Nitrogen Bridgehead Compounds, Part 68 [1]. Studies on Quinolizine Derivatives. Part 2 [2]. Synthesis of 1,3-Disubstituted-4*H*-quinolizine Derivatives.

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Quinolizine compounds **1** and **2** or their monocyclic tautomers **3** and **4** have been synthesized using 2-pyridineacetic acid derivatives **6a**, **b**, **A**, **B** and ethoxymethylenemalonic acid derivatives **7a**, **b**, **c** in base catalyzed or thermic reaction. In the 6-unsubstituted series, both the 4-oxo and 4-imino derivatives could have been obtained, in the 6-substituted series, however the 4-oxo ones only, whereas instead of the 4-imino derivatives, their monocyclic tautomers **3**, **4** have been isolated. In the 6-unsubstituted series, the primarily formed 4-imino compounds have been rearranged into 4-oxo ones under stronger conditions. The structure of the isolated compounds have been proved by ultraviolet, infrared and ^{1}H nmr spectra, that of **3B=C** by X-ray analysis as well.

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Quinolizine is one of the simplest nitrogen bridgehead heterocycles. The parent skeleton and its saturated and fused derivatives are of wide-spread occurence in natural compounds [3]. Numerous biologically active alkaloids contain the quinolizine moiety [4] as well.

Some of the 1-aza-analogues of the quinolizine skeleton, the pyrido[1,2-*a*]pyrimidine derivatives, reveal advantageous pharmacological activity [5]. These compounds are isosters of the appropriate quinolizine derivatives. It might be interesting and useful to compare their chemical and pharmacological properties.

In the present paper, we report the synthesis of compounds of types **1**, **2**, **3**, and **4** [6] (Scheme 1).

