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Synthesis and Mass Spectra of Some 2*H*-Pyrano(2,3-*b*)quinolin-2-ones

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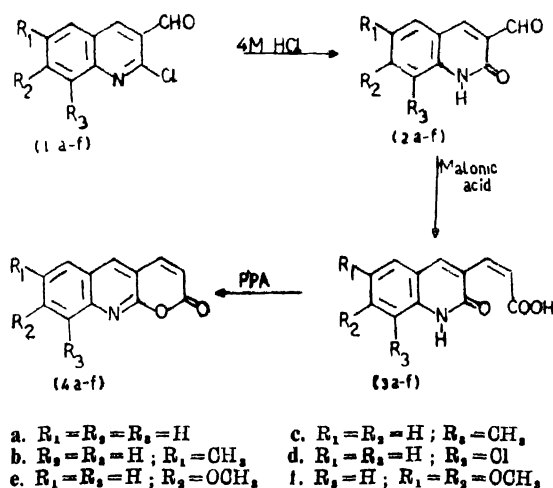
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2*H*-Pyrano(2,3-*b*)quinolin-2-ones are of interest in that they are linear benzaza analogues of coumarins which have gained considerable importance because of their biological and chemical properties¹. As very little work^{2,3} has been done earlier on the synthesis of 2*H*-pyrano(2,3-*b*)quinolin-2-ones, a scheme of synthesis of these compounds was undertaken. The present work describes the synthesis of some new 2*H*-pyrano(2,3-*b*)quinolin-2-ones and their mass spectral fragmentation including that of the parent one. 3-Formyl-2-quinolones (2*a-f*), which may be considered as benzaza analogues of salicylaldehyde were taken as starting materials and were obtained by the acid hydrolysis of 2-chloro-3-formylquinolines (1*a-f*), which in turn were prepared according to the procedure described in literature⁴. 3-Formyl-2-quinolones (2*a-f*) were then condensed with malonic acid under the conditions of Knoevenagel reaction when 3-(2-oxo-1,2-dihydro-3-quinolyl)acrylic acids (3*a-f*) were obtained in 78-82% yield. The acrylic acids (3*a-f*) were then cyclised by employing polyphosphoric acid as cyclising agent and the desired 2*H*-pyrano(2,3-*b*)quinolin-2-ones (4*a-f*) were obtained in yields varying from 69 to 95% (Scheme 1).

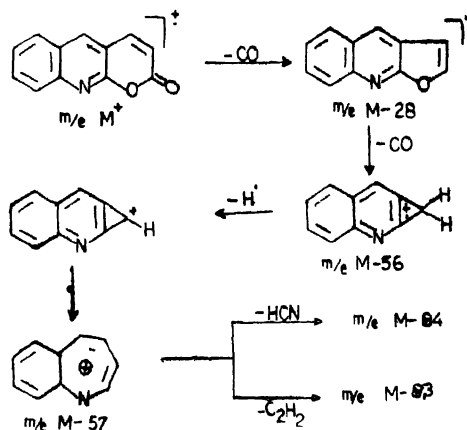
Pyranoquinoquinolines (4*a-f*) exhibit very characteristic pmr spectra. The protons at positions 3 and 4 appear as sharp doublets (J 10 Hz) in the region of δ 6.7-6.9 and 8.25-8.5, respectively, and proton at position 5 appears as a singlet in the region of δ 9-9.4. The signals due to the aromatic protons and methoxyl protons appear in the expected regions.

Mass spectra of the pyranoquinolines (4*a-d*) are also determined. All show intense molecular ion peak as one would expect of this aromatic system. Compounds 4*a* and 4*b* also show half mass peaks corresponding to the doubly charged molecular ion.



Scheme 1

In each case a peak is exhibited at $M-28$ owing to the loss of CO, characteristic of pyrones. Since the subsequent decomposition of $M-CO$ is similar to that of furo(2,3-*b*)quinoline, it might be reasonably inferred, on the lines of the fragmentation of benzofuran⁵ as shown for the parent compound 4*a* in Scheme 2. The ion m/e 140, may possibly have a structure corresponding to benzodehydro-tropilium ion. In case of 4*d* fragments corresponding to ³⁷Cl isotope are also observed.



Scheme 2

Experimental

Hydrolysis of 2-chloro-3-formylquinolines (1*a-f*): A mixture of 2-chloro-3-formylquinoline (0.0104 M) and aqueous hydrochloric acid (35 ml; 4 M) was heated under reflux for 1 h, and then allowed to cool to room temperature. After 1 h the reaction mixture was poured on to crushed ice, when 3-formyl-2-quinolone separated as a yellow solid. It was filtered, washed with water, dried and recrystallised from aqueous acetic acid. M.p., yield, ir and analytical data of 2*a-f* are given in Table 1.

