Tetrahedron Vol. 25, pp. 5217 to 5226. Pergamon Press 1969. Printed in Great Britain

ORGANIC PHOTOCHEMICAL REACTIONS—VI[1]

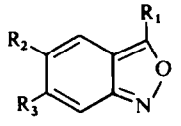
PHOTOCHEMICAL AND THERMAL RING CONTRACTIONS OF 2-METHOXY- AND 2-AMINO-3-ACYL-3*H*-AZEPINES

M. OGATA, H. MATSUMOTO and H. KANŌ
Fukushima-ku, Osaka, Japan

(*Received in Japan* 11 *April* 1969; *Received in the UK for publication* 9 *July* 1969)

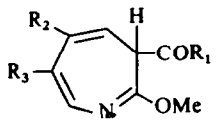
Abstract—Photolysis of 3-benzoyl-2-methoxy-3*H*-azepine (IIa) in methanol led to 7-benzoyl-2-methoxy-3-azabicyclo[2.1.0]hepta-2,4-diene (IVa), 2-methoxy-3-phenacylpyridine (Va) and 2-phenylfuro[2.3-*b*]-pyridine (VIa). This reaction was extended to 3-benzoyl-5-chloro- and -6-chloro-2-methoxy-3H-azepines (IIb, c) and 3-acetonyl-2-methoxy-3*H*-azepine (IId) which underwent analogous conversion into the corresponding pyridine derivatives (Vb–d and VIb), respectively. Pyrolysis of IIa–c gave similar pyridine derivatives. Thermal rearrangement of 2-amino-3-acyl-3*H*-azepines (IIIa–c) gave pyrrolo[2.3-*b*]pyridine derivatives (XIa–c) or 2-diethylamino-3-phenacylpyridines (XIIa, b). A tentative mechanism of these ring contractions is presented.

WE HAVE reported that the photolysis of anthranils (I) in methanol or ether containing amines yield corresponding 2-methoxy- or 2-amino-3-acyl-3*H*-azepines (II or III).[1] A closer investigation of the rearrangement, revealed a novel ring contraction of the azepines II and III into pyridine derivatives.



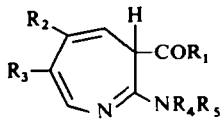
I

a: $R_1 = C_6H_5$, $R_2 = R_3 = H$
b: $R_1 = C_6H_5$, $R_2 = Cl$, $R_3 = H$



II

c: $R_1 = C_6H_5$, $R_2 = H$, $R_3 = Cl$
d: $R_1 = CH_3$, $R_2 = R_3 = H$



III

Photolysis and pyrolysis of 3-*acyl*-2-*methoxy*-3H-*azepines* (II)

Irradiation of 3-benzoyl-2-methoxy-3*H*-azepine (IIa) in methanol gave two isomers of the azepine IIa (IVa and Va), together with a small amount of the third product (VIa) whose molecular formula corresponds to IIa minus MeOH (Table 1). The IR (Table 1) and NMR spectra (Table 2) of Va show the presence of the benzoyl, methoxy, methylene and =CH—CH=CH— (aromatic) groups which suggest its formulation as 2-methoxy-3-phenacylpyridine. Treatment of Va with methanolic hydrogen chloride gave an amide, 3-phenacyl-2(1*H*) pyridone (VIIIa). The compound VIIIa was treated with phosphorous oxychloride and with methanolic ammonia (in a sealed tube) to yield 2-phenyl-pyrrolo[2.3-*b*]pyridine (IXa), which was identical with an authentic sample obtained from 2-benzoylamino-3-methyl-pyridine by Robison's method.[2] Formulation of VIa as 2-phenyl-furo[2.3-*b*]pyridine was suggested by the

analytical (Table 1) and spectral data (Experimental). Actually VIa was obtained by treatment of VIIIa with polyphosphoric acid.

Although the product IVa could not be isolated and readily converted to an amide (VIIa) on passage through an alumina column, the presence of IVa was deduced from the NMR spectrum of the crude photolysis mixture. Its NMR spectrum shows three OMe proton signals at 6·45, 6·23 and 6·13 τ (each assignable to the OMe group of IIa, IVa and Va) and signals of three methine protons (2H, 7·02–7·52 τ, multiplet; 1H, 7·97 τ, triplet, J = 3·5 Hz) besides signals of other groups (Fig. 1). The IR spectrum of the amide VIIa (Table 1) suggests the presence of the —CONH— and C_6H_5CO— groups. Its NMR spectrum in d_5-pyridine shows two olefinic proton signals at 3·76 τ (doubling quartet, J = 8·0, 5·0, 1·0 Hz) and at 4·67 τ (broad quartet, J = 8·0, 5·0 Hz), a NH proton signal at −0·5 τ, signals of three methine protons at 6·8–7·6 τ, and an aromatic 5-proton signals at 1·8–2·1, 2·4–2·7 τ. When deuterium oxide was added, the signal at 3·76 τ turned into a doubling doublet (J = 8·0, 1·0 Hz), the signal at 4·67 τ shows a sharp doubling quartet (J = 8·0, 5·0, 1·0 Hz) and the NH-proton signal disappears (Fig. 2). The spectral data and the conversion of VIIa to VIIIa by treatment with methanolic hydrogen chloride, supports the structure 7-benzoyl-3-azabicyclo-[4.1.0]hept-4-en-2-one for the product VIIa. Therefore the photoproduct IVa from which VIIa was derived should be formulated as 2-methoxy derivative of VIIa.