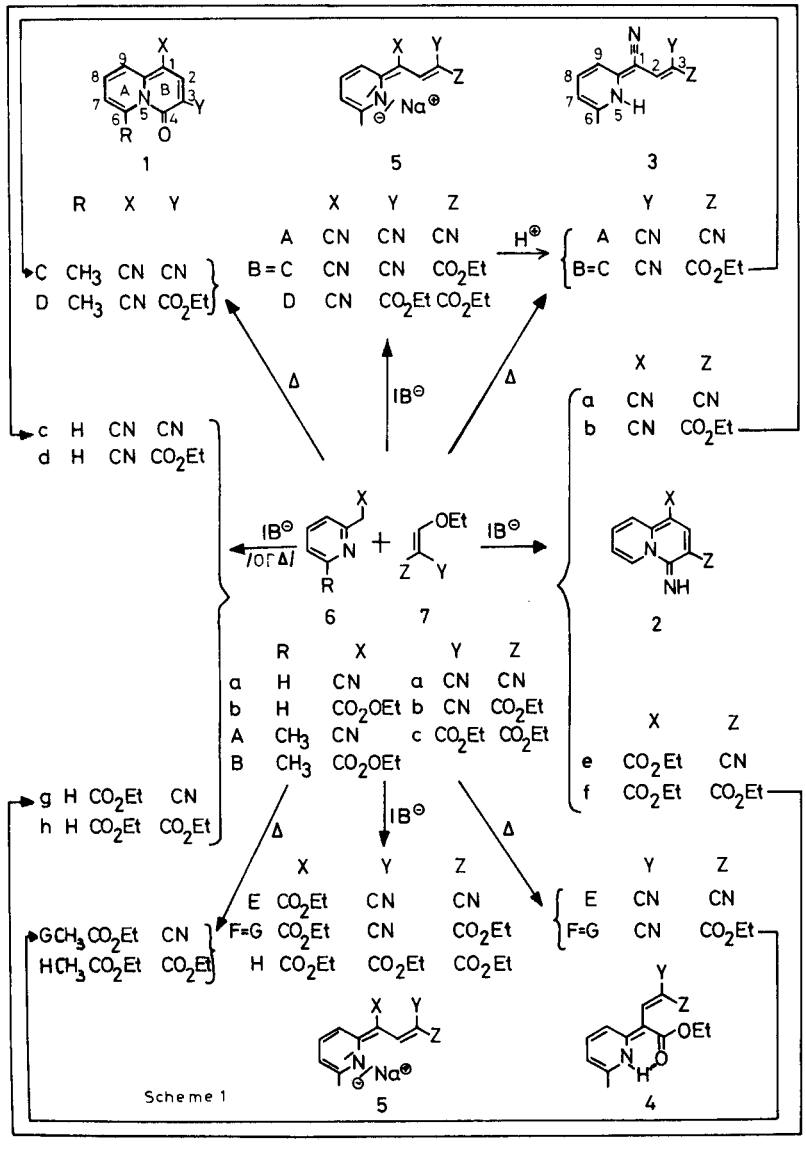
For ring closure, the method of Boekelheide and Lodge [7,8] and that of Thyagarajan [9] have been used, because it gives the possibility to introduce numerous substituents into the ring B. The basic feature of the method is that a 2-pyridineacetic acid derivative **6** is reacted with an ethoxymethylenemalonic acid derivatives **7** in thermic or base catalyzed reaction. The selected four 2-pyridineacetic acid derivatives **6a**, **b**, **A**, **B** and the three ethoxymethylenemalonic acid derivatives **7a**, **b**, **c**, in an appropriate reaction, may afford 16 quinolizine derivatives. Although, several of these compounds are known in the literature [3,7-19], in certain cases the published structures are given erroneously, or not proved rigorously. Govindachari *et al.* [9], Hill *et al.* [12], and Buchman and Duchna [10] have synthesized compounds **2b** and **2f** and assigned a bicyclic structure to them. Likewise, Kobayashi and Matsuda [13] have prepared compound **2a** and correctly assigned a bicyclic structure to it on the basis of the N-H stretching band in the infrared spectrum, but without giving any further spectroscopic details. In an analogous manner, Awaya [14] and Ceder [18] have synthesized compounds **3A** and **4E**, but erroneously, a bicyclic structure has been assigned to them. Kurata [17] has also assigned the erroneous bicyclic structures to compounds **3A** and **4E**, whereas the correct monocyclic structure has been given to compound **4F=G**.

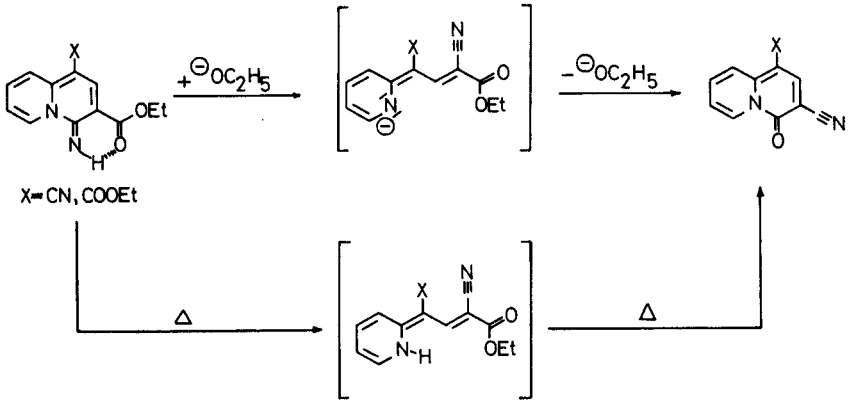
In order to compare systematically the structural as well as the chemical and spectroscopic properties, an appropriate series of compounds has been synthesized. Thus, it became feasible to elucidate the correct structures and to study certain chemical as well as spectroscopic regularities.

Results and Discussion.

