

Nitrogen Bridgehead Compounds. Part 35 [1]. Structures of α -Formyl-2,3-polymethylene-3,4-dihydroquinazolin-4-ones

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The structures of the title compounds bearing a five-, six- or seven-membered *A* ring have been investigated by uv and ^1H and ^{13}C nmr spectroscopy. The imine-enol-enamine (I-II-III) tautomerism of these compounds depends greatly on the ring size. A significant solvent-dependence is observed only for the five-membered-ring compounds **1** and **2**, which in ethanolic solution exist predominantly in the imine form I, and in chloroform solution in the enol form II. The compounds with a six-membered *A* ring, **3** and **4**, are mainly in the enamine form III. On protonation, **3** and **4** change into the *E* and *Z* isomeric mixture of the enol tautomer II. The seven-membered-ring compound **5** is a mixture of the imine I and the enamine III tautomers.

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The 6-formyltetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-4-ones **3** and **4** [2,3] and their homologues [2-4] **1**, **2** and **5** with five- and seven-membered *A* ring, are of interest as starting materials [5] for rutecarpine alkaloids [6] and homologues. The structures of these compounds have not been studied in detail previously to this report.

For **1-5** three tautomeric structures have to be considered: the imine I, the enol II and the enamine III forms (see Scheme 1). The pyrroline derivative **1** was described by Shakhidoyatov *et al* [4] as the enol II, on the basis of the ir and ^1H nmr spectral data, the chemical behaviour and the red colour reaction with ferric chloride. Later, without further investigation or evidence, the same structure was assumed for the homologues **3** and **5** [2,3].

Synthesis.

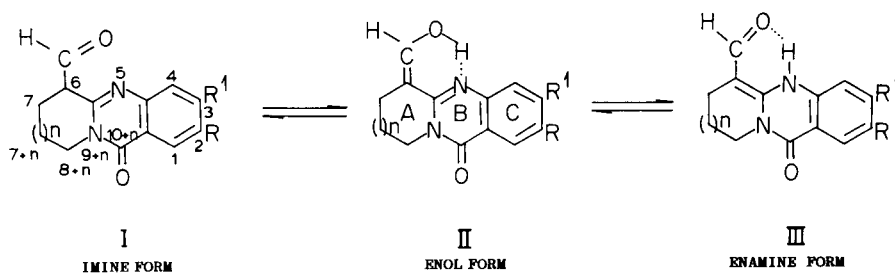
The formyl derivatives **1-5** were prepared from **6-11** by Vielsmeier-Haack formylation (see Scheme 2). Vielsmeier-Haack formylation failed to proceed in only one case, from

the azepino[2,1-*b*]quinazoline (**10**), which is in agreement with an earlier observation [2]. The pyrrolo[2,1-*b*]quinazolines **6** and **7**, subjected to Vielsmeier-Haack formylation and treated in the usual manner (poured onto ice and neutralized with 20% aqueous sodium carbonate), afforded the dimethylaminomethylene derivatives **12** and **13**. Compounds **8**, **9** and **11** under similar conditions furnished the formyl derivatives **3**, **4** and **5**. The azepino derivatives **5** was obtained in 86% yield, against the 6% yield of an earlier report [4]. From the dimethylamino derivative **13**, the formyl compound **2** was prepared directly by alkaline hydrolysis, while **12** was first transformed with sodium acetate to the acetoxymethylene derivative **14**, and the latter was deacetylated by the Zemplén method [7] to the formyl derivative **1**.

UV Study.

The spectra of the starting materials **6**, **8**, **10** ($\text{R} = \text{R}' = \text{H}$) and **9**, **11** ($\text{R} = \text{NO}_2$, $\text{R}' = \text{H}$) in ethanol are very si-

