu,* ibid. *13,* 1047 (1983).

[12] *A. Gül & Ö. Bekâroğlu,* Synth. React. Inorg. Metal-Org. Chem. *12,* 889 (1982); *N. Tan & Ö. Bekâroğlu,* ibid. *13,* 667 (1983).

[13] *C. Bank, K. Trefzer, A. Gül & Ö. Bekâroğlu,* J. Chem. Res. *1984,* 168.

[14] *K. Harsanyi, C. Gönczi & D. Korbonits,* Liebigs Ann. Chem. *1973,* 190.

[15] *K. Harsanyi, C. Gönczi, G. Horvath & D. Korbonits,* Chem. Ber. *105,* 805 (1972).

[16] 'Methoden der Organischen Chemie-Stickstoff Verbindungen 1-Vol X/4', Georg Thieme Verlag, Stuttgart, 1968, p. 278.

[17] *F. Eloy & R. Leaners,* Chem. Rev. *1962,* 165.

[18] *R.A. Bowie, M.D. Gardner, D.G. Neilson, K.M. Watson, S. Mahmood & V. Ridd,* J. Chem. Soc. *1972,* 2395.

[19] *P. Yates, O. Meresz & L.S. Weiler,* Tetrahedron Lett. *1968,* 3929.

[20] *F.W. Mclafferty,* 'Interpretation of Mass Spectra', W.A. Benjamin, Inc., London, 1973, p. 36.

[21] *Q.N. Porter & J. Baldas,* 'Mass Spectrometry of Heterocyclic Compounds', Wiley-Interscience, New York, 1971.