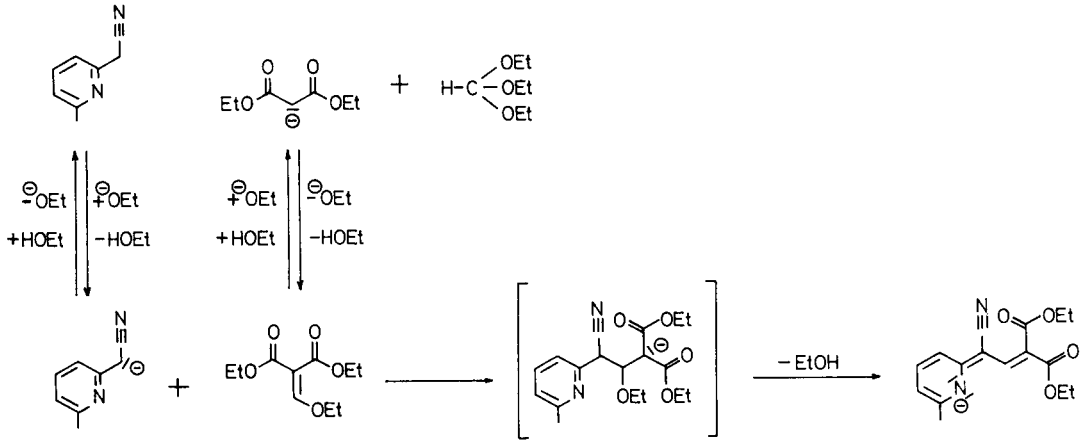
The preparation of the compounds can be realized *via* base-catalyzed or thermic reaction (Scheme 1). If the starting 2-pyridineacetic acid derivatives is an 6-unsubstituted one **6a,b**, according to the literature [15], in the presence of a catalytic amount of sodium ethoxide, the bicyclic 4-oxo- **1c**, **d**, **g**, **h**, or 4-imino-derivatives **2a**, **b**, **e**, **f** have been directly obtained. The former series of compounds **1c**, **d**, **g**, **h** can be prepared under thermic conditions as well, however, the base-catalyzed reaction gives the desired product in higher yield and purity.

If the structure of the starting ethoxymethylenemalonic acid derivative (in the case of **7b**) permits the formation of 4-oxo- as well as 4-imino-derivatives, these latter ones **2b**, **f** are formed under mild conditions (relatively low temperature, and short reaction time), while the former ones **1c**, **g** only under more vigorous conditions. The 3-ethoxycarbonyl-4-iminoquinolizine derivatives can be transform-


1
5
3
R X Y
C CH3 CN CN
D CH3 CN CO2Et
X Y Z
A CN CN CN
B=C CN CN CO2Et
D CN CO2Et CO2Et
H⊕
Y Z
A CN CN
B=C CN CO2Et
Δ
IB⊖
c H CN CN
d H CN CO2Et
X Z
a CN CN
b CN CO2Et
IB⊖ /or Δ/
6
7
2
R X Y Z
a H CN a CN CN
b H CO2OEt b CN CO2Et
A CH3 CN c CO2Et CO2Et
B CH3 CO2OEt
X Z
e CO2Et CN
f CO2Et CO2Et
g H CO2Et CN
h H CO2Et CO2Et
X Y Z
E CO2Et CN CN
F=G CO2Et CN CO2Et
H CO2Et CO2Et CO2Et
Y Z
E CN CN
F=G CN CO2Et
G CH3 CO2Et CN
H CH3 CO2Et CO2Et
5
4
Scheme 1


X=CN, COOEt
+⊖OC2H5
-⊖OC2H5
Δ
Δ

Scheme 2



Scheme 3

ed into the more stable 4-oxo-ones either by thermic reaction **2b** → **1c** [10] or by ethanolic sodium ethoxide at 50° **2f** → **1g**. The rearrangement can be interpreted by ring opening and recrystallization (Scheme 2).

