over $CaCl_2$, evaporated and the residue was distilled under reduced pressure to give 68.0 g (41.6%) of colorless liquid boiling at 89—90°/0.14 mm. *Anal.* Calcd. for $C_9H_{10}OS$: C, 65.02; H, 6.06. Found: C, 64.91; H, 6.00

Ethyl 2-Amino-5-piperidinomethyl-4,5-dihydrothiophene-3-carboxylate——To a solution prepared by dissolving 2.3 g of Na in 300 ml of abs. EtOH was added 15 g of ethyl cyanoacetate. The mixture was refluxed during 15.7 g of piperidinopropylene sulfide was added dropwise over a period of 1 hr. Refluxing was continued for an additional 1 hr. After removal of the solution, by distillation under reduced pressure, the residue was poured into cold H_2O and extracted with ether. The extracts were dried over Na_2SO_4 and evaporated to dryness. Recrystallization of the residue from EtOH gave 6.1 g (22.6%) of colorless prisms melting at 86—88°. *Anal.* Calcd. for $C_{13}H_{22}O_2N_2S$: C, 57.76; H, 8.20; N, 10.36. Found: C, 57.87; H, 8.34; N, 10.38. IR ν_{max}^{KBr} cm^{-1}: 3375, 3275 (NH_2); 1638 (CO).

Ethyl 2-Amino-5-morpholinomethyl-4,5-dihydrothiophene-3-carboxylate——One-tenth mole (15.9 g) of morpholinopropylene sulfide was allowed to react with 15 g of ethyl cyanoacetate in the presence of 2.3 g of Na by the procedure described above. The product was recrystallized from EtOH to give 7.3 g (26.8%) of colorless prisms melting at 115—117°. *Anal.* Calcd. for $C_{12}H_{20}O_3N_2S$: C, 52.93; H, 7.40; N, 10.29. Found: C, 52.78; H, 7.46; N, 10.06. IR ν_{max}^{KBr} cm^{-1}: 3370, 3275 (NH_2); 1643 (CO). NMR ($CDCl_3$) τ: 8.85 (3H, triplet, CH_3), 7.65—7.35 (7H, multiplet, $\begin{matrix}CH_2\\CH_2\end{matrix}>N\text{-}CH_2\text{–}CH$), 7.40—6.80 (2H, multiplet, ring CH_2), 6.35 (4H, triplet, $O<\begin{matrix}CH_2\\CH_2\end{matrix}$), 5.90 (2H, quartet, CH_2-Me), 3.85 (2H, NH_2). Mass Spectrum *m/e*: 272 (M^+).

Ethyl 2-Amino-5-phenoxymethyl-4,5-dihydrothiophene-3-carboxylate——The reaction was carried out using 2.3 g of Na, 16.6 g of phenoxypropylene sulfide and 15 g of ethyl cyanoacetate by the procedure described above. The product was recrystallized from EtOH to give 11.1 g (39.8%) of colorless prisms melting at 105—108°. *Anal.* Calcd. for $C_{14}H_{17}O_3NS$: C, 60.20; H, 6.14; N, 5.02. Found: C, 59.91; H, 6.26; N, 4.98. IR ν_{max}^{KBr} cm^{-1}: 3370, 3280 (NH_2); 1647 (CO). NMR ($CDCl_3$) τ: 8.78 (3H, triplet, CH_3), 7.14—6.90 (2H, multiplet, ring CH_2), 6.50—5.95 (3H, multiplet, O-CH_2-CH), 6.03 (2H, quartet, CH_2-Me), 3.98 (2H, NH_2), 3.40—2.75 (5H, multiplet, phenyl hydrogen). Mass Spectrum *m/e*: 279 (M^+).

γ-Phenoxypropylmalonic Acid from Ethyl 2-Amino-5-phenoxymethyl-4,5-dihydrothiophene-3-carboxylate——Desulfurization of ethyl 2-amino-5-phenoxymethyl-4,5-dihydrothiophene-3-carboxylate with Raney nickel aluminum alloy by the procedure described by Schwenk[10] gave γ-phenoxypropylmalonic acid, which was identified with an authentic sample[11] by the mixed melting point determination and IR comparison.

Acknowledgement We are grateful to Mr. K. Takeda for measurements of NMR and Mass Spectra and to Miss M. Sato for IR data. We also thank Mrs. K. Shiraki and Yoshitomi Seiyaku Co., Ltd. for microanalytical data.

