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CONDENSED BENZOPYRANS VI. 8 *H*-PYRANO[3,2-*f*]QUINOXALINES

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The basic ring system *8H*-pyrano[3,2-*f*]quinoxaline and its alkyl, aryl and oxo derivatives (5a-5d) were prepared by the reaction of 5,6-diaminocoumarin with appropriate 1,2-dicarbonyl compounds.

Key words: Pyrano[3,2-*f*]quinoxalines, coumarins, ^{1}H NMR Spectra.

Introduction

Of the various isomeric pyranoquinoxalines only a handful have been mentioned in literature. A 3,4-dihydro-3-methyl-1-ol, derivative of pyrano [3,4-b]quinoxaline (**1**), was obrtained and spectroscopically identified from the action of pyransome dehydratase, of Phanerochaete chrysosporium on osones and the labile intermediate trapped by o-phenylenediamine (Gabriel *et al* 1993). Some derivatives of the system pyrano [3,2-*f*] quinoxaline (**2**) and pyrano [2,3-*f*] quinoxaline (**3**) were prepared from the 6- or 5-hydroxyquinoxalines respectively by their reactions with a,b-unsaturated aldehydes and organotitanium compounds such as titanium tetraethoxide. These pyranoquinoxalines, however, contained aryl groups at 8-(or 9-) position (R_1=R_2=aryl), and various such derivatives are claimed to display photochromism and to have use in ophthalmic optics (Guglielmetti *et al* 1993; Pozzo *et al* 1994; Hara and Momota 1996; Samat *et al* 1997; Pozzo *et al* 1997).

During our continuous interest in condensed benzopyrans containing nitrogen heterocyclic systems we had earlier reported the synthesis of systems with fused pyrrole (Khan and de B Morley 1978, 1979), pyridine (Khan and Gemal 1977, 1978), imidazole (Khan and Caldas 1987) and 1,2,3-triazole rings (Khan and Caldas 1986). In this communication we wish to report our results on the synthesis of *8H*-pyrano[3,2-*f*]quinoxaline ring system.

Experimental

The ^{1}H nuclear magnetic resonance spectra were obtained on a Hitachi Perkin-Elmer R20B spectrometer operating at 60 MHz with tetramethylsilane as internal standard. The infrared absorption spectra were taken by Perkin-Elmer model 727 spectrophotometer. The samples were measured in potassium bromide disks. Melting points were determined with a Fisher-Johns apparatus and are uncorrected. Elemental analyses were carried on a Perkin-Elmer model 240.

8-Oxo-8H-Pyrano[3,2-f]quinoxaline (5a): A mixture of 0.2 g de 5,6-diaminocoumarin (4) (Khan and Caldas 1986), 0.66 g of glyoxal, 10 ml of water and a few drops of hydrochloric acid was heated under reflux for two hours. On cooling the precipitate was filtered off and crystallized from ethanol (activated charcoal). **5a** was obtained as colorless crystals, mp 215-216°C. Yield 0.05 g (20%). Infra red (cm^{-1}) : 1760 (CO lactone); ^{1}H nmr (deuteriochloroform): d6.58 (d, 1H, J=10Hz, H-9), 7.68 (d, 1H, J=10 Hz, H-6), 8.16 (d, 1H, J=10 Hz, H-5), 8.84 (s, 2H, H-2 & H-3), 8.85 (d, 1H, J=10 Hz, H-10).

Anal. Calcd. for $C_{11}H_6N_2O_2$: C, 66.67, H, 3.05, N, 14.14; Found, C, 66.54, H, 3.07, N, 13.91.

2,3-Dimethyl-8-oxo-8H-pyrano[3,2-f] quinoxaline (5b): Using the method for the preparation of **5a**, from 0.1g of 4 and 0.5 ml of diacetyl, 0.1 g (80%) of 5b, was obtained as yellow crystals from dimethylsulfoxide. mp 225-226°C. Infrared (cm^{-1}) : 1720 (CO lactone), ^{1}H nmr (trifluoroacetic acid): d2.70 (s, 3H, CH_3), 2.75 (s, 3H, CH_3) 6.60 (d, 1H, J=10 Hz, H-9), 7.68 (d, 1H, JH=9Hz, H-6), 8.05 (d, 1H, J=9 Hz, H-5), 8.82 (d, 1H, J=10 Hz, H-10).

Anal. Calcd. for $C_{13}H_{10}N_2O_2$: C, 69.02, H, 4.46, N, 12.38; Found, C, 68.87, H, 4.45, N, 12.03.