Using a 6-methyl-2-pyridineacetic acid derivatives as starting material, **6A,B**, considerable transformation occurs only in the presence of one equivalent of sodium ethoxide, and the sodium salt of the intermediate monocyclic compounds (**5A, B=C, D, E, F=G, H**) can be isolated. This structure gives an insight into the reaction mechanism of the ring closure as well (Scheme 3). Simultaneously with the base-catalyzed Michael addition, a competing reaction can also take place in which the ethoxymethylenemalonic acid derivative, by the action of sodium ethoxide, decomposes into its starting materials in a retro-Claisen reaction. Decomposition becomes the main reaction when the starting compound is 6-methyl-2-pyridineacetic acid ester (**6B**), because in this case, the first step of the Michael addition, *i.e.* the deprotonation is significantly slower. Since under the conditions employed the Michael addition is kinetically a second-order reaction, whereas the decomposition of ethoxymethylenemalonic acid derivatives is a pseudo first-order one, the predominance of the Michael addition can be achieved by increasing the concentration of the reactants.

Using 6-methyl-2-pyridyneacetic acid derivatives **6A, B** as starting materials, the formation of bicyclic compounds can be achieved by thermal ring closure only, and provided that there is a possibility for the formation of 4-oxo-derivatives **1C, D, G, H**. The formation of 4-imino compounds could not have been detected even under more vigorous conditions, although the corresponding monocyclic intermediates **3A, B=C, 4E, F=G** are formed in mild reaction. These monocyclic compounds can be transformed into the appropriate 4-oxo bicyclic ones when the structural conditions are given **3B=C** → **1C**, **4F=G** → **1G**. It should be noted that **3A** and **3B=C** can also be obtained by acidification of the corresponding monocyclic sodium salts **5A, B=C**. However, the analogous **4E** and **4F=G** compounds are not accessible in this way because the corresponding **5E**, and **5F=G** compounds undergo, by the action of acid, to another transformation which is being now studied [20].

Consequently, stability of the quinolizine derivatives studied by us are different from each other in two aspects: 1. The higher stability of 4-oxo over that of 4-iminoquinolizines is due to the stronger interaction between ring nitrogen and carbonyl group. 2. The lower stability of ring B in the 6-methylquinolizine derivatives compared to the 6-unsubstituted ones is a result of the steric strain between the methyl and oxo, or imino groups in peri-position. Therefore, the ring-chain tautomeric equilibrium is shifted in the 6-methyl derivatives to the monocyclic **3, 4** in the 6-unsubstituted ones to the bicyclic **2** form. The existence of

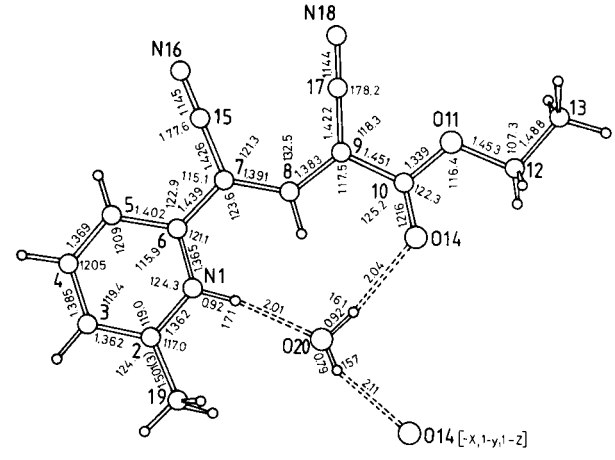


Figure 1. Molecular diagram for **3 B=C** with numbering, bond lengths, hydrogen bonds and bond angles (e.s.d.'s are in the range of 0.03 Å and 0.4°, respectively).

the steric strain is further supported by an X-ray diffraction analysis of the aza-analogues 4-oxopyrido[1,2-*a*]pyrimidine derivatives, carried out by Simon [21]. It has been found that the C(4)-N(5) bond length is 174.2 ppm, which corresponds to a C_{sp^3}-N bond length. Likewise to that of the 6-substituted pyrido[1,2-*a*]pyrimidin-4-ones [22], the lower stability of the ring B is also indicated by the fact that the 4-oxoquinolizine derivative **1D** can be thermally rearranged into 8-cyano-5-ethoxy-2-methylquinoline [2].