The signals of three methine-protons observed in the NMR spectrum of IVa or VIIa are assignable to the cyclopropane ring protons (H_1, H_6, and H_7), whose lower-field chemical shift can be attributed to the conjugation effect of the carbonyl or double bond.[3] The small coupling constant ($J_{7-1} = J_{7-6}$ = 3·5 Hz) of the one proton signal (assigned to the H_7-proton) of the cyclopropane ring suggests that both of H_1 and H_6 are *trans* to H_7.[4]

Photolysis of the analogous azepines (IIb, c and IId) in methanol gave the corresponding pyridine derivatives (Vb, c and Vd) as the major or sole product. In the case of IIb, 4-chloro-2-phenyl-furo[2.3-*b*]pyridine (VIb) and 3-benzoyl-5-chloro-2-oxo-3H-

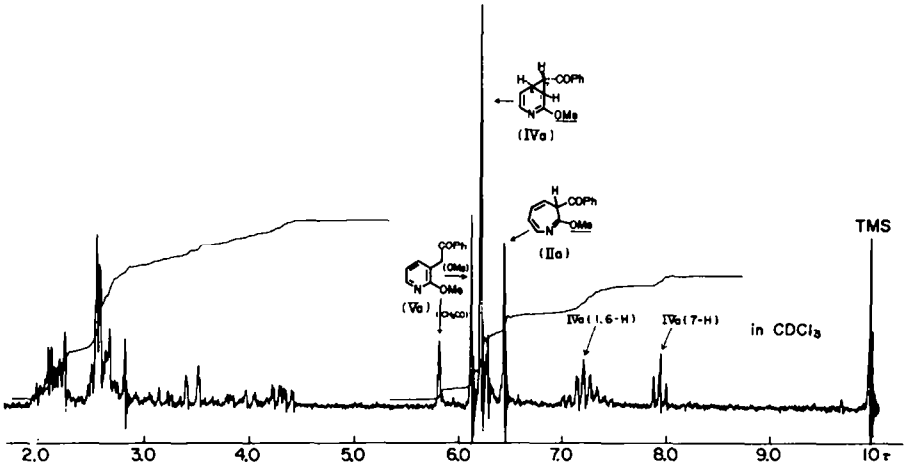


FIG. 1 NMR spectrum of Photoproduct mixture (IIa, IVa and Va).

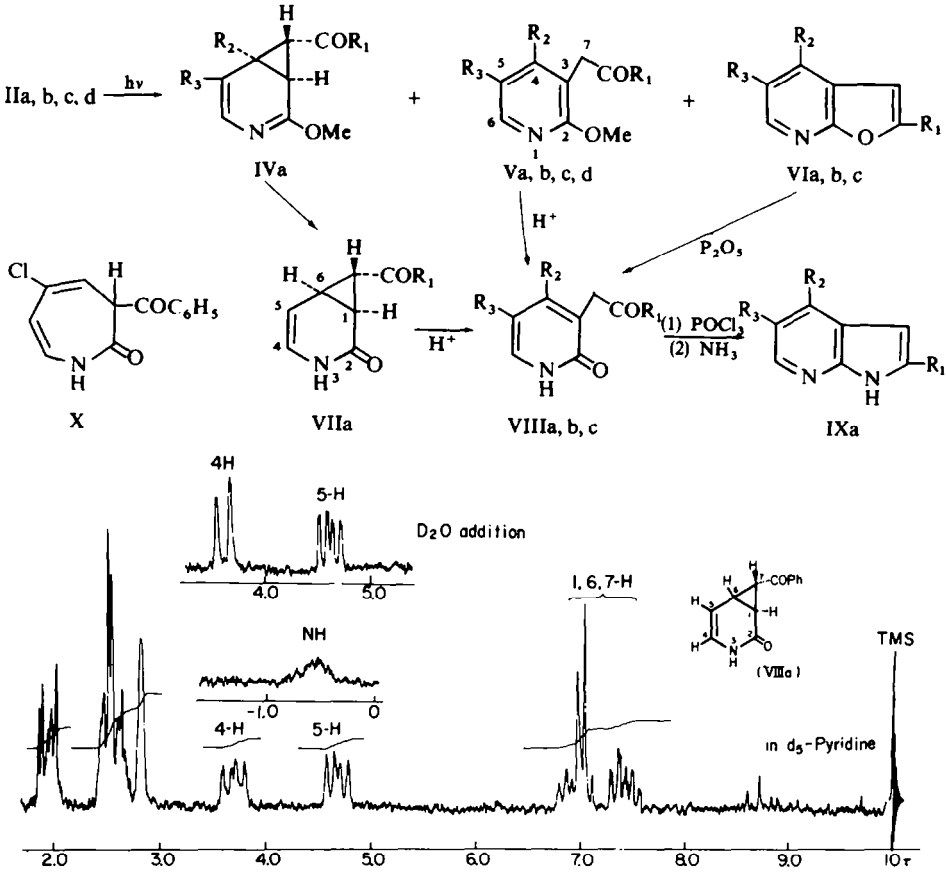


FIG. 2 NMR spectrum of 7-benzoyl-3-azabicyclo[4.1.0]hept-4-en-2-one (VIIa)

azepine (X) were also produced with a recovery of IIb (Table 1). These products were formulated similarly in accordance with their physical data (Tables 1 and 2). Further evidence for the structures of VIb and Vc was obtained by the following transformations. The product VIb was hydrogenated with Pd-C in methanolic ammonia to yield VIa, and Vc was converted to the corresponding furo[2.3-*b*]pyridine (VIc) through an amide (VIIIc) by the same procedure as Va → VIa. Catalytic hydrogenation of VIc gave VIa.