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Organic Photochemical Reactions. VIII.[1] Photocyclization of N-Acryloyl Heteroaromatic Amines

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As an extension of the photochemical cyclization of methacrylanilides,[3] we attempted the photocyclization of N-acryloyl heteroaromatic amines. Irradiation of various N-substituted acrylamides in benzene solution through pyrex glass with a high pressure mercury arc lamp in an argon atmosphere at room temperature afforded photoproducts (I—X). De-

1) Part VII: M. Ogata, H. Matsumoto, and H. Kano, *Chem. Pharm. Bull.* (Tokyo) **18**, 964 (1970).
2) Location: *Fukushima-ku, Osaka.*
3) P.G. Cleveland and O.L. Chapman, *Chem. Commun.*, **1967**, 1064.

hydrogenation of I with selenium dioxide in acetic acid yielded known 2-hydroxy-1,8-naphthyridine (XI).[4] From this result and from the nuclear magnetic resonance (NMR) spectrum (Table II), I wasass igned as 1,2,3,4-tetrahydro-2-oxo-1,8-naphthyridine. The NMR spectrum of photoproduct II was also consistent with the expected structure, 1,2,3,4-tetrahydro-3-methyl-2-oxo-1,8-naphthyridine. Photocyclization of 3-substituted-2-aminopyridine derivatives did not occur; N-(3-methyl-2-pyridyl)methacrylamide was recovered unchanged after irradiation, and N-(3,5-dibromo-2-pyridyl)methacrylamide gave a trace amount of 3,5-dibromopyridine. Dehydrogenation of compound III with selenium dioxide in acetic acid yielded the known 2-hydroxy-3-methyl-1,5-naphthyridine (XII).[5] This fact, and the NMR spectrum of compound III, led to its assignment as 1,2,3,4-tetrahydro-3-methyl-2-oxo-1,5-naphthyridine.

Table I. Photolysis of Various N-Substituted Acrylamides

Starting acrylamide derivatives	Product (s)	Yield (%)
N-(2-Pyridyl)acrylamide	I	17.1
N-(2-Pyridyl)methacrylamide	II	78.0
N-(3-Pyridyl)methacrylamide	III	53.1
	IV	22.2
N-(4-Pyridyl)methacrylamide	V	71.6
N-(4-Pyrimidyl)methacrylamide	VI	24.0
N-(5-Pyrimidyl)methacrylamide	VII	13.7
N-(2-Pyrazyl)methacrylamide	VIII	19.4
N-(1-Methyl-4-imidazolyl)methacrylamide	IX	6.0
N-(1-Phenyl-4-pyrazolyl)methacrylamide	X	2.6
N-(2-Chloro-3-pyridyl)methacrylamide	XIII	24.7

