[Chem. Pharm. Bull.
21(9)2019—2025(1973)]

UDC 547.785.5.04 : 547.314.2.04

Studies on Heterocyclic Compounds. XIII.[1] Reaction of 2-Aminobenzazoles with Acetylenic Compounds

Haruo Ogura, Mitsuo Kawano, and Tsuneo Itoh

School of Pharmaceutical Sciences, Kitasato University[2]

(Received February 21, 1973)

Reaction of 2-aminobenzazoles such as 2-amino-benzothiazole, -benzoxazole, and -benzimidazole with acetylene compounds was reported comparing with the condensation product of these benzazoles and ethoxy methylenemalonate. In the former case, 2-oxo compounds were obtained while 4-oxo compounds were the product in the latter condensation. The structure of these products was confirmed from nuclear magnetic resonance and mass spectra.

Previously, we reported the synthesis of tricyclic azole series, such as thiazolo[3,2-*a*]-benzimidazoles,[3,4] thiazolo[2,3-*b*]benzothiazoles,[5] and imidazo[2,1-*b*]benzothiazoles,[6] imidazo-[2,1-*b*]benzoxazoles,[7] and imidazo[1,2-*a*]benzimidazoles.[8] Antaki and Petrow[9] already reported the synthesis of 2-methyl-4-oxopyrimido[2,1-*b*]benzothiazole, -benzoxazole, and -benzimidazole from the reaction of ethyl β-aminocrotonate with 2-aminobenzothiazole (I), 2-aminobenzoxazole (II), and 2-aminobenzimidazole (III). Recently, Shiokawa and Ohki[10] reported the synthesis of 2,10-dimethyl-4-oxo-10*H*-pyrimido[1,2-*a*]benzimidazole from ethyl acetoacetate with 1-methyl-2-aminobenzimidazole. Recently, Dunwell and Evans[11] reported the reaction of 2-aminothiazoles and 2-aminobenzothiazoles with propiolic acid and its esters and obtained 7*H*-thiazolo[3,2-*a*]pyrimidin-7-ones and 2*H*-pyrimido[2,1-*b*]benzothiazol-2-ones, respectively, and not obtained any alternative isomeric 5*H*-thiazolo[3,2-*a*]pyrimidin-5-ones and 4*H*-pyrimido[2,1-*b*]benzothiazol-4-ones.

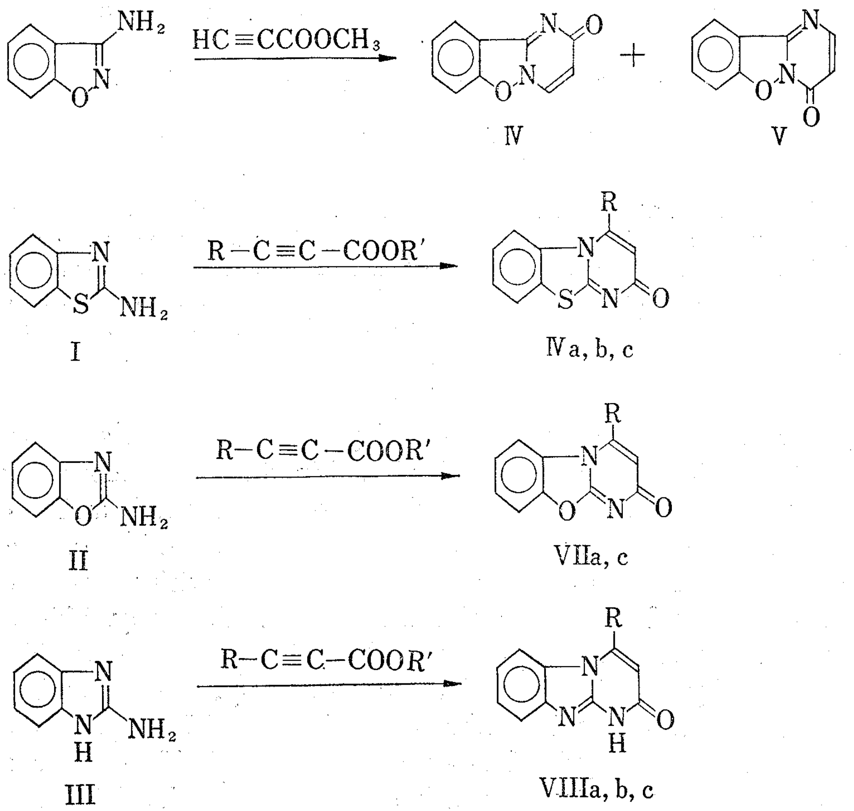
On the other hand, Reimlinger, *et al.*[12] reported about the reaction of methyl propiolate with 3-aminobenzisoxazole, with 2-amino-*s*-triazolo[1,5-*a*]pyridine, with 3-aminoindazole, and with 2-aminobenzimidazole. Only in the case of 3-aminobenzisoxazole, they obtained 15% of 2*H*-pyrimido[1,2-*b*]benzisoxazol-2-one (IV) and 8% of the alternative isomeric 4-oxo compound (V).