SCHEME 1



SCHEME 2

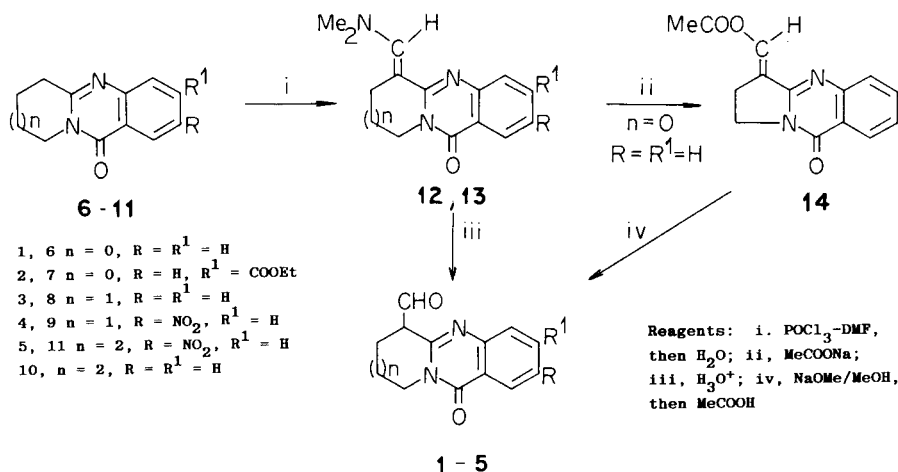


Table 1

UV Data on 2,3-Polymethylene-3,4-dihydroquinazolin-4-ones **1-11** in Ethanol

Compound	n	R	R'	λ max (ϵ)
1	0	H	H	355i (820), 336i (1640), 314 (4630), 303 (4990), 293 (3780), 266 (19500), 225 (25500)
2	0	H	COOEt	350i (1720), 336 (5380), 322 (6480), 312i (5500), 278 (7440), 268 (9050), 235 (39200)
3	1	H	H	355i (17100), 345 (18260), 282i (5150), 275 (6400), 223 (19300)
4	1	NO_2	H	384 (24600), 299 (8400), 234i (17400), 224 (19700)
5	2	NO_2	H	390i (4840), 326 (13900), 213 (30400)
6	0	H	H	314 (3310), 302 (3900), 293i (2850), 269i (7360), 265 (7700), 224 (26300)
7	0	H	COOEt	336 (3090), 322 (7840), 312i (2770), 276 (5610), 264i (6990), 225 (26900)
8	1	H	H	317 (2970), 306 (3550), 296i (2900), 275i (7300), 268 (7480), 225 (26900)
9	1	NO_2	H	324 (11970), 224i (21100), 212 (22360)
10	2	H	H	317 (3260), 305 (4200), 296i (3330), 274i (8330), 267 (8860), 225 (10800)
11	2	NO_2	H	323 (13260), 220i (24100), 213 (26800)

i = inflexion.

milar within each series, independent of the ring size, indicating that they contain the same type of chromophoric system, *i.e.* the quinazoline moiety. In turn, depending on the ring size, the spectra of the products **1-5** differ substantially from one another (see Table 1 and Figure 1), suggesting that the products are present as an equilibrium mixture with various tautomer (I-III) compositions.

The spectra of the products **1-5** did not show a concentration-dependence in the range $10^{-4} - 2.5 \cdot 10^{-6}$ mol/l. The solvent-dependence was pronounced in the five-membered ring series **1** and **2**, but for **3**, **4** and **5** only a very weak, if any, solvent-dependence was observed (see Table 2).

In the five-membered ring series the formyl derivatives **1** and **2** in ethanol exhibited very similar spectra to those of the parent compounds **6** and **7**, apart from a weak absorption and band beyond 330 nm, which appears only for the formyl derivatives. In chloroform, dimethylsulphoxide, (DMSO) and dioxane, however, the spectra of the formyl

derivatives were quite different from those of the starting materials. The spectra of the starting material **6** and of the formyl derivative **1** in various solvents are shown in Figure 2.

Figure 2 and Table 1 suggest that in ethanolic solution **1** and **2** exist mainly in the imine tautomeric form I, where the formyl group is not conjugated with the quinazoline moiety. In chloroform, DMSO and dioxane the enol II or/and the enamine III forms must predominate over the imine form I. The ratio of II and III in solution may vary with the solvent, and this may cause the slight changes in the uv spectra in Figure 2.