Structures of the Products.

In structure elucidation of the compounds, two problems arise. It has to be established whether monocyclic or bicyclic compounds, and having been employed ethoxymethylenecyanoacetic acid ester **7b** as reagent, if 4-oxo, or 4-imino compounds are formed. The formation of bicyclic 4-oxo-derivatives can be easily proved by ^{1}H nmr spectroscopy, because it always implies the elimination of an ethoxy group. In cases, however, when there is a possibility for the formation of 4-imino derivatives, this is not so easy anymore, because the 4-imino derivatives and the corresponding monocyclic compounds have ring-chain tautomerism relationship. Ring B of the 4-imino derivatives opens and recyclizes very easily, in certain cases even by the action of the solvent. This may serve as an explanation for the fact mentioned previously that in the literature several incorrect or unreliable structures are described. The spectra of the synthesized compounds will be discussed in details in a forthcoming paper, now we should like to draw the attention to the fact, only, that the formation of the bicycle implies a considerable paramagnetic shift of the C(9)-H of the ^{1}H nmr spectrum of compounds having an ethoxycarbonyl group in position 1 (Table 1). In compounds **1g** and **1G**, the existence of a cyano stretching band in the infrared spectra rules out the 4-imino-bicyclic structure. In cases where the structure of the starting compounds permits the formation of 4-imino-bicycles, significant differences can be observed in the spectra of 6-substituted and 6-unsubstituted series of compounds. The 4-imino-bicyclic structure of compound **2f** is supported by the strong paramagnetic shift of C(9)-H mentioned above and by two ethoxy groups observed in the ^{1}H nmr spectrum, moreover by the lack of a cyano stretching band in the infrared spectrum and a sharp band of medium intensity at 3280 cm^{-1} which is characteristic of the NH stretching band of the C(4)=NH moiety. The latter band can also be observed in compounds **2a**, **b**, **e**, proving again 4-imino-bicyclic structure. This is further supported by the presence of an ethoxy group in **2b**, and by the considerable paramagnetic shift of C(9)-H observed in compound **2e**. In the 6-methyl series the spectra are quite different. In the compound **4F=G** the number of ethoxy groups is unchanged, nevertheless in the infrared spectrum a cyano stretching band can be observed. Thus, the compound is neither 4-oxo, nor 4-imino quinolizine derivatives but it should be of monocyclic structure. This is also supported by the fact that the C(9)-H signal showed no paramagnetic shift. The NH signal at 14.2 δ ppm indicates a hydrogen bond of chelate character. The ^{1}H nmr and the solution infrared spectra of compound **4E** are very similar to those of **4F=G**. Therefore a monocyclic structure should be assigned to it as well. In the ^{1}H nmr spectrum of compound **3B=C**, one ethoxy group is present, however, the NH valence stretching band in the infrared spectrum is significantly different in position, shape and intensity from those of the 6-unsubstituted 4-imino-bicyclic derivatives. Therefore the compound **3B=C** should also be of monocyclic structure.

Table 1

Characteristic ^{1}H NMR and IR Data on Compounds **Ic**, **d**, **g**, **h**, **1C**, **D**, **G**, **H**, **2a**, **b**, **e**, **f**, **3A**, **B=C** and **4E**, **F=G**

	C(9)-H (δ ppm)	NH (cm^{-1})
1c	8.10	
1d	7.96	
1g	9.08	
1h	9.18	
1C	7.82	
1D	7.71	
1G	9.18	
1H	8.97	
2b	7.86	3280
2e	8.96	3280
2f	9.00	3280
2a		3280
3A	7.43	3260-3160
3B=C	7.37	3250-3170
4E	7.58	3100-2500
4F=G	7.56	3100-2500

The structure of **3B=C** is also confirmed by X-ray analysis. The molecular diagram, bond lengths, hydrogen bonding and bond angles are given in the Figure 1. Bond lengths indicate delocalized system including N(1)-C(9)-atoms. The solvent water molecule participates in three hydrogen bonds twice as donor, once as acceptor.