The present report describes the reaction of I, II, and III with acetylenic compounds. 2-Aminobenzothiazole (I) readily reacted with ethyl propiolate (R=H, R′=Et), ethyl phenylpropiolate (R=C_6H_5, R′=Et), or dimethyl acetylenedicarboxylate (R=COOMe, R′=Me), to yield 2-oxopyrimido[1,2-*a*]benzothiazoles (VIa, b, c). Similarly, 2-aminobenzoxazole (II) reacted with ethyl propiolate or dimethyl acetylenedicarboxylate to yield 2-oxopyrimido-[1,2-*a*]benzoxazoles (VIIa, c). Although, the reaction of II and ethyl phenylpropiolate

---

[1] Presented before the 91st Annual Meeting of the Pharmaceutical Society of Japan, April 1971, p. 669.
[2] Location: *Shirokane, Minato-ku, Tokyo, 108, Japan.*
[3] H. Ogura, T. Itoh, and Y. Shimada, *Chem. Pharm. Bull.* (Tokyo), **16**, 2167 (1968).
[4] H. Ogura, T. Itoh, and K. Kikuchi, *J. Heterocyclic Chem.*, **6**, 797 (1969).
[5] H. Ogura, T. Itoh, M. Ogiwara, and T. Okamoto, *Yakugaku Zasshi*, **89**, 469 (1969).
[6] H. Ogura and T. Itoh, *Chem. Pharm. Bull.* (Tokyo), **18**, 1981 (1970).
[7] H. Ogura, T. Itoh, and S. Sugimoto, *Chem. Pharm. Bull.* (Tokyo), **18**, 2204 (1970).
[8] H. Ogura and T. Itoh, *Kitasato Arch. Exptl. Med.*, **42**, 65 (1969).
[9] H. Antaki and V. Petrow, *J. Chem. Soc.*, 551 (1951).
[10] Y. Shiokawa and S. Ohki, *Chem. Pharm. Bull.* (Tokyo), **19**, 401 (1971).
[11] D.W. Dunwell and D. Evans, *J. Chem. Soc.* (*C*), **1971**, 2094.
[12] H. Reimlinger, M.A. Peiren, and R. Merényi, *Chem. Ber.*, **105**, 794 (1972).

did not afford any cyclized compound (VIIb) and only the starting material was recovered. The reaction of 2-aminobenzimidazole (III) proceeded in a similar manner to yield 2-oxopyrimido[1,2-*a*]benzimidazoles (VIIIa, b, c). In these cases, only 2-oxo derivatives were obtained, and not obtained any alternative isomeric 4-oxo compounds.



a : R=H, b :R=C_6H_5, c : R=$COOCH_3$
R′ =CH_3 or C_2H_5

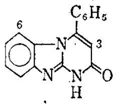
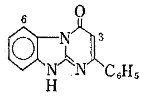
Chart 1

The structure of these products was determined from their nuclear magnetic resonance (NMR), mass, and infrared (IR) spectra. In the NMR spectra of VI, VII, and VIII, chemical shift of the proton at C-6 appeared at δ 7.0—8.0 ppm ($CDCl_3$). This was confirmed by comparing the NMR spectra of 2-oxo-4-phenylpyrimido[1,2-*a*]benzimidazole (VIIIb) and 4-oxo-2-phenyl compound (IX), which was prepared from the condensation of III and ethyl benzoylacetate.

Table I summarizes the NMR and IR data of these compounds (VIIIb and IX). The proton at C-6 in the 4-oxo compound (IX) had shifted to a lower field (8.35 ppm) by the paramagnetic anisotropic effect of C-4 carbonyl group. On the other hand, C-6 proton in the 2-oxo compound (VIIIb) appeared at 7.0—7.8 ppm. The IR spectra of these compounds showed the presence of an amide group, which also supported this structural elucidation. This conclusion may be applicable to confirm the position of the oxo group to the cyclized products of amino heterocycles with acetylenic compound reported by Reimlinger, *et al.*[12]