Pyrolysis of 3-benzoyl-2-methoxy-3*H*-azepines (II) also caused the ring contraction into pyridine derivatives. Heating IIa in decaline at 250° for 2 hr gave Va (6·1%) and VIIIa (1·2%) with recovery of IIa (52·4%). Similar pyrolysis of IIb at 200° for 2 hr gave Vb (6·2%) and VIb (2·5%) with recovery of IIb (2·8%) and that of IIc at 150° for 2 hr gave Vc (3·4%) and VIIIc (0·9%) with recovery of IIc (14·4%).

Photolysis and pyrolysis of 2-(*substituted amino*)-3-*acyl*-3*H*-*azepines* (III)

Unlike the anthranil rearrangement 1 → III, irradiation of Ia in ether containing aniline led to the formation of 1,2-diphenyl-pyrrolo[2.3-*b*]-pyridine (XIa, R_4 = Ph; 9·7%). The structure of XIa (R_4 = Ph) was established by the analytical and NMR

TABLE 1. PHOTOLYSIS OF IIa–d

Starting material	Product	Yield (%)	M.p.[a] (°C)	Recryst. solvent	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N	IR[b] (cm^{-1})
IIa	Va	16·9	160 (0·15 mm)	—	$C_{14}H_{13}NO_2$	73·99	5·77	6·16	73·82	5·91	6·10	1590, 1681 (N)
	VIa	<0·05	91–91·5	MeOH	$C_{13}H_9NO$	79·98	4·65	7·17	80·19	4·67	7·19	
	VIIa	25·0	171–175 (d)	MeOH	$C_{13}H_{11}NO_2$	73·22	5·20	6·57	73·10	5·44	7·03	1653, 1675, 3200, 3070 (N)
IIb	Vb	9·6	150 (0·005 mm)	-	$C_{14}H_{12}NO_2Cl$	64·23	4·62	5·34	64·35	4·69	5·46	1573, 1686 (f)
	VIb	3·0	102–103	MeOH	$C_{13}H_7NOCl$	67·99	3·51	6·10	67·71	3·32	6·24	
	X[1]	7·1										
IIc	Vc	50·8	76–77	MeOH	$C_{14}H_{12}NO_2Cl$	64·23	4·62	5·34	64·28	4·74	5·15	1580, 1597, 1675 (N)
IId	Vd	1·4	liquid	—	$C_9H_{11}NO_2$	65·44	6·71	8·48	64·79	6·55	7·54	1619, 1719 (f)

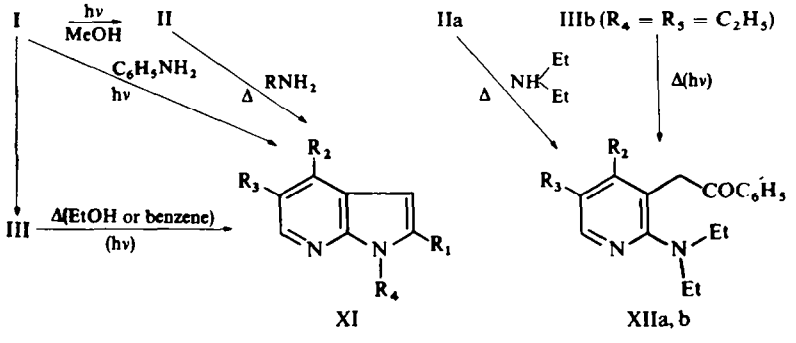
[a] Boiling point indicated bath temperature.
[b] N and f in parentheses indicated Nujol mull. and neat film.

TABLE 2. NMR SPECTRAL PARAMETERS OF PYRIDINE DERIVATIVES

Compound	Solvent	Chemical shift (τ) 4H	5H	6H	—CH_2—	OMe	—COPh	Coupling constant (Hz) $J_{4,5}$	$J_{4,6}$	$J_{5,6}$
Va	CCl_4	~2·4–2·7	3·25	~2·4–2·7	5·90	6·13	~1·8–2·2 ~2·4–2·7	7·5	—	5·0
Vb	CCl_4	—	3·13	2·88	5·50	6·13	~1·9–2·1 ~2·4–2·7	—	—	5·0
Vc	$CDCl_3$	~1·8–2·1	—	~2·3–2·6	5·80	6·13	~1·8–2·1 ~2·3–2·6	—	?	—
	C_6D_6	~2·0–2·3	—	~2·8	6·25	6·37	~2·0–2·3 ~2·8–3·0	—	2·5	—
Vd	$CDCl_3$	2·62	3·17	1·92	6·37	6·07	7·83 (CH_3CO)	7·5	2·0	5·0
VIIIa	d_6-DMSO	~2·3–2·8	3·89	~2·3–2·8	5·88	—1·60 (NH)	~1·8–2·2 ~2·3–2·8	6·5	?	6·5
VIIIc	d_6-DMSO	~2·3–2·7	—	~2·3–2·7	5·83	—1·82 (NH)	~1·9–2·1 ~2·3–2·7	—	?	—

spectral data (Experimental). This result suggests that the 2-anilino derivative IIIa initially formed was further converted to XIa (R_4 = Ph). Actually, photolysis of IIIb (R_4 = Ph, R_5 = H) gave XIb (R_4 = Ph; 4·2%) with recovery of IIIb (20·3%).