In the six-membered ring series the spectra of the formyl compounds **3** and **4** did not resemble those of the starting materials. On this basis we ruled out the predominance of the imine structure I, in the formyl derivatives **3** and **4**. The 9-formyltetrahydropyrido[1,2-*a*]pyrimidin-4-ones, the two rings of which are identical with the **A** and **B**

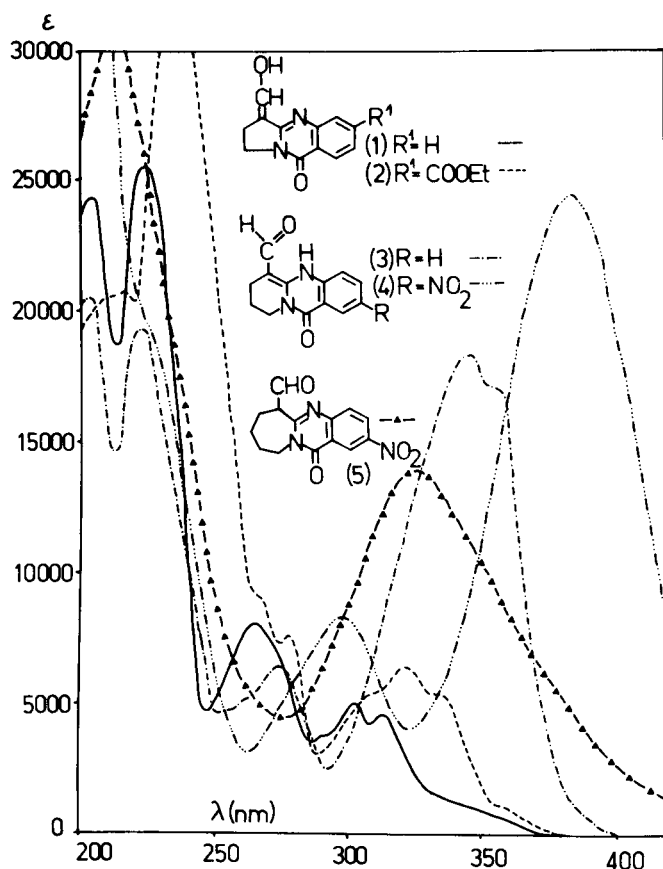


Figure 1. UV Spectra of compounds 1-5 in ethanol.

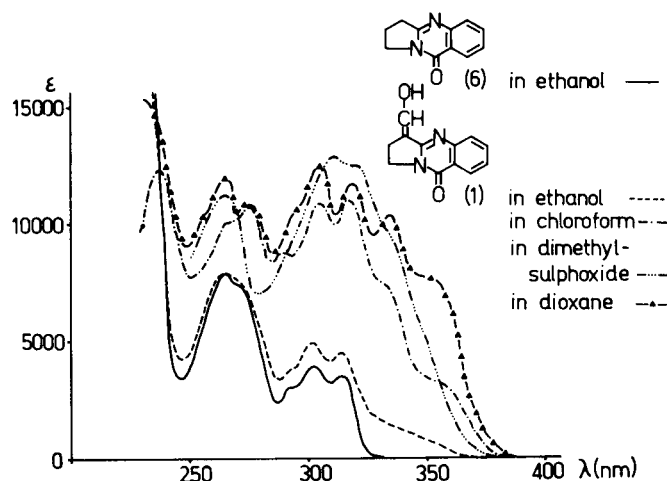


Figure 2. UV Spectra of compound 1 in various solvents and compound 6 in ethanol.

rings of the present tricyclic compounds, were earlier demonstrated to have the enamine structure [8]. By analogy, we assume that the tricyclic derivative 3 and 4 also have the enamine form III.

As the spectra of 1 and 2 in chloroform, DMSO and dioxane are not similar to the spectra of 3 and 4, we presume that in these solvents 1 and 2 have not the enamine III but the enol form II.

In the spectrum of the azepino derivative 5, an absorption maximum appears at 326 nm. This suggests that the imine form of 5 is also present in the equilibrium mixture.