This reaction process may be represented by the sequence shown in Chart 2. An intermolecular proton transfer from an amino group at C-2 position may be considered (A), and this introduced an intermediate (B) with an olefinic group attached to the cyclic nitrogen atom rather than on the amino group and this intermediate (B) underwent cyclization. This conclusion is similar to the reactions of 3-amino-2-cyclohexenone with methyl propiolate and

Table I. NMR and IR Data of VIIIb and IX

		 VIIIb	 IX
NMR (DMSO-d_6)	3-H	δ 5.81 ppm	δ 6.30 ppm
	6-H	7.0—7.8	8.35
IR (KBr)	NH	3410 cm^{-1}	—
		3610	3650
	CO	1650	1680

of ethyl 2-(benzimidazolyl)acetate with methyl acetylenedicarboxylate,[13] and to the reaction of N-alkyl-6-aminouracils with dimethyl acetylenedicarboxylate.[14]

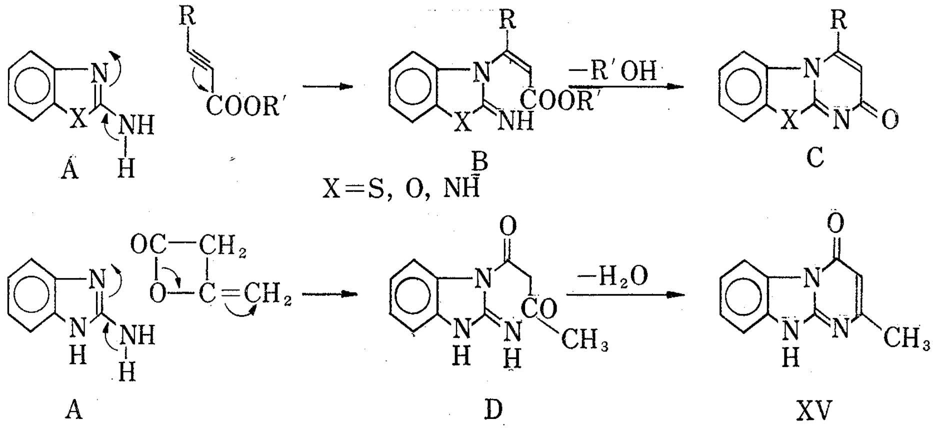


Chart 2

In the condensation reaction of 2-aminobenzothiazole (I) or 2-aminobenzoxazole (II) with diethyl ethoxymethylenemalonate under the same condition as the above-cited reaction with acetylenic compounds, open-chain compounds, X (X=S) or XII (X=O), were obtained. These open-chain compounds further cyclized to 3-ethoxycarbonyl-4-oxopyrimido[2,1-*b*]-benzazole, XI (X=S) or XIII (X=O), on being heated with Dowtherm A. On the other hand, condensation of 2-aminobenzimidazole (III) with diethyl ethoxymethylenemalonate resulted in cyclization and gave 3-ethoxycarbonyl-4-oxopyrimido[2,1-*b*]benzimidazole (XIV). Condensation reaction of III with diketene or ethyl acetoacetate afforded 2-methyl-4-oxopyrimido-[2,1-*b*]benzimidazole (XV) in a good yield.

When 4-oxo compound (IX) was methylated with methyl iodide under basic condition, 10-methyl derivative (XVI) was obtained. This was assumed since comparison of the methylated product (XVI), which was obtained from the cyclization of 2-amino-1-methylbenzimidazole (XVII) and ethyl benzoylacetate, proved them to be identical. On the other hand, 2-oxo compound (VIIIb) was methylated under the same condition described above to yield 1-methyl compound (XIX), and not obtained any 10-methyl compound (XVIII). This was confirmed by comparison of XVIII, prepared from XVII and ethyl phenylpropiolate. Alkylation did not took place under neutral or acidic conditions. From this experiment, tautomeric system in which the 10-H isomer (IX) would be expected to predominate in 4-oxo compound under basic condition. On the other hand, 1-H isomer (VIIIb) would be expected in 2-oxo compound under basic condition.

---

[13] N. Finch and C.W. Gemenden, *J. Org. Chem.*, **35**, 3114 (1970).
[14] H. Ogura and M. Sakaguchi, *Chem. Letters*, **1972**, 657.