Photolysis of IIIb (R_4 = R_5 = Et) in ethanol gave 4-chloro-2-diethyl-amino-3-phenacylpyridine (XIIb).

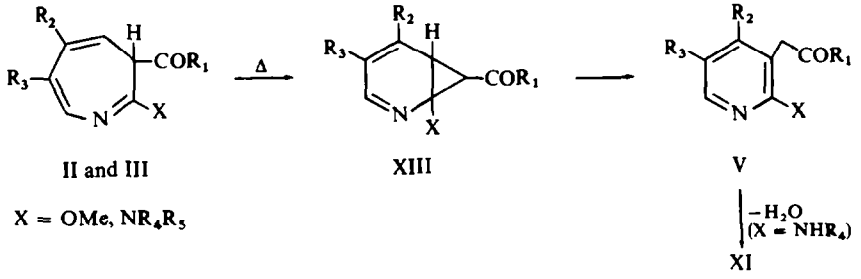


R_4 = H(≡IX), C_6H_5, n-Bu

Similar ring contraction proceeds more readily upon heating II in amines or III in ethanol or benzene under reflux. Thus heating IIa in aniline, ethanolic ammonia, or diethylamine gave the corresponding pyrrolo[2.3-*b*]pyridines XIa (R_4 = Ph; 25·3%), IXa (3·4%) or 2-diethylamino-3-phenacylpyridine (XIIa; 52·5%), respectively. The compounds IIIb (R_4 = Ph, R_5 = H; R_4 = n-Bu, R_5 = H; R_4 = R_5 = Et) and IIId (R_4 = Ph, R_5 = H) were heated under reflux in ethanol or benzene and gave the corresponding pyridine derivatives, XIb (R_4 = Ph; R_4 = n-Bu), XIIb and XId (R_4 = Ph). The NMR spectra of these pyrrolo[2.3-*b*]pyridines are all consistent with the assigned structures.

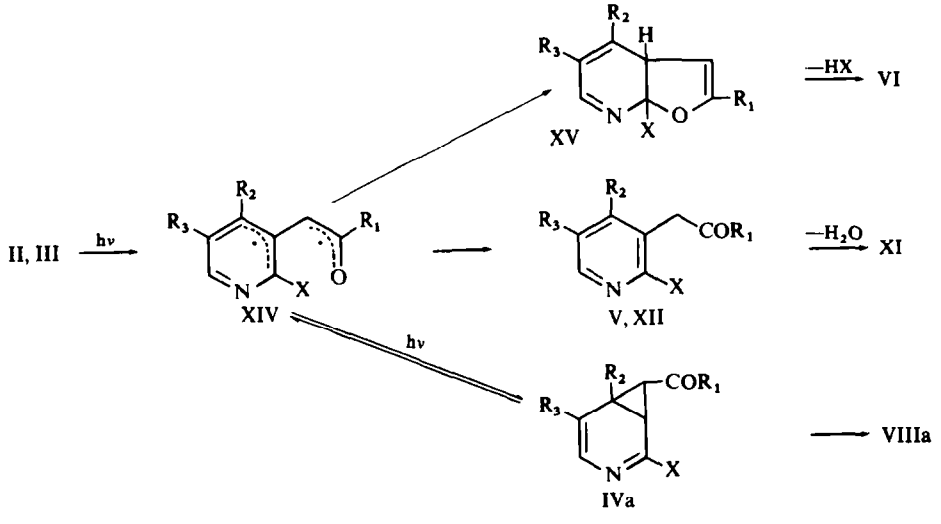
DISCUSSION

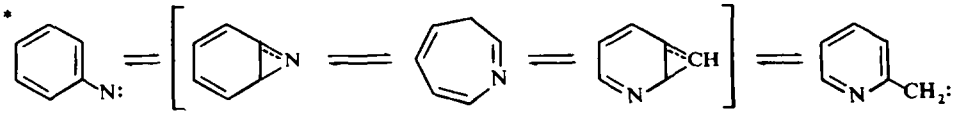
The reaction scheme for the thermal rearrangement can be envisaged as involving an azanorcaradiene intermediate (XIII) described below. Rupture of the cyclopropane



ring of XIII followed by hydrogen shift gives V, some of which further undergo dehydrative cyclization to yield XI. A similar intermediate (or transition state) was suggested by Crow and Wentrop[5] for the thermal interconversion of 2-pyridylcarbene and phenylnitrene,* and thermal isomerization of some cycloheptatrienes into the corresponding toluene derivatives[6] are supposed to proceed *via* norcaradiene intermediates according to Woodward and Hoffmann rule[7] (disrotatory). The ease of the thermal rearrangement of III as compared with that of II is noticeable but the reason is not clear.