Table 2

UV Data on α -Formyl-2,3-polymethylene-3,4-dihydroquinazolin-4-ones 1-5

Compound	n	R	R'	Solvent	λ max (ϵ)
1	0	H	H	Chloroform	350i (7660), 335 (10400), 319 (11600), 306 (13900), 289 (8730), 275 (10800), 266 (10220)
				DMSO	350i (3150), 333i (9910), 320i (12600), 311 (12850), 284i (9730), 266 (11450)
				dioxane	350i (3300), 330i (8090), 317 (11800), 304 (12500), 294i (10350), 275 (10830), 265 (11800)
2	0	H	COOEt	Chloroform	350i (9100), 334 (11700), 317 (14700), 305 (15500), 294i (12500), 277 (14200)
				DMSO	356 (2640), 334 (8480), 319 (11800), 309 (12300), 298i (10100), 266 (11000)
				dioxane	350i (5570), 331i (9070), 316 (12900), 305 (13800), 296i (11600), 277i (12200), 264 (14790)
3	1	H	H	Chloroform	357i (23000), 347 (24350), 283i (5900), 276 (7800),
				DMSO	360i (17900), 345 (20600), 286i (5300), 278 (6960), 270 (6300)
				dioxane	354i (19000), 343 (20700), 283i (7000), 275 (17200), 268i (15800), 253i (5900), 242i (8100)
4	1	NO ₂	H	Chloroform	388 (29850), 300 (10100)
				DMSO	396 (24410), 306 (10560)
				dioxane	384 (28500), 297 (10450), 232i (9800), 224 (11250)
5	2	NO ₂	H	Chloroform	393 (13940), 300 (4220)
				DMSO	380 (13520)
				dioxane	389 (12570), 300 (9200), 225 (22800)

i = inflexion.

Table 3

¹H NMR Data on α -Formyl-2,3-polymethylene-3,4-dihydroquinazolin-4-ones **1-5** in Deuteriochloroform

Compound	n	R	R'	Tauto-		Ratio %	1-H	2-H	3-H	4-H	NH	6-H	7-H ₂	8-H ₂	9-H ₂	10-H ₂	-CHO or =CH-O	OH
				mer	Isomer													
1	0	H	H	I II	— Z	5 95	8.18 dd			— 7.3-7.8 —	—	—	2.98 m	4.20 m	—	—	10.04 7.41 t [a]	6.60 br
2	0	H	COOEt	I II	— Z	5 95	8.20 m	7.90 dd	—	8.07 m	—	—	2.97 m	4.20 m	—	—	10.04 7.50 t [b]	10.44 br
3	0	H	H	III	—	100	8.02 d	7.13 m	7.55 dd	7.08 m	14.75 br	—	2.52 t	1.97 m	3.94 t	—	8.72 d [c]	—
3 [d]	1	H	H	II II	Z E	75	8.27 d	7.5- 7.7 m	7.92 t	7.5- 7.7 m	—	—	2.64 t	2.13 m	4.18 m	—	7.84 s 8.42 s	—
4	1	NO ₂	H	III	—	100	8.94 d [e]	—	8.38 dd	7.21 d [f]	14.71 br	—	2.60 t	2.00 m	4.00 t	—	8.80 d [g]	—
5	2	NO ₂	H	I	—	39	9.08 d	—	8.45 dd	7.67 d [h]	—	3.83 m [i]					ax 3.58 m [j,k] eq 5.18 dd [j,l]	10.23
				III	—	62	8.90 d	—	8.36 dd	7.20 d [m]	15.52 br	—		2.5- 2.8 m	— 1.3-2.2 m —			4.30 t

[a] $J_{7,}$ = CH-1.8 Hz. [b] $J_{7,}$ = CH-2.0 Hz. [c] $J_{\text{NH,CHO}}$ = 1.2 Hz. [d] in deuteriochloroform:TFA = 1:1. [e] $J_{1,3}$ = 2.0 Hz. [f] $J_{3,4}$ = 9.0 Hz. [g] $J_{\text{NH,CHO}}$ = 1.5 Hz. [h] $J_{3,4}$ = 8.5 Hz. [i] $J_{6,7\text{ax}}$ = 7.0 Hz. [j] $J_{10\text{ax},10\text{eq}}$ = 15 Hz. [k] $J_{10\text{ax},9\text{ax}}$ = 10 Hz. [l] $J_{10\text{eq},9\text{ax}}$ = 6.0 Hz. [m] $J_{3,4}$ = 8.5 Hz. [n] $J_{\text{NH,CHO}}$ = 1.2 Hz.