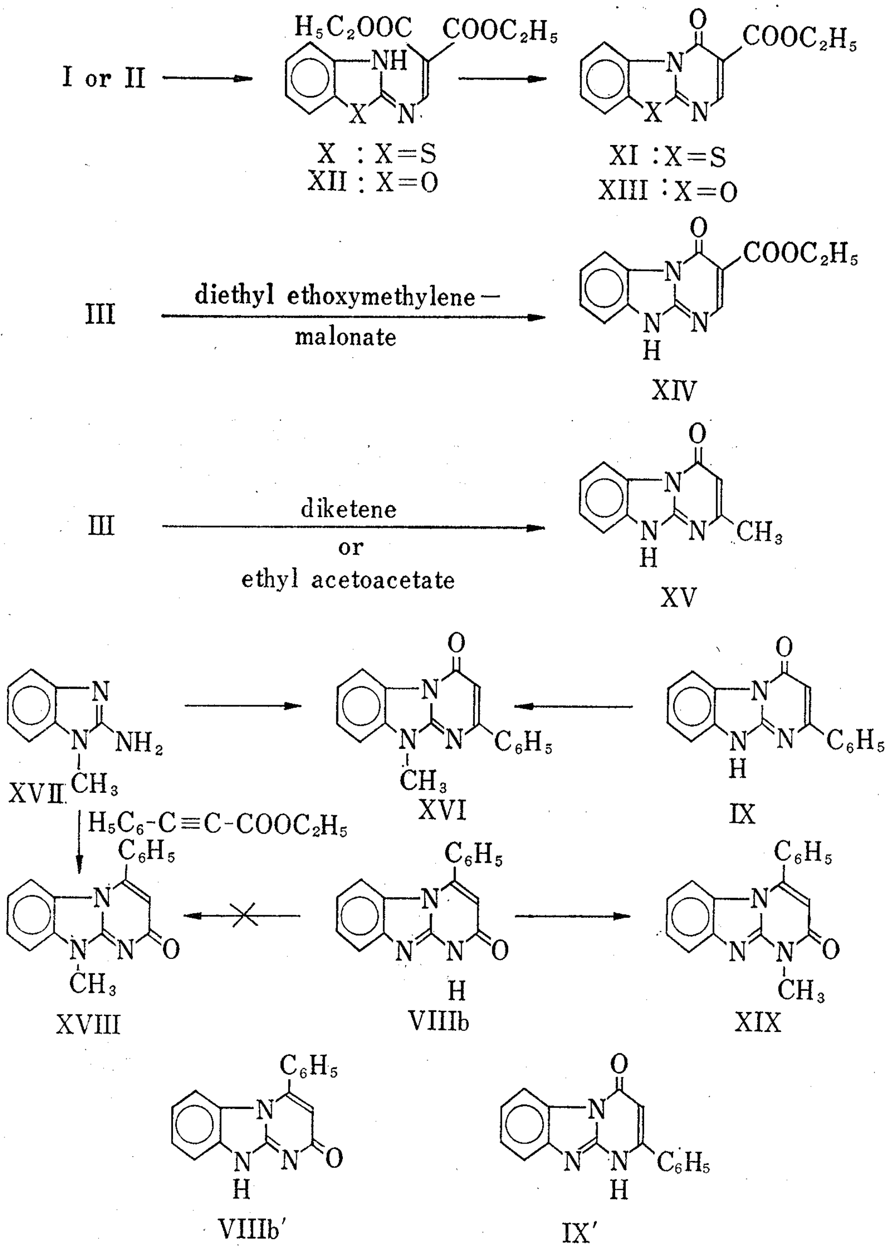
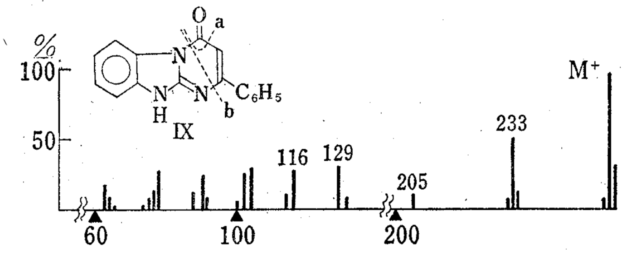
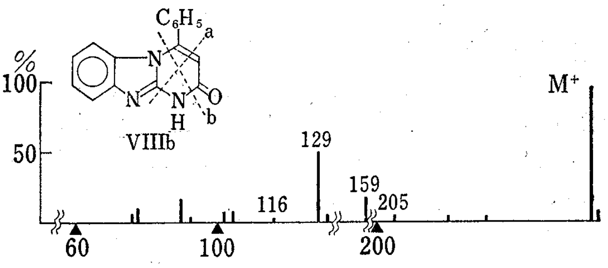


Chart 3



m/e	Formula	Calcd.	Found
261 (M+)	$C_{16}H_{11}ON_3$	261.090	261.090
233	$C_{15}H_{11}N_3$	233.095	233.095
205	$C_{14}H_9N_2$	205.077	205.078
129	C_9H_5O	129.034	129.035
116	$C_7H_4N_2$	116.037	116.037