As for the photoisomerization of azepines, it has been reported that 1-ethoxycarbonyl-1*H*-azepine, like cycloheptatriene,[6] isomerizes to a 2-azabicyclo[3.2.0]-heptadiene derivative;[8] however, little is known concerning the 3*H*-azepine system. A tentative mechanism has been advanced to explain the formation of the various products, though the detailed reaction mechanism is not possible at present.





In contrast to the thermal disrotatory process, the conrotatory photoisomerization of the azepine system II or III into the corresponding azanorcaradiene system XIII would require a greater activation energy. Thus, the conrotatory isomerization of II or III to the corresponding pyridine system may force the C_2—C_3 bond scission of the azepine ring to give a diradical intermediate (or transition state; XIV). Intramolecular cyclization of XIV can produce a dihydrofuro[2.3-*b*]pyridine derivative (XV) which gives the product VI losing HX. An alternative intramolecular cyclization of XIV gives IVa, which is converted to the lactam VIIIa by hydrolysis. Hydrogen shift of XIV would produce the pyridine derivative V or XII and the product V (X = NHR_4) undergoes cyclization to the pyrrolopyridine derivative XI with loss of water. A photoconversion[9] of IVa into Va (probably *via* XIVa) was suggested by the progress in photolysis of IIa followed by NMR spectroscopy; the initial main product IVa decreased and another product Va increased with time during the photolysis (Table 3).

On the basis of the NMR spectroscopy of IIa, no evidence was obtained of a valence-tautomeric equilibrium between IIa and XIIIa in methanol at room temperature or at 80°. Accordingly, it seems to be unlikely that the initial step of the photolysis involves an azanorcaradiene entity as a direct reactor. The remarkable solvent-dependence* in the photolysis also remained unsolved.

TABLE 3. PHOTOLYSIS OF 3-BENZOYL-2-METHOXY-3H-AZEPINE (IIa)

Irradiation time	Product yield (%)[a] IIa	(IVa)	VIIa	Va
1 hr	(35·8)	(49·4)		(14·8)
2 hr	(15·5) 9·3	(57·0)	25·0	(27·5) 16·9
6 hr	(19·1) 8·9	(19·1)	6·9	(61·8) 20·1

[a] Parenthesis indicates the height ratio of methoxy signal peaks in NMR spectra ($CDCl_3$).

EXPERIMENTAL

All m.ps were taken on a Kofler hot-stage and are uncorrected. NMR spectra were determined with a Varian A-60A instrument, using TMS as an internal standard. Irradiation was carried out with a high pressure mercury arc lamp wity pyrex filter.

General procedure of photolysis of 2-methoxy-3-acyl-3H-azepines (IIa–d). A 1% soln of IIa–d in MeOH was irradiated at room temp. The reaction was followed by UV spectroscopy and TLC. After evaporation of MeOH under vacuum on a water bath, the residue was chromatographed on neutral alumina (activity IV). The products obtained and their physical data are summarized in Table 1 and the NMR spectral data of Va–d and VIIIa, c are listed in Table 2. NMR ($CDCl_3$) of VIa: 1·72 τ (1-H, qu, $J_{4,6}$ = 1·5, $J_{5,6}$ = 5·0 Hz, C_6-H), 1·9–2·2 τ, 2·4–2·9 τ (6-H, m, 2-Ph, C_4-H, C_5-H), and 3·02 τ (1-H, s, C_3-H). NMR ($CDCl_3$) of VIb: 1·82 τ (1-H, d, $J_{5,6}$ = 5·5 Hz, C_6-H), 1·9–2·2 τ, 2·4–2·9 τ (5-H, m, 2-Ph, C_5-H) and 2·93 τ (1-H, s, C_3-H); NMR ($CDCl_3$) of VIc: 1·77 τ (1-H, d, $J_{4,6}$ = 2·0 Hz, C_6-H), 1·9–2·2 τ, 2·4–2·7 τ (6-H, m, 2-Ph, C_4-H) and 3·07 τ (1-H, s, C_3-H).

3-Phenacyl-2(1H)-pyridone (VIIIa)

(a) A soln of 200 mg of Va in 4 ml EtOH and 4 ml 6N HCl was refluxed for 2·5 hr. After evaporation of EtOH, the residue was diluted with water and extracted with ether. The extract was dried over Na_2SO_4

* The photolysis of II in methylene dichloride, cyclohexane and acetonitrile resulted in the recovery of the starting materials.

and evaporated. The crude product was crystallized from Et_2O–CH_2Cl_2 to give VIIIa (11 mg), colorless needles, m.p. 192–197°. Further recrystallization from MeOH gave a pure sample of m.p. 195–201°. (Found: C, 73·31; H, 5·21; N, 6·54. $C_{13}H_{11}N_2O$ requires: C, 73·21; H, 5·20; N, 6·57%).

(b) A soln of 200 mg of VIIa and a drop of conc HCl in 8 ml MeOH was refluxed for 2 min. After cooling the resulting crystalline product (154 mg) (m.p. 195–197°) was collected. Recrystallization from MeOH gave a pure sample of VIIIa, m.p. 195–201°.