NMR Studies.

The ¹H and ¹³C nmr data obtained in deuteriochloroform are compiled in Tables 3 and 4. As a consequence of the poor solubilities of the products, saturated solutions were used: nevertheless, due to the unfavourable signal to noise ratio, the low-intensity signals of the ¹³C spectrum of **2** could not be identified, and for **1** and **4** no acceptable ¹³C spectra were obtained.

In rationalizing the spectra, we kept in view that prototropic processes taking place between a carbon atom and a heteroatom are slow in relation to the nmr time scale, and thus the signals of the individual tautomers can be distinguished. This should be the case when interconversion from I to II or III occurs, while the prototropic processes between two heteroatoms are fast, and only time-averaged signals can be observed (interchange between tautomers II and III) [9].

In our structural study the most informative nmr data were the chemical shifts of the protons of the formyl or the hydroxymethylene group, and the signals of the 6-H and N-H protons and the C-6 atom.

The ¹H nmr spectra of the five-membered ring compounds **1** and **2** in deuteriochloroform exhibited signals at 7.41 and 7.50 ppm, respectively, which were assigned to the =CH- proton of the hydroxymethylene group of form II, whereas the six-membered ring compounds **3** and **4** dis-

played signals at 8.72 and 8.80 ppm, respectively, which were assigned to the proton of the formyl group of form III. However, the chemical shift of a formyl group is to be expected at lower field [10] and thus the above chemical shifts must be time-averaged values: this is indicative of a fast equilibrium between forms II and III, favouring the enol form II, in **1** and **2** and the enamine form III in **3** and **4**.

For the bicyclic analogues of **3** and **4** (i.e. for the 9-formyltetrahydropyridopyrimidines) the enol-amine equilibrium ratio was established [1] by ¹⁵N nmr investigation to be 1:7.

In the spectra of **1** and **2** an additional signal, with an intensity of about 5%, was recognized at 10.04 and 10.05 ppm, respectively. This signal is likely to relate to the proton of the formyl group of tautomer I. Non-conjugated formyl protons are expected to appear in this range [10]. The formyl proton of **5**, with a seven-membered A ring, also appears in this region (see later).

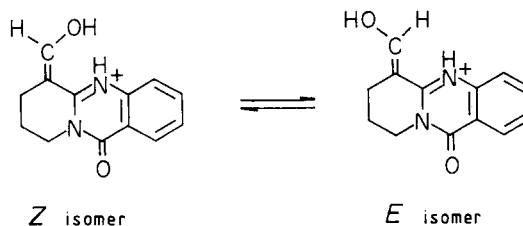
The protonation of **3** in a 1:1 mixture of deuteriochloroform and trifluoroacetic acid (TFA) was also studied. Protonation took place at the oxygen atom of the formyl group (the formyl group of form III can be considered as a part of a vinylogous amide), consequently an enol type structure II was formed and Z:E isomers resulted. This explains the red colour reaction observed on the action of a

Table 4
¹³C NMR Data on α-Formyl-2,3-polymethylene-3,4-dihydroquinazolin-4-ones in Deuteriochloroform

Compound	n	R	R'	Tautomer	Isomer	C-1	C-2	C-3	C-4	C-4a	C-5a	C-6	C-7	C-8	C-9	C-10	C-(10+n)	C-(10+n)a	CHO	=CH-
2	0	H	COOEt	[a] H	Z	127.0 [b]	125.5 [b]		125.1 [b]		157.4	102.9	20.9	45.4	—	—	159.9	122.7	—	159.6
3	1	H	H	III	—	127.6	123.7	135.0	117.0	139.3	150.4	91.0	22.4	20.7	41.9	—	159.9	116.1	182.8	—
3 [d]	1	H	H	II	Z	128.3 [c]	129.0 [c]	137.6	118.7	136.3	154.0	96.6	23.0	20.4	44.5	—	159.7	—	—	164.9
				II	E	128.6 [c]	128.6 [c]	118.2	137.1	157.1	102.2	19.6	44.3	—	159.3	—	—	—	161.1	
5	2	NO ₂	H	I	—	123.8	143.8	128.8	118.9	144.6	150.7	56.1	27.6	25.1	26.2	42.9	160.0	116.6	195.4	—
				III	—	124.6	129.7	129.7	118.9	144.6	150.7	99.4	27.8	25.0	25.6	43.4	—	—	184.4	

[a] ¹³C NMR data: 165.2; 61.6; 14.3. [b] and [c] interchangeable. [d] In deuteriochloroform:TFA 1:1.