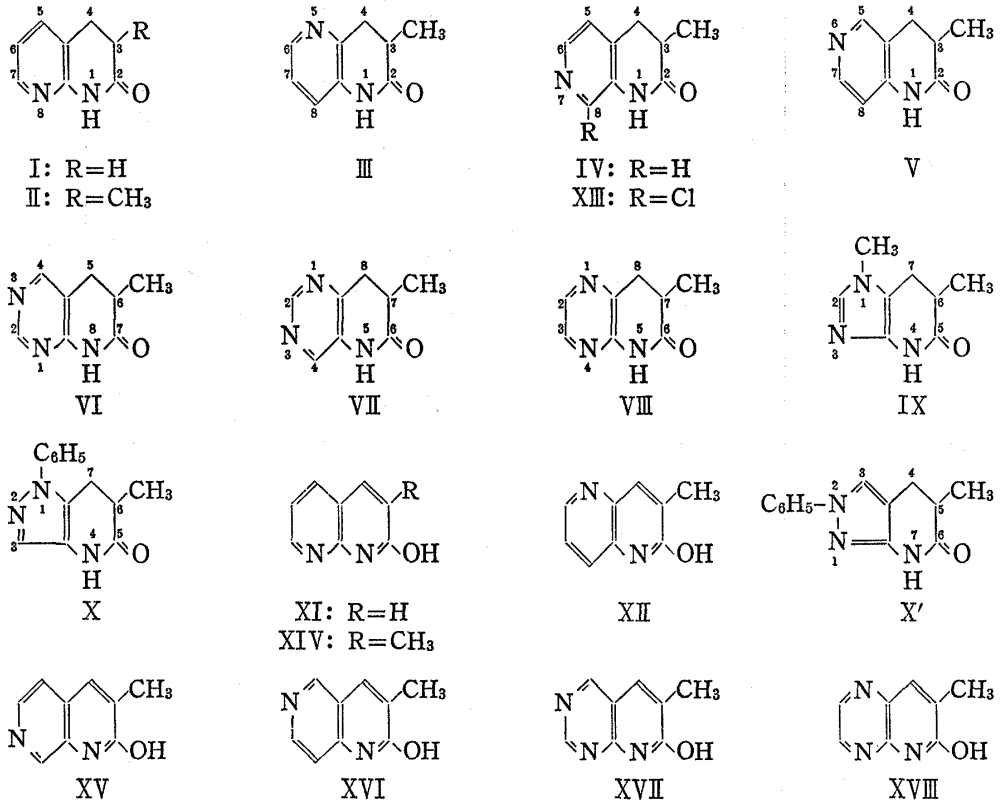


Chart 1

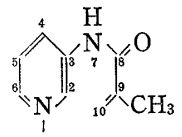
4) E.M. Harves and D.G. Wibberley, *J. Chem. Soc.*, **1967**, 1564.
5) H. Rapoport and A.D. Batcho, *J. Org. Chem.*, **28**, 1753 (1963).

TABLE II. NMR Spectra Parameters of the Compounds[a] (I—X, XIII)

Compd.	Chemical shifts (τ) (multiplicities)								Spin-spin couplngs (Hz)		
	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8			
I[b]	−0.30(bs)	—	[6.7—7.2(m)]		2.43(bq)	3.07(q)	1.92(q)	—	J_{H_5,H_6} 7.5;	J_{H_5,H_7}, 2.0;	J_{H_6,H_7} 5.0
II[b]	−0.38(bs)	—	[CH_3 8.87 (d) H_3, H_4 6.9—7.4(m)]		2.37(bq)	3.06(q)	1.88(q)	—	J_{CH_3,H_3} 6.0; J_{H_6,H_7} 5.0	J_{H_5,H_6} 7.0;	J_{H_5,H_7} 2.0
III[b]	0.50(bs)	—	[CH_3 8.68 (d) H_3, H_4 6.4—7.3(m)]		—	1.72(q)	2.85—2.94(m)	—	J_{CH_3,H_3} 6.0;	J_{H_6,H_7} 3.5;	J_{H_6,H_8} 2.5
IV[b]	−0.16(bs)	—	[CH_3 8.87(d) H_3, H_4 6.7—7.4(m)]		2.82(bd)	[1.84—1.95(m)]			J_{CH_3,H_3} 6.0;	J_{H_5,H_6} 4.5	
V[b]	−0.33 (bs)	—	[CH_3 8.87(d) H_3,H_4 6.7—7.2 (m)]		[~1.78(m)]			3.20(d)	J_{CH_3,H_3} 6.0;	J_{H_7,H_8} 5.0	
VI[b]	—	1.35(s)	—	1.58(s)	[CH_3 8.88(d) H_5,H_6 6.8—7.5(m)]		—	0.83(bs)	J_{CH_3,H_6} 6.5		
VII[c]	—	1.17(s)	—	1.78(s)	1.00(bs)	—	[CH_3 8.87(d) H_7,H_8 6.8—7.3(m)]		J_{CH_3,H_7} 6.5		
VIII[b]	—	[H_2,H_3 1.90(s)]		—	−0.37(bs)	—	[CH_3 8.85(d) H_7H_8 6.7—7.3(m)]		J_{CH_3,H_7} 6.5		
IX[c]	CH_3 6.45(s)	2.83(s)	—	1.60(bs)	—	[CH_3 8.68(d) H_6,H_7 6.8—7.5(m)]		—	J_{CH_3,H_6} 6.5		
X[c]	[~2.54(m)	—	2.54]	1.84(bs)	—	[CH_3 8.68(d) H_6,H_7 6.7—7.3(m)]		—	J_{CH_3,H_6} 6.5		
XIII[c]	0.39(bs)	—	[CH_3 8.88(d) H_3,H_4 6.7—7.3(m)]		2.73(bd)	2.02(d)	—	—	J_{CH_3,H_3} 6.0;	J_{H_5,H_6} 4.5	

a) The spectra were recorded on a Varian A-60 spectrometer with TMS as internal standard. b=broad, d=doublet, s=singlet, m=multiplet *b*) DMSO, *c*) $CDCl_3$