2-Phenyl-furo[2,3-b]*pyridine* (VIa)

A mixture of 48 mg and 0·5 ml polyphosphoric acid was heated at 150° for 1·5 hr. After cooling, the reaction mixture was diluted with water and extracted with ether. The extract was dried over Na_2SO_4 and evaporated to give 24 mg of colorless prisms, m.p. 89–91°. Crystallization from dil MeOH afforded a pure sample of m.p. 91–91·5°. This was identical with the sample obtained by photolysis of IIa.

2-Chloro-3-phenacylpyridine

A mixture of 400 mg of VIIa and 2 ml $POCl_3$ was heated at 100° for 4 hr. After evaporation of $POCl_3$, the residue was diluted with ice water, and extracted with $CHCl_3$. Evaporation of $CHCl_3$ gave a residue which was chromatographed on neutral alumina (activity IV). Elution with benzene gave the title compound (101 mg), pale yellow needles, m.p. 63–64° (after recrystallization from pet. ether). (Found: C, 67·39; H, 4·32; N, 6·47. $C_{13}H_{10}NOCl$ requires: C, 67·25; H, 4·41; N, 6·05%). Evaporation of the fraction eluted with CH_2Cl_2–MeOH (10:1) yielded starting material (114 mg).

2-Phenyl-pyrrole[2.3-b]*pyridine* [IXa = XIa (R_4 = H)]

(a) A soln of 80 mg 2-chloro-3-phenacylpyridine in 10 ml sat. MeOH–NH_3 was heated in a sealed tube at 100° for 24 hr. After cooling, the solvent was evaporated and the residue was extracted with benzene. The extract was chromatographed on neutral alumina (activity IV). Elution with benzene gave the starting material (35 mg). Further elution with benzene–ether(1:1) gave IXa (4 mg) as colorless scales, m.p. 204–205° (after crystallization from MeOH). This was identical with an authentic sample prepared by the known method (b).[2]

(b) A mixture of 2·5 g 2-benzoylamino-3-methylpyridine, 15 ml abs EtOH and 900 mg Na was heated at 350° for 20 min. The reaction mixture was diluted with water and extracted with ether. The extract was washed with water, dried over Na_2SO_4 and evaporated. The residue was chromatographed on neutral alumina (activity IV). Elution with benzene gave IXa as colorless scales (39 mg), m.p. 205–206° (after recrystallization from MeOH). (Found: C, 80·38; H, 5·19; N, 14·42. $C_{13}H_{10}N_2$ requires: C, 80·31; H, 5·19; N, 14·15%); NMR ($CDCl_3$): ~ −2·8 τ (—NH), 1·72 τ (1-H, qu, J = 5·0, 1·5 Hz, C_6-H), 2·0–2·2 τ (1-H, m, C_4-H), 2·4–2·7 τ, 2·0–2·2 τ (5-H, m, C_2-Ph), 2·93 τ (1-H, qu, J = 8·0, 5·0 Hz, C_5-H) and 3·23 τ (1-H, s, C_3-H).

(c) A mixture of 1 g of IIa and 15 ml saturated EtOH–NH_3 was heated at 100° for 3 hr in a sealed tube. After evaporation of the solvent, the residue was treated in the same way as for (a) to yield IX (18 mg) and 967 mg of the starting material.

2-Benzoylamino-3-methylpyridine

A mixture of 9 g 2-dibenzoylamino-3-methylpyridine prepared by the method by Seide,[10] 200 ml EtOH and 10 ml of 10% NaOH was heated on a water bath for 10 min. After evaporation of EtOH, the residue was neutralized with dil HCl and extracted with $CHCl_3$. The extract was dried over $MgSO_4$ and evaporated. The residue was washed with CH_2Cl_2-isopropyl ether to give a solid (4·75 g), m.p. 126–126·5°. (Found: C, 73·56; H, 5·70; N, 13·12. $C_{13}H_{12}N_2O$ requires: C, 73·56; H, 5·70; N, 13·20%).

Catalytic hydrogenation of 4-chloro- and 5-chloro-3-phenyl-furo[2.3b]*pyridine* (VIb *and* VIc)

A mixture of 40 mg of VIb, 10 ml MeOH, 0·5 ml sat MeOH–NH_3 and 50 mg of 8% Pd-C was subjected to hydrogenation. One mole of H_2 per mole of VIb was absorbed. The catalyst was filtered off, then the filtrate was evaporated and the residue was extracted with ether. Removal of the solvent left a solid, which was crystallized from MeOH to give colorless prisms (3 mg), m.p. 91–91·5°. This was identical with VIa prepared from VIIIa.

Similarly, 21 mg of VIa was obtained from 100 mg of VIc.

5-Chloro-3-phenacyl-2(1H)*pyridone* (VIIIc)

A soln of 100 mg of Vc in 2 ml EtOH and 2 ml 6N HCl was refluxed for 3 hr. After cooling, the resulting

crystalline product (84 mg) was collected, m.p. 230–235°. (Found: C, 62·93; H, 4·19; N, 5·81. $C_{13}H_{10}NO_2Cl$ requires: C, 63·04; H, 4·07; N, 5·66%).