Fig. 1



m/e	Formula	Calcd.	Found
261 (M+)	$C_{16}H_{11}ON_3$	261.090	261.090
205	$C_{14}H_9N_2$	205.077	205.075
129	C_9H_5O	129.034	129.034
116	$C_7H_4N_2$	116.037	116.036

Fig. 2

Mass spectra of 2-oxo compound (VIIIb) and 4-oxo compound (IX) are shown in Figure. 2-Oxo compound (VIIIb) shows a base peak at molecular ion (*m/e* 261), a peak at *m/e* 205 (M-C_2H_2ON) corresponding a cleavage at a, and a strong peak at *m/e* 129 (C_9H_5O) corresponding a cleavage at b [C_9H_6O(*m/e* 130)-H]. On the other hand, 4-oxo compound (IX) shows a base peak at molecular ion (*m/e* 261), a strong peak at *m/e* 233 (M-CO) corresponding a scission a, and a peak at *m/e* 129 (C_9H_5O) corresponding a cleavage at b similar to that of VIIIb.

Experimental

Melting points were determined with a Yamato melting point apparatus Type Mp. 1, and are uncorrected. NMR spectra were measured in $CDCl_3$ with a Varian T-60 spectrometer unless otherwise stated and tetra-

Table II. 4-Substituted 2-Oxobenzazoles

Compound	X	R	mp (°C)	Yield (%)	Mass spectrum *m/e* (M^+)	IR ν_{max}^{KBr} cm^{-1} (carbonyl)	UV λ_{max}^{EtOH} nm (log ε)
VIa	S	H	272 (yellow needles)	66	202	1635	230(4.40), 241(4.32), 263(4.11), 301(4.15)
VIb	S	C_6H_5	241 (yellow needles)	10	278	1635	233(4.98), 250(4.09), 306(4.18)
VIc	S	COOMe	203 (white needles)	52	260	1725 1650	229(4.24), 250(4.09), 265(4.05), 300(3.98)
VIIa	O	H	257 (white needles)	55	186	1625	243(4.18), 292(4.30)
VIIc	O	COOMe	207 (white needles)	58	244	1735 1625	243(4.04), 310(3.84)
VIIIa	NH	H	313—315 (white needles)	69	185	1675	239(4.22), 249(4.05)
VIIIb	NH	C_6H_5	300 (white needles)	21	261	1650	242(4.46), 305(4.03)
VIIIc	NH	COOMe	221 (pale yellow powder)	73	243	1740 1690	213(4.35), 239(4.42)

Compound	Formula	Analysis (%)						NMR δ (ppm)
		Calcd.			Found			
		C	H	N	C	H	N	
VIa	$C_{10}H_6ON_2S$	59.39	2.99	13.85	59.18	2.92	13.73	6.51 (1H, doublet, 3-H, $J_{3,4}$=8.0 Hz), 7.51—7.97 (4H, multiplet, aromatic protons), 8.85 (1H, doublet, 4-H, $J_{4,3}$=8.0 Hz) (CD_3OD)
VIb	$C_{16}H_{10}ON_2S$	69.05	3.62	10.06	68.86	3.61	9.86	6.30 (1H, singlet, 3-H), 7.50—7.80 (9H, multiplet, aromatic protons) ($CDCl_3$)
VIb	$C_{12}H_8O_3N_2S$	55.38	3.10	10.76	55.18	3.09	10.76	4.13 (3H, singlet, $COOCH_3$), 6.63 (1H, singlet, 3-H), 7.20—7.70 (4H, multiplet, aromatic protons) (CD_3COCD_3)
VIIa	$C_{10}H_6O_2N_2$	64.52	3.25	15.05	64.78	3.34	14.99	7.45 (1H, doublet, 3-H, $J_{3,4}$=8.0 Hz), 7.85—8.31 (4H, multiplet, aromatic protons), 9.15 (1H, doublet, 4-H, $J_{4,3}$=8.0 Hz) (CF_3COOH)
VIIc	$C_{12}H_8O_4N_2$	59.02	3.30	11.47	59.08	3.31	11.59	4.12 (3H, singlet, $COOCH_3$), 6.69 (1H, singlet, 3-H), 7.33—7.89 (4H, multiplet, aromatic protons), ($CDCl_3$)
VIIIa	$C_{10}H_7ON_3$	64.86	3.81	22.69	64.73	3.74	22.86	6.05 (1H, doublet, 3-H, $J_{3,4}$=5.0 Hz), 7.10—8.00 (4H, multiplet, aromatic protons), 8.70 (1H, doublet, 4-H, $J_{4,3}$=5.0 Hz) (DMSO-d_6)
VIIIb	$C_{16}H_{11}ON_3$	73.55	4.24	16.08	73.49	4.36	16.08	5.81 (1H, singlet, 3-H), 6.6—7.7 (9H, multiplet, aromatic protons) (DMSO-d_6)
VIIIc	$C_{12}H_9O_3N_3$	59.26	3.73	17.28	59.05	3.66	17.20	3.70 (3H, singlet, $COOCH_3$), 6.50 (1H, singlet, 3-H), 7.05—7.75 (4H, multiplet, aromatic protons) (DMSO-d_6)