It is very probable that **3A** and likewise other monocyclic 1-cyano-derivatives have a similar side chain conformation. In 1-ethoxycarbonyl-derivatives, however, a chelate type hydrogen bridge can be demonstrated in solid state by the ir spectrum as well as in solution by ^{1}H nmr spectroscopy, consequently, their structure corresponds rather to **4** (Scheme 1).

Table 2

Physical and Analitical Data of Compounds **1c-h**, **1C-H**, **2a**, **b**, **e**, **f**, **3A**, **B=C** *and* **4E**, **F=G**

Starting compounds	Product	Method	time min	Reaction temp. °C	Catalyst mmole NaOEt	Yield %	Mp °C	Molecular formula	Analyses (%) Calculated/(Found) C	H	N
6A+7b	**1C**	C	90	180-185		54	245-249 [a]	$C_{12}H_7NO$	68.92 (68.80)	3.35 (3.50)	20.09 (20.15)
6A+7c	**1D**	C	120	180-190		70	170-172 [a]	$C_{14}H_{12}N_2O_3$	65.63 (65.64)	4.69 (4.80)	10.94 (10.93)
4F=G	**1G**	C	10	240-245		45	138-140 [b]	$C_{14}H_{12}N_2O_3$	65.63 (65.50)	4.69 (4.83)	10.94 (10.90)
6B+7c	**1H**	C	120	160-170		65	124-125 [b]	$C_{16}H_{17}NO_5$	63.40 (63.24)	5.61 (5.80)	4.62 (4.29)
6a+7b	**1c**	c	60	160-165		40	255-257 [c]	$C_{11}H_5N_3O$			
6a+7c	**1d**	A	45	25	1.0	55	180-182 [c]	$C_{13}H_{10}N_2O_3$	64.46 (64.21)	4.13 (4.48)	11.56 (11.77)
6b+7b	**1g**	A	120	50	1.0	41		$C_{13}H_{10}N_2O_3$	64.49 (64.40)	4.13 (4.25)	11.56 (11.77)
		C	60	160-165		70	198-200 [c]				
		D	120	50	1.0	90					
7b+7c	**1h**	A	30	25	1.0	52	135-138 [c]	$C_{15}H_{15}NO_5$	63.21 (63.24)	5.18 (5.30)	4.85 (4.82)
6a+ 7a	**2a**	A	60	25	0.5	50	194-196 [c]	$C_{11}H_6N_4$	68.05 (67.94)	3.09 (3.27)	28.85 (28.76)
		C	30	140-150		45					
6a+7b	**2b**	A	60	25	0.25	60	178-180 [c]	$C_{13}H_{11}N_3O_2$	64.75 (64.51)	4.56 (4.67)	17.42 (17.63)
6b+7a	**2e**	A	60	25	1.0	68	220-224 [c]	$C_{13}H_{11}N_3O_2$	64.75 (64.50)	4.13 (4.38)	17.42 (17.65)
		C	60	150		45					
6b+7b	**2f**	A	45	25	0.25	60	124-127 [b]	$C_{15}H_{16}N_2O_4$	62.53 (62.47)	5.55 (5.61)	9.72 (9.60)
6c+7a	**3A**	B-1	30	25		85	279-283 [d]				
		B-2	5	100		92		$C_{12}H_8N_4$	69.25 (69.50)	3.84 (3.65)	26.91 (27.10)
6A+7b	**3B=C**	B-1	30	25		53	189-193 [c]	$C_{14}H_{13}N_3O_2$	65.91 (65.61)	5.10 (5.15)	16.46 (16.48)
6b+7a	**4E**	B-2	5	100		77	140-143 [d]	$C_{14}H_{13}N_3O_2$	65.91 (65.89)	5.10 (5.20)	16.46 (16.45)
6b+7b	**4F=G**	B-2	5	100		62	139-142 [d]	$C_{16}H_{18}N_2O_4$	63.60 (63.54)	5.96 (6.20)	9.27 (9.45)

Crystallized from [a] acetone, [b] methanol, [c] ethanol, [d] isopropanol.