5-Chloro-2-phenyl-furo[2.3-b]*pyridine* (VIc)

A mixture of 200 mg of VIIIc and 2 ml polyphosphoric acid was heated at 150° for 1·5 hr. The reaction mixture was treated in the same way as for VIIIa to yield 140 mg of VIc as colorless plates, m.p. 159–161° after crystallization from MeOH. (Found: C, 67·79; H, 3·66; N, 5·99. $C_{13}H_8NOCl$ requires: C, 67·99; H, 3·51; N, 6·10%).

Pyrolysis of 3-*acyl*-2-*methoxy*-3H-*azepines* (IIa, IIb *and* IIc)

A mixture of 1·0 g of IIa and 5 ml decalin was heated at 250° for 3 hr. The reaction mixture was chromatographed on neutral alumina (activity IV). Elution with pet. ether–benzene (1:1) gave the starting material (524 mg). Further elution with pet. ether–benzene (1:1) and benzene gave Va (113 mg) as a distillate at bath temp 150° (0·05 mmHg). Recrystallization from n-hexane gave a solid (61 mg), m.p. 68–69°. Finally, elution with (H_2Cl_2–MeOH (9:1) gave VIIIa (11 mg) after washing with CH_2Cl–ether.

Similarly, pyrolysis (200°) of 500 mg of IIb in 3 ml decalin gave Vb (31 mg), VIb (11 mg) and the starting material (14 mg).

Pyrolysis (150°) of 230 mg of IIc in 2 ml decalin gave Vc (8 mg), VIIIc (2 mg) and the unchanged IIc (33 mg).

1,2-*Diphenyl-pyrrolo*[2.3-b]*pyridine* (XIa, $R_4 = C_6H_5$)

(a) A mixture of 1·14 g of IIa and 700 mg aniline was heated at 120° for 4 hr. The reaction mixture was chromatographed on neutral alumina (activity IV). Elution with benzene–pet. ether (1:1) gave a solid, which was recrystallized from MeOH to yield XIa (R_4 = Ph), 346 mg (25·3%), m.p. 130–132°. (Found: C, 84·42; H, 5·12; N, 10·30. $C_{19}H_{14}N_2$ requires: C, 84·42; H, 5·22; N, 10·36%); NMR (CCl_4): 1·83 τ (1-H, doubling d, $J_{4,6}$ = 1·5, $J_{5,6}$ = 5·0 Hz, C_6-H), 2·17 τ (1-H, doubling d, $J_{4,5}$ = 8·0, $J_{4,6}$ = 1·5 Hz, C_4-H), ~2·72, ~ −2·80 τ (10-H, m, N-Ph, C_2-Ph), 3·00 τ (1-H, qu, $J_{4,5}$ = 8·0, $J_{5,6}$ = 5·0 Hz, C_5-H) and 3·40 τ (1-H, s, C_3-H).

(b) A soln of 5·0 g of Ia and 5 ml aniline in 600 ml ether was irradiated for 4 hr. After evaporation of ether under reduced press on a water bath, the residue was chromatographed on neutral alumina (activity IV). Successive elution with pet. ether–benzene (1:1) and benzene–ether (1:1) gave a solid, which was crystallized from EtOH to give XIa (R_4 = Ph), colorless needles, 715 mg (9·7%), m.p. 129–132°.

4-*Chloro*-1,2-*diphenyl-pyrrolo*[2.3-b]*pyridine* (XIb, R_4 = Ph)

(a) A soln of 100 mg of IIIb (R_4 = Ph, R_5 = H) in 10 ml EtOH was refluxed for 2 hr. After evaporation of EtOH, the residue was chromatographed on neutral alumina. The solid from the fraction eluted with benzene was recrystallized from isopropyl ether to give colorless needles (79 mg), m.p. 131–132°. (Found: C, 70·68; H, 4·76; N, 8·57. $C_9H_{13}N_2Cl$ requires: C, 70·70; H, 4·68; N, 8·69%); NMR (CCl_4): 1·96 τ (1-H, d, $J_{5,6}$ = 5·0 Hz, C_6-H), ~2·72 τ, ~2·80 τ (10-H, m, N-Ph, C_2-Ph), 2·93 τ (1-H, d, $J_{5,6}$ = 5·0 Hz, C_5-H) and 3·23 τ (1-H, s, C_3-H).

Similarly the reaction of 100 mg of IIIb (R_4 = Ph, R_5 = H) in benzene gave 83 mg of XIb (R_4 = Ph).

(b) A soln of 780 mg of IIIb (R_4 = Ph, R_5 = H) in 200 ml MeOH irradiated for 3 hr. After evaporation of MeOH, the residue was chromatographed on neutral alumina. Successive elution with pet. ether and pet. ether–benzene (1:1) gave 158 mg of the starting material. The residue from the fraction eluted with benzene was purified using TLC plate (alumina, solvent: benzene–cyclohexane 1:1) to give 31 mg of XIb (R_4 = Ph). The sample was identical with that obtained by procedure (a).