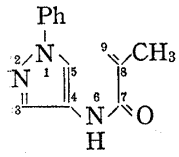
The following reactions were carried out to decide the structure of compound IV. Irradiation of N-(2-chloro-3-pyridyl)methacrylamide in benzene afforded 8-chloro-1,2,3,4-tetrahydro-3-methyl-2-oxo-1,7-naphthyridine (XIII). Catalytic hydrogenation of XIII with palladium charcoal in ethanol containing hydrochloric acid gave IV, which was identical with the compound given by irradiation of N-(3-pyridyl)methacrylamide. From these results, the structure of IV was assigned as 1,2,3,4-tetrahydro-3-methyl-2-oxo-1,7-naphthyridine. In connection with the course of photocyclization, we calculated the free valence numbers (Fr*) for N-(3-pyridyl)methacrylamide by the simple Hückel MO method, using the reaction $Fr^* = \sqrt{3} - \sum P_{ij}^*$, in which P_{ij}^* is the π bond order in the first π-π^* excited state between the atom i and neighboring atom j.[6] The ratio of photocyclization products (III and IV) is in accord with the theoretical prediction that the sum of the free-valence numbers ($\sum Fr^*$) of the 4 and 10 positions is less than that of the 2 and 10 positions. As shown in Table II, the NMR spectra of V, VI, VII, VIII, and IX were also consistent with the expected structures, 1,2,3,4-tetrahydro-3-methyl-2-oxo-1,6-naphthyridine, 5,6,7,8-tetrahydro-6-methyl-7-oxo-pyrido[2,3-*b*]pyrimidine, 5,6,7,8-tetra-hydro-7-methyl-6-oxo-pyrido[3,2-*d*]pyrimidine, 5,6,7,8-tetrahydro-7-methyl-6-oxo-pyrido[2,3-*b*]pyrazine, and 4,5,6,7-tetrahydro-1,6-dimethyl-5-oxo-imidazo[4,5-*b*]pyridine,[7] respectively. The structure 4,5,6,7-tetrahydro-6-methyl-5-oxo-1-phenylpyrazo[4,3-*b*]pyridine was assigned to X from the NMR spectrum, but the alternative structure, 4,5,6,7-tetrahydro-5-methyl-6-oxo-2-phenylpyrazo[3,4-*b*]pyridine (X'), could not be ruled out. According to the theoretical prediction that the sum of free valence numbers of the 3 and 9 positions is less than that of the 5 and 9 positions, photocyclization of N-(1-phenyl-4-pyrazolyl)methacrylamide should be expected to give 4,5,6,7-tetrahydro-6-methyl-5-oxo-1-phenylpyrazo[4,3-*b*]pyridine (X).



Fr_2^* 0.5758, Fr_{10}^* 1.0467, Fr_4^* 0.4860; $\sum Fr_{2,10}^*$ 1.6225, $\sum Fr_{4,10}^*$ 1.5333

$h_{\ddot{N}}=1.5$ $k_{CN}=0.8$
$h_{\dot{O}}=1.0$ $k_{CO}=1.0$
$h_{\dot{N}}=0.5$

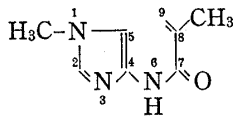
Chart 2



Fr_5^* 0.6853, Fr_8^* 0.2426, Fr_9^* 1.0476; $\sum Fr_{5,9}^*$ 1.7326, $\sum Fr_{8,9}^*$ 1.2902

$h_{\ddot{N}}=1.5$ $k_{CN}=0.8$
$h_{\dot{O}}=1.0$ $k_{CO}=1.0$
$h_{\dot{N}}=0.5$

Chart 3



Fr_5^* 0.7356, Fr_9^* 1.1085; $\sum Fr_{5,9}^*$ 1.8441

$h_{\ddot{N}}=1.5$ $k_{CN}=0.8$
$h_{\dot{O}}=1.0$ $k_{CO}=1.0$
$h_{\dot{N}}=0.5$
$h_{\ddot{N}\text{-}CH_3}=1.4$

Chart 4

Dehydrogenation of compounds II, IV, V, VI, and VIII with selenium dioxide in acetic acid afforded 2-hydroxy-3-methyl-1,8-naphthyridine (XIV), 2-hydroxy-3-methyl-1,7-naphthyridine (XV), -1,6-naphthyridine (XVI), 7-hydroxy-6-methylpyrido[2,3-*b*]pyrimidine (XVII), and 6-hydroxy-7-methylpyrido[2,3-*b*]pyrazine (XVIII), respectively.