Condensation of 3-formyl-2-quinolones 2a-f with malonic acid: A mixture of 3-formyl-2-quinolone (1.54 g; 0.0082 M), malonic acid (1.73 g; 0.0166 M), pyridine (7 ml) and piperidine (10 drops) in ethanol (10 ml) was heated to 100° in an oil bath with stirring for 2 h. The reaction mixture was then cooled and diluted with water when 3-(2-oxo-1,2-dihydro-3-quinolyl)acrylic acid separated as yellow precipitate. It was filtered washed with water and dried. The product obtained was pure enough for further use. M.p., yield, ir, and analytical data of 3a-f are given in Table 1.

Cyclisation of 3-(2-oxo-1,2-dihydro-3-quinolyl)-acrylic acids 3a-d: Acrylic acid (3a-d) (0.8 g; 0.0035 M) was added with vigorous stirring to the

polyphosphoric acid (prepared from 50 g phosphorus pentoxide and 30 ml orthophosphoric acid) maintained at 245°. The reaction mixture was stirred at this temperature for 2 h. The resulting sticky dark brown mass obtained after cooling was poured onto crushed ice. The clear solution thus obtained was made alkaline with sodium hydroxide (4 M) and immediately extracted with chloroform. The chloroform extract was dried over anhydrous sodium sulphate and distilled off when crude 2H-pyrano(2,3-b)quinolin-2-one was obtained as a brown solid. It was purified by sublimation at 240° under reduced pressure.

In case of 3e and 3f, a mixture of orthophosphoric acid (10 ml) and phosphorus pentoxide

TABLE 1—CHARACTERISATION DATA OF COMPOUNDS

Compd. no.	Yield %	M.p. °C	Molecular formula	Analysis % : Found/(Calcd.)			ν_{max} (cm ⁻¹)
				C	H	N	
3a	96	298	C ₁₀ H ₇ NO ₂	69.02 (69.06)	3.92 (4.05)	8.01 (8.09)	1680, 1550, 3150
b	96	275	C ₁₁ H ₉ NO ₂	70.61 (70.58)	4.63 (4.81)	7.44 (7.48)	1660, 1560, 3200
c	96	284	C ₁₁ H ₉ NO ₂	70.81 (70.58)	4.84 (4.81)	7.61 (7.48)	1680, 1560, 1550
d	88	328	C ₁₀ H ₆ NOCl	57.59 (57.83)	2.68 (2.83)	6.76 (6.74)	1680
e	86	263	C ₁₁ H ₉ NO ₂	64.60 (65.02)	4.86 (4.43)	6.66 (6.89)	1680, 1640
f	88	285	C ₁₁ H ₁₁ NO ₂	63.46 (62.80)	4.95 (4.72)	6.14 (6.0)	1680, 1660
4a	81	319	C ₁₂ H ₉ NO ₂	66.67 (66.97)	4.58 (4.18)	6.29 (6.50)	1680, 1260
b	82	297	C ₁₂ H ₁₁ NO ₂	67.83 (68.12)	4.87 (4.80)	6.11 (6.11)	1680, 1280, 3200
c	82	305	C ₁₂ H ₁₁ NO ₂	67.90 (68.12)	4.87 (4.80)	6.02 (6.11)	1680, 1280, 3200
d	73	287	C ₁₂ H ₁₁ ClNO ₂	57.58 (57.71)	3.54 (3.20)	6.10 (5.91)	1700, 1680, 1200
e	78	295	C ₁₂ H ₁₁ NO ₂	63.79 (63.37)	4.59 (4.48)	5.67 (5.71)	1700, 1680, 1260
f	78	325	C ₁₄ H ₁₃ NO ₂	61.17 (61.09)	4.66 (4.72)	5.07 (5.09)	1700, 1680, 1280
5a	81	248	C ₁₂ H ₇ NO ₂	74.05 (73.09)	3.78 (3.55)	6.98 (7.10)	1740, 1620, 1180, 1180
b	95	240	C ₁₂ H ₉ NO ₂	74.16 (73.98)	4.40 (4.26)	6.44 (6.69)	1740, 1620, 1180, 1120
c	95	230	C ₁₂ H ₉ NO ₂	74.20 (73.98)	4.11 (4.26)	6.50 (6.69)	1740, 1620, 1180, 1135
d	69	280	C ₁₂ H ₉ ClNO ₂	62.81 (62.20)	2.67 (2.59)	5.89 (6.04)	1780, 1620, 1180, 1135
e	53	225	C ₁₂ H ₉ NO ₂	67.66 (68.72)	4.5 (3.90)	5.92 (6.16)	1725, 1625, 1180, 1120
f	46	241	C ₁₄ H ₁₁ NO ₂	64.9 (65.86)	3.9 (4.2)	5.8 (5.4)	1720, 1630, 1200, 1120

TABLE 2—MASS SPECTRAL DATA OF 2H-PYRANO(2,3-b)QUINOLIN-2-ONES
m/e (% abundance)