1-*n-Butyl*-4-*chloro*-2-*phenyl-pyrrolo*[2.3-b]*pyridine* (XIb, R_4 = n-Bu)

A soln of 200 mg of IIIb (R_4 = n-Bu, R_5 = H) in 20 ml EtOH was refluxed for 40 min. After evaporation of EtOH, the residue was chromatographed on neutral alumina. The residue from the fraction eluted with benzene was distilled to give XIb (R_4 = n-Bu; 165 mg), as a distillate at bath temp 150° (0·025 mmHg). (Found: C, 71·35; H, 5·92; N, 8·57. $C_{17}H_{17}N_2Cl$ requires: C, 71·70; H, 4·68; N, 9·84%); NMR (CCl_4): 1·90 τ (1-H, d, $J_{5,6}$ = 5·0 Hz, C_6-H), ~2·53 τ (5-H, m, C_2-Ph), 3·00 τ (1-H, s, C_3-H), 3·50 τ (1-H, s, C_3-H) and ~5·5–5·8 τ, ~8·1–9·4 τ (9-H, m, n-Bu).

2-*Methyl*-1-*phenyl-pyrrolo*[2.3-b]*pyridine* (XId, $R_4 = C_6H_5$)

A soln of 100 mg of IIId (R_4 = Ph, R_5 = H) in 10 ml EtOH was refluxed for 3 hr. The reaction mixture

was treated as described, 50 mg of XId (R_4 = Ph) was obtained as a distillate at bath temperature 115–130° (0·05 mmHg). (Found: C, 80·69; H, 5·88; N, 13·33. Calcd. for $C_{14}H_{12}N_2$: C, 80·74; H, 5·81; N, 13·45%); NMR ($CDCl_3$): 1·80 τ (1-H, doubling d, $J_{4,6}$ = 1·5, $J_{5,6}$ = 5·0 Hz, C_6-H), 2·18 τ (1-H, doubling d, $J_{4,5}$ = 8·0, $J_{4,6}$ = 1·5 Hz, C_4-H), ~2·4–2·7 τ (5-H, m, N-Ph), 2·98 τ (1-H, q, $J_{4,5}$ = 8·0, $J_{5,6}$ = 5·0 Hz, C_5–H), 3·67 τ (1-H, s, C_3-H) and 7·67 τ (3-H, d, $J_{CH_3—C_3—H}$ = 0·5 Hz).

2-Diethylamino-3-phenacylpyridine (XIIa)

A mixture of 1 g of IIa and 5 ml Et_2N was heated in a sealed tube at 120° for 4 hr. After evaporation of Et_2N, the residue was chromatographed on neutral alumina. The fraction eluted with pet. ether–benzene (10:1) and benzene was distilled to yield XIIa (24 mg) as a distillate at bath temp 165° (0·25 mmHg). (Found: C, 76·11; H, 7·43; N, 10·39. $C_{17}H_{20}N_2O$ requires: C, 76·08; H, 7·51; N, 10·44%).

4-Chloro-2-diethylamino-3-phenacylpyridine (XIIb)

(a) A mixture of 500 mg of IIIb (R_4 = R_5 = Et) and 20 ml benzene was refluxed for 2 hr. The solvent was evaporated, and the residue was chromatographed on neutral alumina. The fraction eluted with pet. ether–benzene (1:1) was distilled to give XIIb (155 mmHg) as a distillate at bath temp 160° (0·18 mmHg). (Found: C, 67·24; H, 6·32; N, 8·76. $C_{17}H_{19}N_2OCl$ requires: C, 67·43; H, 6·32; N, 9·25%). Elution with pet. ether–benzene (1:1) ~ benzene gave 26 mg of the starting material.

(b) A soln uf IIIb (R_4 = R_5 = Et) in 75 ml EtOH was irridiated for 2 hr. The solvent was evaporated and the residue was chromatographed as for (a) to yield XIIb (39 mg) and that starting material (158 mg).

Acknowledgement—The authors are grateful to Professor Emeritus E. Ochiai of the University of Tokyo and to Dr. K. Takeda, Director of this Laboratory for their interest on this work. Thanks are also due to the members of the Physical Chemistry Department for the spectral measurements, to the members of the Analysis Room for the elemental analysis.

REFERENCES

[1] Part V, M. Ogata, H. Matsumoto and H. Kanō, *Tetrahedron* **25**, 5205 (1969).
[2] M. M. Robison and B. L. Robison, *J. Am. Chem. Soc.* **77**, 457 (1955).
[3] [a] J. D. Holmes and R. Pettit, *Ibid.* **85**, 2531 (1963);
[b] O. L. Chapman and R. A. Fugiel, *Ibid.* **91**, 2151 (1969).
[4] [a] J. D. Graham and M. T. Rogers, *Ibid.* **84**, 2249 (1962);
[b] D. J. Patel, M. E. H. Howden and J. D. Roberts, *Ibid.* **85**, 3218 (1963);
[c] H. M. Hutton and T. Schaefer, *Canad. J. Chem.* **40**, 875 (1962).
[5] W. D. Crow and C. Wentrop, *Tetrahedron Letters* 6149 (1968).
[6] A review is presented by G. Maier, *Angew. Chem.* Internat. Edit. **6**, 402 (1967).
[7] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.* **1**, 17 (1968).
[8] L. A. Paquette and J. A. Barrett, *J. Am. Chem. Soc.* **88**, 1718 (1966).
[8] [a] G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson and G. Klose, *Ibid.* **87**, 1410 (1965);
[b] A. Padwa, E. Alexander and M. Niemcyzk, *Ibid.* **91**, 456 (1969).
[10] O. Seide, *Ber. Dtsch. Chem. Ges.* **57**, 1802 (1924).