Experimental

All melting points were taken on a Kofler hot-stage and are uncorrected. The light source for the photolysis was a high pressure Hg arc lamp with pyrex filter. During irradiation a steady stream of argon was bubbled through the solution.

6) *a*) W.H. Laarhoven, Th. J.H.M. Cuppen, and R.J.F. Nivard, *Rec. Trav. Chim.*, **87**, 687 (1968); *b*) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N.Y., 1961, p. 329.

7) $\sum Fr^*$ calculation for N-(1-methyl-4-imidazolyl)methacrylamide has been made.

General Procedure of Photolysis——The general procedure was that described for the preparation of 1,2,3,4-tetrahydro-2-oxo-1,8-naphthridine (I).

A solution of N-(2-pyridyl)acrylamide (1.22 g) in benzene (400 ml) containing AcOH (2.5 ml) was irradiated for 3 hr with 450 W high pressure mercury arc lamp through pyrex filter. The solvent was evaporated and the residue was chromatographed on alumina to give starting material, 364 mg (29.8%) and I, 375 mg (30.7%). Recrystallization from AcOEt gave I as colorless prisms, 208 mg (17.1%), mp 162—164°.

The yields, spectral data and elemental analysis are shown in Table I, II and III.

Table III. Photoproducts

Product	Recryst. solvent	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N
I	AcOEt	17.1	162—164	$C_8H_8ON_2$	64.85	5.44	18.91	64.62	5.55	18.55
II	AcOEt	78.0	200—200.5	$C_9H_{10}ON_2$	66.65	6.22	17.27	66.77	6.26	17.24
III	AcOEt	53.1	167—168	$C_9H_{10}ON_2$	66.65	6.22	17.27	66.81	6.28	17.10
IV	AcOEt	22.2	210—213	$C_9H_{10}ON_2$	66.65	6.28	17.27	66.37	6.28	16.98
V	iso-PrOH	71.6	254—255	$C_9H_{10}ON_2$	66.65	6.28	17.27	66.98	6.21	17.16
VI	MeOH	24.0	229—230	$C_8H_9ON_3$	58.88	5.56	25.75	58.74	5.42	25.65
VII	iso-PrOH	13.7	245—246	$C_8H_9ON_3$	58.88	5.56	25.75	58.88	5.80	25.47
VIII	iso-PrOH	19.4	195—196	$C_8H_9ON_3$	58.88	5.56	25.75	59.18	5.55	25.48
IX	MeOH-AcOEt	6.0	250—252	$C_8H_{11}ON_3$	58.16	6.71	25.44	57.80	6.93	25.31
X	Bz	2.6	161—162.5	$C_{13}H_{13}ON_3 \cdot \frac{1}{2}H_2O$	66.08	5.97	17.79	66.34	5.86	17.75
XIII	AcOEt	24.7	160—161	$C_9H_8ON_2Cl$	54.96	4.62	14.24	55.25	4.62	14.05

Table IV. Dehydrogenation Products

Product	Recryst. solvent	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N
XI	MeOH	35.0	202—203	$C_8H_6ON_2$	65.75	4.14	19.17	65.57	4.28	18.87
XIV	MeOH	66.5	231—232	$C_9H_8ON_2$	67.48	5.03	17.49	67.41	5.08	17.34
XV	MeOH	15.8	253—254	$C_9H_8ON_2$	67.48	5.03	17.49	67.33	5.02	17.35
XVI	MeOH	36.4	302—303	$C_9H_8ON_2$	67.48	5.03	17.49	67.57	4.95	17.80
XVII	EtOH-$CHCl_3$	90.5	302—303	$C_8H_7ON_3$	59.62	4.38	26.07	60.08	4.53	25.85
XVIII	MeOH	64.7	238—240	$C_8H_7ON_3$	59.62	4.38	26.07	59.59	4.38	25.90

General Procedure of Dehydrogenation——The procedure for the preparation of 2-hydroxy-1,8-naphthyridine (XI) is representative. A solution of I (200 mg) and selenium dioxide (180 mg) in AcOH (4 ml) was heated on a oil-bath at 130° for 23.5 hr. After removal of the precipitate, the filtrate was evaporated and the residue was chromatographed on alumina and elution with $CHCl_3$–MeOH (10:1) gave XI [69 mg (35.0%), colorless needles, mp 203° after recrystallization from MeOH].

The physical properties, spectral data and elemental analysis are shown in Table IV.

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