Lewis acid (ferric chloride) [4]. The signal of the =CH-proton of the hydroxymethylene group of the *Z* and *E* stereoisomers appeared at 7.83 and 8.33 ppm, respectively, with an intensity ratio of 3:1. Assignment was made on the basis of the anisotropic effect of the C(5a)=N(5) double bond, which causes a downfield shift for the *E* isomer.



The spectrum of the seven-membered ring homologue **5** exhibits signals at 8.70 and 10.23 ppm, with an intensity ratio of 3:2. These signals were assigned to the formyl proton of the enamine III and the imine I forms, respectively. Here again the signal at 8.70 ppm must be a time-averaged signal for the appropriate proton of forms II and III, with the latter predominating. Some further evidence as to the presence of the imine tautomer I was found in the spectrum, e.g. the signal of 6-H, observed as a multiplet at 3.83 ppm. Of the possible conformations of the seven-membered **A** ring [11], of the imine I form of **5** one conformation is preferred, as shown by the non-equivalent C(10) H₂ protons. The axial proton appears at 3.58 ppm, and the equatorial proton, as a consequence of the anisotropic effect of the neighbouring carbonyl group at 5.18 ppm.

The ¹³C nmr spectra support the results of the uv and ¹H nmr studies. In the ¹³C nmr spectrum of the five-membered ring compound **2**, the signal appearing as a doublet at 159.6 ppm indicates the predominance of the enol tautomer II. The six-membered ring derivatives **3** and **4** give rise to a doublet at 182.8 and 184.4 ppm, respectively, pointing to the presence of a conjugated formyl group (form III).

The spectrum of **3** in a 1:1 mixture of deuteriochloroform and TFA reveals that on protonation the tautomeric equilibrium II ⇌ III is shifted towards the enolic form II. The signal of the hydroxymethylene carbon atom in the *Z* geometric isomer appears at 164.9 ppm and in the *E* isomer at 161.3 ppm. As a consequence of the γ gauche steric effect, the C-7 signal of the *E* isomer suffers an upfield shift of 3.4 ppm with respect to the signal of the *Z* isomer.

For the azepinoquinazoline **5**, which exists as a mixture of the imine I and enamine III tautomers, the signal of the non-conjugated formyl group appears in the expected region [1], at 195.4 ppm. The conjugated formyl group of the enamine gives rise to a signal at 184.4 ppm. The tautomers of **5** can also be distinguished on the basis of the signal of the C-6 atom: in accordance with its sp³ character in the imine tautomer I the C-6 atom gives a signal at 56.1 ppm,

whereas its sp^2 character in the enamine tautomer III leads to a signal at 99.4 ppm.

EXPERIMENTAL

The melting points are uncorrected. The uv spectra were recorded with a UNICAM SP-800 spectrophotometer, 1H and ^{13}C nmr spectra in deuteriochloroform solution (TMS as the internal standard) with a JEOL-FX-100 spectrometer. The formylpyridoquinazolinone (3) was prepared by a procedure described in reference 3 [mp 206-208°, from ethanol (lit [3] mp 199-201°)].

6-Formyl-6,7,8,10-tetrahydropyrrolo[2,1-*b*]quinazolin-10-one (1).

To a solution of 6-(acetoxymethylene)-6,7,8,9-tetrahydropyrrolo[2,1-*b*]quinazolin-10-one (14) [2] (10 mmoles) in ethanol (40 ml) sodium ethoxide, prepared from sodium (0.23 g) and ethanol (30 ml) was added. The mixture was kept at 25° for 0.5 hour and the pH of the mixture was then adjusted to 7 with acetic acid. The mixture was evaporated to dryness, the residue was treated with water and the crystalline product was filtered off (1.4 g, 65%), crystallized from ethanol-chloroform, to give formylpyrroloquinazoline (1), mp 207-209° [lit [4] 205-206° (from acetone)].