methylsilane was used as an internal standard. Ultraviolet (UV) spectra were determined with a Hitachi EPS-3 spectrophotometer and IR spectra with a Shimadzu IR-27G spectrometer. Mass spectra were taken with a Japan Electron Optics spectrometer.

General Procedure for 4-Substituted 2-Oxopyrimido[2,1-*b*]benzazoles (VIa,b,c; VIIa,c; VIIa,b,c) (Table II)——To a solution of 2-aminobenzazole (5 mmole) in EtOH (20 ml), acetylene compound (5 mmole) was added, and the solution was warmed under reflux for 0.5—3 hr. After ice-cooling, separated crystals were recrystallized from MeOH (VIa,b,c; VIIa,c; VIIIb) or dimethylformamide (VIIIa,c).

4-Oxo-2-phenyl-10*H*-pyrimido[1,2-*a*]benzimidazole (IX)——A solution of 2-aminobenzimidazole (0.7 g; 5 mmole) and ethyl benzoylacetate (0.9 g; 5 mmole) in EtOH (20 ml) was warmed under reflux for 3 hr. When cooled, the separated crystals were recrystallized from MeOH to yield 0.5 g (46%) of IX as white needles, mp 296—297°. *Anal.* Calcd. for $C_{16}H_{11}ON_3$: C, 73.55; H, 4.24; N, 16.08. Found: C, 73.32; H, 4.31; N, 15.97. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1680 (C=O), 1550, 730 (phenyl). UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ε): 254 (4.47), 288 (4.22), 345 (3.97). Mass Spectrum *m/e*: 261 (M^+). NMR (Me_2SO-d_6) δ (ppm): 6.70 (1H, singlet, 3-H), 7.45—8.21 (8H, multiplet, aromatic protons), 8.35 (1H, multiplet, 6-H).

2-(2,2-Diethoxycarbonylimino)benzothiazole (X)——A solution of 2-aminobenzothiazole (0.7 g) and diethyl ethoxymethylenemalonate (1.0 g) in EtOH (20 ml) was warmed under reflux for 3 hr. After evaporation of the solvent to 2 ml, the separated white needles were recrystallized from MeOH to yield 0.98 g (66%) of X, mp 109°. *Anal.* Calcd. for $C_{15}H_{16}O_4N_2S$: C, 56.24; H, 5.03; N, 8.74. Found: C, 56.06; H, 5.12; N, 8.69. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1685, 1650 (ester). UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ε): 213 (3.56), 260 (2.82), 330 (3.59). Mass Spectrum *m/e*: 320 (M^+). NMR (CD_3COCD_3) δ (ppm): 1.35 (3H, triplet, $COOCH_2C\underline{H}_3$), 1.40 (3H, triplet, $COOCH_2C\underline{H}_3$), 4.35 (2H, quartet, $COOC\underline{H}_2CH_3$), 4.40 (2H, quartet, $COOC\underline{H}_2CH_3$), 7.27—8.00 (4H, multiplet, aromatic protons), 8.80 (1H, singlet, 1-H).

3-Ethoxycarbonyl-4-oxopyrimido[2,1-*b*]benzothiazole (XI)——A solution of X (0.8 g) in Dowtherm A (20 ml) was heated under reflux for 0.5 hr. When cooled petr. ether was added to the reaction mixture to separate white crystals. Recrystallization from MeOH yielded 0.43 g (63%) of XI as white needles, mp 147°. *Anal.* Calcd. for $C_{13}H_{10}O_3N_2S$: C, 56.93; H, 3.67; N, 10.21. Found: C, 56.88; H, 3.66; N, 10.06. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1715 (ester), 1680 (C=O). UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ε): 237 (4.19), 245 (4.19), 280 (3.55), 345 (4.42), 358 (4.43). Mass Spectrum *m/e*: 274 (M^+). NMR δ (ppm): 1.30 (3H, triplet, $COOCH_2C\underline{H}_3$), 4.45 (2H, quartet, $COOC\underline{H}_2CH_3$), 7.46—7.85 (3H, multiplet, aromatic protons), 8.70 (1H, singlet, 2-H), 9.10 (1H, triplet, 6-H).