2,3-Diphenyl-8-oxo-8H-pyrano[3,2-f]quinoxaline (5c): Similarly from 0.10g of 4 and 0.12 g of benzil, 0.12 g of 5c was obtained as yellow crystals from dimethylsulfoxide, mp 293-294°C, yield 60%. Replacing water with ethanol for the

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*Author for correspondence, [c]Present address reaction raised the yield of 5c to 73%. Infrared (cm^{-1}): 1740 (CO lactone); ^{1}H nmr (trifluoroacetic acid): δ 6.59 (d, 1H, J=10 Hz, H-9), 7.20 (m, 10H, Ph), 7.72 (d, 1H, J=10 Hz, H-6), 8.15 (d, 1H, J=10 Hz, H-5), 8.85 (d, 1H, J=10Hz, H-10).

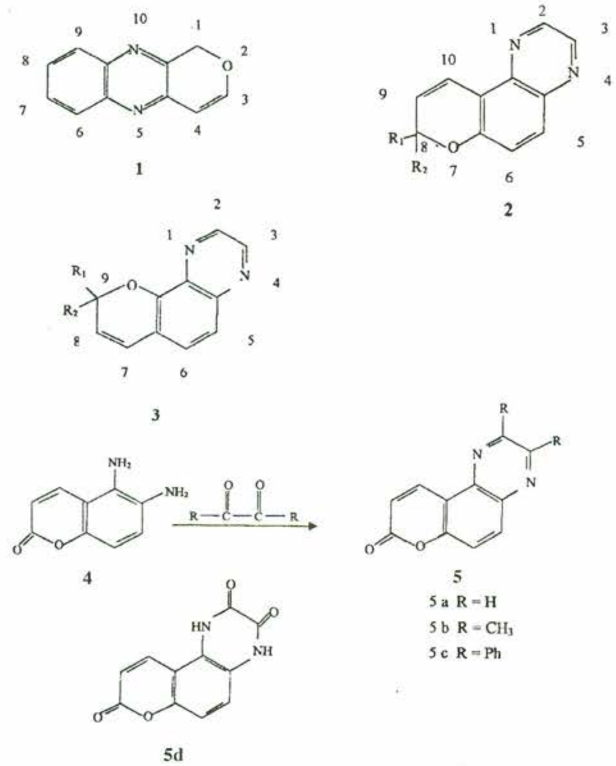
Anal. Calcd. for $C_{23}H_{14}N_2O_2$: C, 78.84, H, 4.03, N, 8.00; Found, C, 78.66, H, 4.09, N, 7.93.

8H-Pyurano[3,2-f)quinoxaline-2,3,8-trione-(5d): Following the method for the synthesis for 5a -5c, 0.1 g of 4 and 0.5 mL of diethyl oxalate, 5d was obtained as rose colored crystals from dimethylsulfoxide, mp>300°C, yield 84%. Infrared (cm^{-1}) : 3100-3000 (br. NH) and 1750-1650 (br. CO amide & lactone). Not very soluble in usual organic solvents for ^{1}H nmr spectrum.

Anal. Calcd. for $C_{11}H_6N_2O_4$: C, 57.40, H, 2.63, N, 12.17; Found, C, 57.62, H, 2.70, N, 11.90.

Results and Discussion

The key starting material for the synthesis of various *8H*-pyhrano[3,2-*f*]quinoxalines is 5,6-diaminoicoumarin (4) which was earlier obtained from coumarin by its successive nitration and reduction (Khan and Caldas 1986). This diaminocoumarin was condensed with 1,2-dicarbonyl compounds for the construction of the quinoxaline ring (Cheeseman 1963; Cheeseman and Werstiuk 1978). The synthesis of various *8H*-pyrano [3,2-*f*]quinoxalines is presented in the scheme 1.



Scheme 1

The condensation of 4 with glyoxal produced the basic ring system of 8*H*-pyrano[3,2-*f*]quinoxalines (5a). Its infrared spectrum was devoid of any absorption bands in the 3200 - 3500 cm^{-1} region indicating disappearance of the two amino groups. This evidence together with its ^{1}H nuclear magnetic resonance spectrum which displayed four doublets at δ 6.58, 8.85, 8.16 and 7.86, with coupling constants of 10 Hz for the protons at positions 9, 10, 5 and 6 respectively and two protons singlet at 8.84 for the protons at 2 and 3 positions, indicated the formation of the desired ring system 5a. The infrared and ^{1}H nuclear magnetic resonance spectra for the compounds 5b-5d, together with their elemental analyses helped, in establishing their structure (see experimental). The compound 5d exists mainly in the "dilactam" form (infrared absorption in the region 3100-3000 cm^{-1} and 1750-1650 cm^{-1} for "lactam" NH and CO respectively).

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