5a	5b	5c	5d
197(100) 169(44.6)	211(100) 189(84.6)	211(100) 189(84.85)	231(100) 203(50.5)
141(19.7) 140(12.39)	155(2.6) 154(16.78)	155(11.11) 154(8)	175(19.3) 174(3)
114(7) 113(4.2)	140(4.7) 129(3.4)	128(3.8) 127(68)	148(2.6) 147(1.7)
98(1.2) 88(2.5)	127(6) 115(1.2)	115(1.38) 102(3)	140(22.6) 113(3.1)
75(1.7) 70.5(4.72)	105.5(2.5) 97(7.2)	91.5(3.4) 87(1)	101.5(3.3) 87.5(9)
63(2.5) 51(1.7)	63(3.8) 51(4.2)	77(6.8) 63(4.2) 51(4.2)	69.5(2.8) 63(4.2) 50(2.5)

(10 g) was heated on a water bath for 2 h. Acrylic acid(3e, f) (1 g) was added to the above clear solution and stirred at room temperature for 36 h. The reaction mixture was then poured into water (50 ml) and the solution was neutralised with sodium bicarbonate, when pyranoquinolin-2-one was separated as pale yellow solid. It was filtered, dried and sublimed at 280° under reduced pressure. M.p., yield, ir and analytical data of 4a-f are given in Table 1. Mass spectral data are given in Table 2.

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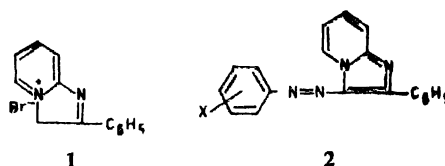
Synthesis of Some 3-Arylazo-1-aza-2-phenylpyrrocoline Derivatives

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1-Aza-2-phenylpyrrocolinium bromide (1) has been synthesised¹ and the greater electrophilicity of position 3 over position 1 in the azapyrrocoline nucleus has been established by nitration² and ethoxy methylation reactions³. A calculation based on the FEMO theory has also reached the same conclusion⁴. We report here the synthesis of some 3-arylazo-1-aza-2-phenylpyrrocolines (2) to adduce further support on greater electrophilicity of position 3.



All the compounds were synthesised in excellent yield by the reaction of different aryldiazonium chlorides with 1-aza-2-phenylpyrrocoline. The structures of the compounds were confirmed by their elemental and spectral analysis. The infrared spectra of the compounds exhibit bands in the region 1630-1590 cm^{-1} due to $\text{N}=\text{N}$ stretching. The diazo compounds absorb light in the range, 366-395 nm due to $n-\pi^*$ transition⁵. Both the values of

TABLE I—PHYSICAL AND ANALYTICAL DATA OF AZO COMPOUNDS (2)

\bar{X}	M.p. °C	Yield %	Molecular formula	λ_{max} nm	ϵ_{max} $\times 10^{-4}$	Analysis % : Found/(Calcd.)		
						C	H	N
H	125	70	$\text{C}_{10}\text{H}_{14}\text{N}_4$	380	0.694	75.98 (76.51)	4.50 (4.69)	18.50 (18.79)
<i>p</i> -CH ₃	90	75	$\text{C}_{10}\text{H}_{16}\text{N}_4$	395	1.058	76.28 (76.92)	4.98 (5.12)	17.64 (17.94)
<i>o</i> -Cl	135	80	$\text{C}_{10}\text{H}_{13}\text{N}_4\text{Cl}$	387	0.591	68.12 (68.57)	3.92 (3.90)	16.68 (16.84)
<i>p</i> -Cl	155	80	$\text{C}_{10}\text{H}_{13}\text{N}_4\text{Cl}$	389	0.993	67.98 (68.57)	3.79 (3.90)	16.50 (16.84)
<i>o</i> -OMe	98	90	$\text{C}_{10}\text{H}_{16}\text{N}_4\text{O}$	397	0.912	72.82 (73.17)	4.71 (4.87)	16.85 (17.07)
<i>p</i> -OMe	120	70	$\text{C}_{10}\text{H}_{16}\text{N}_4\text{O}$	366	0.912	72.95 (73.17)	4.55 (4.87)	16.75 (17.07)
<i>m</i> -NO ₂	115	85	$\text{C}_{10}\text{H}_{13}\text{N}_4\text{O}_2$	370	0.898	65.97 (66.47)	3.61 (3.79)	19.91 (20.40)
<i>p</i> -NO ₂	127	65	$\text{C}_{10}\text{H}_{13}\text{N}_4\text{O}_2$	370	0.885	65.87 (66.47)	3.59 (3.79)	19.86 (20.40)
<i>p</i> -SO ₃ H	142	75	$\text{C}_{10}\text{H}_{14}\text{N}_4\text{SO}_3$	377	0.586	59.90 (60.31)	3.61 (3.70)	14.80 (14.81)
<i>o</i> -COOH	160	80	$\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_2$	372	0.901	69.81 (70.17)	3.98 (4.09)	16.12 (16.97)
<i>p</i> -NH ₂	132	65	$\text{C}_{10}\text{H}_{15}\text{N}_5$	371	0.679	78.85 (74.18)	4.12 (4.22)	21.92 (21.62)