2-(2,2-Diethoxycarbonylethyleneimino)benzoxazole (XII)——A solution of 2-aminobenzoxazole (0.7 g) and diethyl ethoxymethylenemalonate (1.1 g) in EtOH (20 ml) was warmed under reflux for 3 hr. After evaporation of the solvent to 2 ml, separated pale brown plates were recrystallized from MeOH to yield 0.95 g (61%) of XII, mp 105—107°. *Anal.* Calcd. for $C_{15}H_{16}O_5N_2$: C, 59.21; H, 5.30; N, 9.21. Found: C, 59.08; H, 5.27; N, 9.11. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1730, 1650 (ester). UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ε): 315 (3.84). Mass Spectrum *m/e*: 304 (M^+). NMR (CD_3OD) δ (ppm): 1.40 (6H, triplet, $(COOCH_2C\underline{H}_3)_2$), 4.30 (2H, quartet, $COOC\underline{H}_2CH_3$), 7.40—7.70 (4H, multiplet, aromatic protons), 8.70 (1H, singlet, 1-H).

3-Ethoxycarbonyl-4-oxopyrimido[2,1-*b*]benzoxazole (XIII)——A solution of XII (0.7 g) in Dowtherm A (20 ml) was heated under reflux for 1 hr. When cooled, petr. ether was added to separate white crystals, whose recrystallization from MeOH gave 0.38 g (61%) of XIII as white leaflets, mp 158°. *Anal.* Calcd. for $C_{13}H_{10}O_4N_2$: C, 60.47; H, 3.90; N, 10.85. Found: C, 60.46; H, 3.91; N, 10.80. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1710 (ester), 1690 (C=O). UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ε): 234 (4.27), 323 (4.33). Mass Spectrum *m/e*: 258 (M^+). NMR δ (ppm): 1.40 (3H, triplet, $COOCH_2C\underline{H}_3$), 4.41 (2H, quartet, $COOC\underline{H}_2CH_3$), 7.10—7.50 (3H, multiplet, aromatic protons), 8.30 (1H, multiplet, 6-H), 8.86 (1H, singlet, 2-H).

3-Ethoxycarbonyl-4-oxo-10*H*-pyrimido[1,2-*a*]benzimidazole (XIV)——A solution of III (0.7 g) and diethyl ethoxymethylenemalonate (1.0 g) in EtOH (20 ml) was warmed under reflux for 5 hr. After cooling, separated pale yellow crystals were recrystallized from DMF to yield 0.75 g (51%) of XIV as pale yellow needles, mp 292—295°. *Anal.* Calcd. for $C_{13}H_{11}O_3N_3$: C, 60.70; H, 4.31; N, 16.33. Found: C, 60.50; H, 4.60; N, 16.53. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1720 (ester), 1645 (C=O). UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ε): 248 (4.31), 273 (4.11), 291 (4.01). NMR (CF_3COOH) δ (ppm): 1.30 (3H, triplet, $COOCH_2C\underline{H}_3$), 4.30 (2H, doublet, $COOC\underline{H}_2CH_3$), 6.9—7.6 (3H, multiplet, aromatic protons), 8.20 (1H, multiplet, 6-H), 8.70 (1H, singlet, 2-H).

2-Methyl-4-oxo-10*H*-pyrimido[1,2-*a*]benzimidazole (XV)——a) From Diketene: To a cold solution of III (0.7 g) in dry benzene (20 ml), diketene (2 ml) was added under stirring. Separated white powder was crystallized from MeOH to yield 0.9 g (60%) of XV as colorless needles, mp and mixed mp with the sample prepared from b showed 285—287°.

b) From Ethyl Acetoacetate: A solution of III (0.7 g) and ethyl acetoacetate (2 ml) in EtOH (20 ml) was warmed under reflux for 3 hr. After cooling, separated white crystals were recrystallized from MeOH to yield 1.1 g (73%) of XV as colorless needles, mp 287—288°. *Anal.* Calcd. for $C_{11}H_9ON_3$: C, 66.32; H, 4.55; N, 21.09. Found: C, 66.09; H, 4.60; N, 20.92. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 2950 (CH_3), 1680 (C=O), 1380 (CH_3). NMR (CF_3COOH) δ (ppm): 2.70 (3H, singlet, CH_3), 6.45 (1H, singlet, 3-H), 7.70—8.0 (3H, multiplet, aromatic protons), 8.30 (1H, multiplet, 6-H).

