The Reaction of Ethyl 4*H*-Pyran-4-one-2-carboxylate with 1,2-Diaminobenzene

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Ethyl 4*H*-pyran-4-one-2-carboxylate was allowed to react with 1,2-diaminobenzene and related diamines. The resulting products were found to be 8*H*-5,6-dihydro-6,8-dioxopyrido[1,2-*a*]quinoxaline and derivatives. The synthesis 3*H*-5,6-dihydrobenzo[*g*]pyrido[1,2-*a*]quinoxaline-3,5-dione (**2c**) constitutes the synthesis of a derivative of previously unknown benzo[*g*]pyrido[1,2-*a*]quinoxaline ring system.

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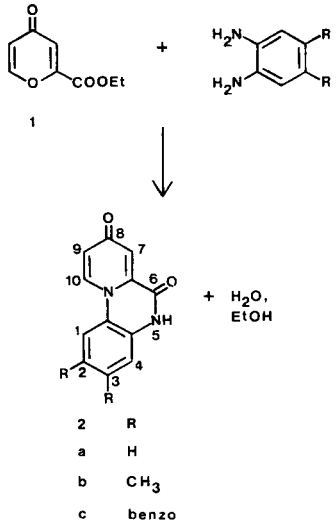
Recently the results of reactions of ethyl chromone-2-carboxylate and related esters with 1,2-diaminobenzene and similar amines were described [1]. In this paper I should like to report results of reactions of ethyl 4*H*-pyran-4-one-2-carboxylate (ethyl comanate) **1** with 1,2-diaminobenzene and related amines. The reaction of **1** with 1,2-diaminoethane had been found to produce 2*H*-1,3,4,8-tetrahydro-1,8-dioxopyrido[1,2-*a*]pyrazine [2]. I have found that direct heating of the same ester with 1,2-diaminobenzene gave the structurally similar 8*H*-5,6-dihydro-6,8-dioxopyrido[1,2-*a*]quinoxaline **2a**. A small amount of ethanol was also isolated from this reaction.

Very little is known about compounds containing this three ring system, although its formation was suggested many years ago by reaction of saccharides with 1,2-diaminobenzene [4]. This suggestion, however, was shown to be in-correct some years later [5]. Recently it was reported that reaction of diethyl chelidonate (diethyl 4*H*-pyran-4-one-2,6-dicarboxylate) with 1,2-diaminobenzene gave the 10-carbethoxy derivative of compound **2a** [6]. The only other similar compounds so far reported are nitro derivatives of 7,8,9,10-tetrahydropyrido[1,2-*a*]quinoxalin-6-one [7]. In this paper I wish to present more information on the physical and spectral properties of this relatively unexplored ring system.



The mass spectrum of compound **2a** indicates a molecular mass of 212 and its ir spectrum contains two strong bands at 1690 cm^{-1} and 1640 cm^{-1} which are likely to be due to the carbonyl groups of the quinoxaline and pyridone moieties of the compound [8]. A weaker band at 3220 cm^{-1} due to the N-H group is also observed in the ir spectrum. Bands at 1685 cm^{-1} 1630 cm^{-1} and 3200 cm^{-1}

Table

Spectral Data of Compounds 2a-2c

Compound	UV [a] max	UV [a] log	IR [b] Wavenumbers cm^{-1}	^1H NMR [c] delta values
2a	209	4.62	1690, 1640,	9.55 d, J = 7, 1H
	231sh	4.35	1580, 1560,	8.52 d, J = 3, 1H
	273	4.10	1280	8.3-8.1 m, 1H
	332	4.24		7.9-6.9 m, 4H [d]
				12.0 s, 1H [e]
				8.85 d, J = 7, 1H
				8.1-7.8 m, 1H
				7.3-7.1 m, 3H
				6.95 d, J = 3, 1H
				6.52 dd, J = 7, 3, 1H
2b	211	4.54	1685, 1620,	9.54 d, J = 7, 1H
	278	4.10	1545, 1395,	8.51 d, J = 3, 1H
	342	4.23	1270	7.98 s, 1H
	358	4.22		7.86 dd, J = 7, 3, 1H
				7.38 s, 1H
				2.50 s, 6H
2c	228	4.63	1690, 1640,	9.72 d, J = 7, 1H
	288	4.40	1620, 1585,	8.72 s, 1H
	357	4.32	1330	8.54 d, J = 3, 1H
				8.2-7.5 m, 6H [d]

[a] Spectra in ethanolic solutions. [b] Spectra of suspensions in bromoform. The wavenumbers of the five strongest bands, rounded to the nearest 5 cm^{-1}, are reported. [c] Solvent deuterated trifluoroacetic acid/deuterated chloroform 1:1 with TMS as the internal standard. This solvent obscures the N-H signal. [d] This signal included the double doublet for the H nucleus in position 9. [e] Solvent deuterated dimethyl sulfoxide; note N-H signal.