EXPERIMENTAL

Melting points are uncorrected. Yields were not optimized. The ir spectra were recorded in potassium bromide pellets with Unicam SP-1200 spectrophotometer; uv spectra in ethanolic solutions with Unicam SP8-100 spectrophotometer; ^1H nmr spectra in DMSO-d_6 solutions (TMS as the internal standard) with Jeol JNM-PS 100 spectrometer.

Method A.

To a solution of pyridyl compound **6** (1 mmole) in ethanol (2 ml) was added ethoxymethylene derivative **7** (1 mmole) and 1*M* ethanolic sodium ethoxide. The mixture was stirred and the precipitated products were filtered off and recrystallized. The reaction temperature, time, yield and the solvent for recrystallization are given in Table 2.

Method B-1.

To an ethanolic solution of pyridyl compound (**6**) (1 mmole) was added ethoxymethylene derivative **7** (1 mmole) and 1 *M* ethanolic sodium ethoxide (1 ml). The mixture was stirred at room temperature for 1 hour. The reaction mixture was evaporated to dryness *in vacuo*. The obtained product was dissolved in ethanol (4 ml) and 2*M* aqueous hydrochloric acid was added to the solution (2 ml). The mixture was stirred at ambient temperature for 0.5 hour. The precipitated solid product was filtered off and washed with ethanol, than diethyl ether. The obtained products were recrystallized.

Method B-2.

A mixture of pyridyl compound **6** (1 mmole) and ethoxymethylene derivative **7** (1 mmole) was heated at 100°. After 5 minutes the mixture

was cooled to room temperature and treated with isopropanol and diethyl ether. The precipitated solid products were filtered off and recrystallized.

Method C.

A mixture of 6-methylpyridyl compound (1 mmole) and ethoxymethylene derivative **7** (1 mmole) was heated in the presence of some drops of diglyme. The ethanol was destillated out from the reaction mixture. The reaction time, temperature, crystallization solvent and yield are given in Table 2.

Method D.

To a solution of 4-iminoquinolizine (**2f**) in ethanol (4 ml) 1 *M* ethanolic sodium ethoxide (1 ml) was added and the reaction mixture was stirred at 50° for 2 hours. The precipitated yellow solid **1g** was filtered off, washed with ethanol and diethyl ether. The yield and solvent for recrystallization are given in Table 2.

X-Ray Crystal Structure of **3B=C**.

Crystal data for **3B=C** are: $C_{14}H_{13}N_3O_2 \cdot H_2O$, M = 273.3; monoclinic, a = 7.771(1), b = 7.955(4), c = 22.346(4)Å, β = 94.75(3)°, V = 1377 Å^3, D_c = 1.32 gcm^{-3}, F(OOO) = 576, Mo-Kα radiation, λ = 0.7107 Å, μ(Mo-K) = 1.03 cm^{-1}, space group $P2_1/c$, Z = 4. Data were collected on an Enraf-Nonius CAD-4 diffractometer with monochromated Mo-Kα radiation up to O = 25°; 2122 out of 2433 reflections were considered observed [I > δ(I)]. All calculations were carried out on a PDP 11/34 minicomputer by the use of the Enraf-Nonius SDP program package (Version 18) with local modifications. The structure was solved by the direct method. The set with the best combined figure of merit revealed all non-hydrogen atoms (R = 0.36). After full matrix refinement for the non-hydrogen atoms, the difference map gave the positions of all hydrogen atoms and then they were refined isotropically. The refinement concluded with R = 0.042, R_w = 0.063 for 2122 reflections. The weighting scheme was $w = 1/[\delta^2(F_o) + 0.01F_o^2]$. Atomic co-ordinates are given in Figure 1.

Acknowledgement.

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