10-Methyl-4-oxo-2-phenyl-10*H*-pyrimido[1,2-*a*]benzimidazole (XVI)——a) Methylation of IX: To a stirred solution of IX (0.26 g; 1 mmole) and KOH (0.06 g) in EtOH (30 ml), MeI (0.15 g) was added. After standing at room temperature over-night, EtOH was removed. The residual solid was recrystallized from $CHCl_3$ to yield 0.1 g (36%) of XVI as white needles, mp 217—218°. *Anal.* Calcd. for $C_{17}H_{13}ON_3$: C, 74.17; H, 4.76; N, 15.26. Found: C, 74.01; H, 4.67; N, 14.96. IR ν_{max}^{KBr} cm^{-1}: 1670 (C=O), 1550, 735 (phenyl). UV λ_{max}^{EtOH} nm (log ε): 255 (4.00), 287 (4.00), 347 (3.00); $\lambda_{max}^{0.1N\ NaOH/EtOH}$: 254 (4.00), 298 (4.00); $\lambda_{max}^{0.1N\ HCl/EtOH}$: 253 (4.00), 287 (4.00), 348 (3.00). Mass Spectrum *m/e*: 275 (M^+). NMR ($CDCl_3$) δ (ppm): 3.90 (3H, singlet, N-CH_3), 6.65 (1H, singlet, 3-H), 7.35—8.10 (8H, multiplet, aromatic protons), 8.40 (1H, singlet, 6-H).

b) From 2-Amino-1-methylbenzimidazole (XVII): A solution of XVII (0.98 g) in ethyl benzoylacetate (2.6 g) was heated at 160° for 5 hr. After cooling, MeOH was added to the reaction solution to precipitate XV. Recrystallization from MeOH gave 1.1 g (60%) of XV, mp and mixed mp 218—219°.

10-Methyl-2-oxo-4-phenyl-2*H*,10*H*-pyrimido[1,2-*a*]benzimidazole (XVIII)——A solution of XVII (0.73 g, 0.05 mole) and ethyl phenylpropiolate (0.87 g, 0.05 mole) in EtOH (20 ml) was heated under reflux for 3 hr. After evaporate the organic solvent under reduced pressure, residual crystals were recrystallized from $CHCl_3$ to obtain 0.42 g (31%) of XVIII as white needles, mp 235°. *Anal.* Calcd. for $C_{17}H_{13}ON_3$: C, 74.17; H, 4.76; N, 15.26. Found: C, 73.95; H, 4.88; N, 15.14. IR ν_{max}^{KBr} cm^{-1}: 1685 (C=O), 1530, 730 (phenyl). UV λ_{max}^{EtOH} nm (log ε): 241 (4.00), 307 (3.00); $\lambda_{max}^{0.1N\ NaOH/EtOH}$: 240 (4.00), 295 (4.00); $\lambda_{max}^{0.1N\ HCl/EtOH}$: 242 (4.00), 294 (3.00). Mass Spectrum *m/e*: 275 (M^+). NMR ($CDCl_3$) δ (ppm): 3.90 (3H, singlet, N-CH_3), 6.30 (1H, singlet, 3-H), 7.30—7.80 (9H, multiplet, aromatic protons).

1-Methyl-2-oxo-4-phenyl-1*H*,2*H*-pyrimido[1,2-*a*]benzimidazole (XIX)——To a stirred solution of VIIIb (0.26 g, 1 mmole) and KOH (0.06 g) in EtOH (30 ml), MeI (0.15 g) was added. After standing at room temperature over-night, EtOH was removed, and then extracted with $CHCl_3$. Evaporation of dried $CHCl_3$ solution left 0.06 g (22%) of XIX as white needles, mp 222—224°. *Anal.* Calcd. for $C_{17}H_{13}ON_3$: C, 74.17; H, 4.76; N, 15.26. Found: C, 73.96; H, 4.81; N, 14.98. IR ν_{max}^{KBr} cm^{-1}: 1675 (C=O), 1550, 740 (phenyl). UV λ_{max}^{EtOH} nm (log ε): 252 (4.00), 296 (3.00); $\lambda_{max}^{0.1N\ NaOH/EtOH}$: 251 (4.00), 298 (4.00); $\lambda_{max}^{0.1N\ HCl/EtOH}$: 253 (4.00), 288 (3.00). Mass Spectrum *m/e*: 275 (M^+). NMR ($CDCl_3$) δ (ppm): 3.80 (3H, singlet, N-CH_3), 6.26 (1H, singlet, 3-H), 7.25—7.70 (9H, multiplet, aromatic protons).