Ethyl 6-Formyl-10-oxo-6,7,8,10-tetrahydropyrrolo[2,1-*b*]quinazoline-3-carboxylate (2).

A. 10-Oxo-6,7,8,10-tetrahydropyrrolo[2,1-*b*]quinazoline-3-carboxylic acid [12] (23.0 g, 0. mole) was refluxed during 10 hours in ethanol (600 ml) containing 10% of dry hydrogen chloride. The solution was evaporated to dryness, the residue dissolved in water (400 ml) and the aqueous solution neutralized with sodium bicarbonate and extracted with ethyl acetate 4 × 50 ml. The combined extracts were decolorized with charcoal, dried (sodium sulfate) and evaporated. The residue was filtered off, washed with acetone, dried (8.5 g, 33%) and crystallized from ethanol, to give ethyl 10-oxo-6,7,8,10-tetrahydropyrrolo[2,1-*b*]quinazoline-3-carboxylate (7) mp 127-129°.

Anal. Calcd. for $C_{17}H_{14}N_2O_3$: C, 65.11; H, 5.46; N, 10.85. Found: C, 64.96; H, 5.37; N, 10.93.

B. To a cooled solution of the ester 7 (5 mmoles) in DMF (50 mmoles), phosphorus oxychloride (10 mmoles) was added, dropwise at 15-20°. The mixture was stirred at 25° during 1 hour and at 60° during 3 hours. After the mixture had cooled it was poured onto 50 g crushed ice and the pH of the aqueous phase was adjusted to 7 with 20% aqueous sodium carbonate. The precipitated ethyl 6-(dimethylaminomethylene)-10-oxo-6,7,8,10-tetrahydropyrrolo[2,1-*b*]quinazoline-3-carboxylate (13) was filtered off (1.45 g, 92%) and crystallized from ethanol, mp 203°.

Anal. Calcd. for $C_{17}H_{14}N_2O_3$: C, 65.16; H, 6.11; N, 13.41. Found: C, 64.86; H, 5.96; N, 13.35.

C. The 6-dimethylaminomethylene compound 13 (4 mmoles) was stirred in 0.5 *N* hydrochloric acid (10 ml) during 24 hours at 25°. The precipitated crystals were filtered off, washed with water, dried (1.05 g, 92%) and crystallized from ethyl acetate, to give the formyl derivative (2), mp 184°.

Anal. Calcd. for $C_{17}H_{14}N_2O_4$: C, 62.93; H, 4.93; N, 9.78. Found: C, 62.64; H, 4.84; N, 9.66.

6-Formyl-2-nitro-6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (4).

To a cooled solution of 2-nitro-6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one [3] (5 mmoles) in DMF (100 mmoles), phosphorus oxychloride (10 mmoles) was added dropwise at 15-20°. The reaction mixture was stirred at 25° during 6 hours, after the mixture had cooled it was poured onto 50 g crushed ice and the pH of the aqueous phase was adjusted to 7 with 20% aqueous sodium carbonate. The precipitated crystals were filtered off (1.25 g, 93%) and crystallized from acetic acid, then it was heated under reflux in ethanol to give the formylpyridoquinazoline 4, mp 259°.

Anal. Calcd. for $C_{13}H_{11}N_3O_4$: C, 57.24; H, 4.06; N, 15.38. Found: C, 57.44; H, 4.00; N, 15.70.

6-Formyl-2-nitro-6,7,8,9,10,12-hexahydroazepino[2,1-*b*]quinazolin-12-one (5).

2-Nitro-6,7,8,9,10,12-hexahydroazepino[2,1-*b*]quinazolin-12-one [3] (5 mmoles) was formylated as described above, to give the formylazepinoquinazolinone 5 (1.23 g, 86%) which was recrystallized from acetonitrile, mp 200-202° (lit [3] mp 179-181°).

Anal. Calcd. for $C_{14}H_{12}N_3O_4$: C, 58.74; H, 4.26; N, 14.68. Found: C, 59.16; H, 4.38; N, 14.78.

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