have been reported for 2*H*-1,3,4,8-tetrahydro-1,8-dioxopyrido[1,2-*a*]pyrazine [3]. The ^{1}H nmr spectra of compounds **2a**, **b** and **c** also contain signals for the hydrogen nuclei of their pyridone moieties which are strikingly similar to the ones assigned to the analogous nuclei of 2*H*-1,3,4,8-tetrahydro-1,8-dioxopyrido[1,2-*a*]pyrazine [3]. Only compound **2a** was sufficiently soluble in dimethyl sulfoxide for measurement of the ^{1}H nmr spectrum, which contained the N-H signal at 12.0 ppm.

Reaction of ethyl comanate **1** with 4,5-dimethyl-1,2-diaminobenzene and with 2,3-diaminonaphthalene gave analogous compounds 8*H*-5,6-dihydro-2,3-dimethyl-6,8-dioxopyrido[1,2-*a*]quinoxaline (**2b**) and 3*H*-5,6-dihydrobenzo[*g*]pyrido[1,2-*a*]quinoxaline-3,5-dione (**2c**). The condensations leading to these two compounds were carried out in acetic acid. All spectra of **2b** and **2c** supported the proposed structures. All compounds **2a**, **2b** and **2c** are almost colorless and it was difficult to recrystallize them because of their slight solubility/temperature gradient.

EXPERIMENTAL

Melting points were determined on a Mel-temp apparatus and are uncorrected. The ir spectra were taken on a Perkin-Elmer 1330 spectrometer, the uv spectra on a Perkin-Elmer Lambda 6, and the ^{1}H nmr spectra on a Hitachi Perkin-Elmer R 24-A instrument. The analyses were carried out by Baron Consulting Co., Analytical Services, Orange CT, 06477, Dr. H. Agahigian, Director.

8*H*-5,6-Dihydro-6,8-dioxopyrido[1,2-*a*]quinoxaline **2a**.

A mixture of ethyl comanate **1** (0.85 g) and 1,2-diaminobenzene (0.55 g) was heated in a xylene vapor bath to 135°. The mixture melted, but resolidified at the reaction temperature and a small amount of ethanol was collected and identified by its ir spectrum. The solid which had formed was cooled and washed with hot alcohol to give 0.65 g of crude product. Recrystallization from water (with charcoal), followed by sublimation at about 300° and 1.5 mm gave the analytical sample, mp >360°; ms: 212 (M^+, 100), 213 (M+1, 14), 184 (M-28, 75), 155 (M-57, 18), 129, 103, 78. For other spectral data see the Table.

Anal. Calcd. for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.20. Found: C, 68.09; H, 3.53; N, 13.48.

8*H*-5,6-Dihydro-2,3-dimethyl-6,8-dioxopyrido[1,2-*a*]quinoxaline **2b**.

A mixture of ethyl comanate **1** (0.84 g), 4,5-dimethyl-1,2-diaminobenzene (0.68 g) and 10 ml of acetic acid was heated to reflux. Heating was suspended when a solid formed, which was collected after cooling and washed with warm ethanol, yield 0.6 g. Recrystallization from water-acetic acid, 1:1 once with charcoal gave pale yellow material, mp >360°; ms: 240 (M^+, 83), 241 (M+1, 15), 212 (M-28, 100), 197 (M-43, 20), 183 (M-57, 16), 169, 168, 116, 115, 103, 78, 77, 76. For other spectral data, see the Table.

Anal. Calcd. for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.80; H, 4.83; N, 11.69.

3*H*-5,6-Dihydrobenzo[*g*]pyrido[1,2-*a*]quinoxaline-3,5-dione **2c**.

This compound was obtained by refluxing a mixture of ethyl comanate **1** (1.68 g), 2,3-diaminonaphthalene (1.58 g) and 25 ml of acetic acid. The solid which formed after about 45 minutes was collected after cooling, washed with ethanol and ether, yield 1.1 g. Repeated recrystallization from acetic acid and from aqueous acetic acid, 1:1, once with charcoal gave the pale yellow product mp >360°; ms: 262 (M^+, 75) 263 (M+1, 14), 234 (M-28, 100), 205 (M-57, 27), 179, 152, 140, 126, 103, 89, 76, 75, 63, 39. For other spectral data, see the Table.

Anal. Calcd. for $C_{16}H_{10}N_2O_2$: C, 73.27; H, 3.84; N, 10.68. Found: C, 73.01; H, 3.59; N, 10.52.

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