[Chem. Pharm. Bull. 31(8)2899—2904(1983)]

Studies on Ketene and Its Derivatives. CXVII.[1] Reaction of Dichloroketene with Ethyl *N*-(2-Pyridyl)formimidates

NOBUYA KATAGIRI,*[,a] RYUJI NIWA,[b] and TETSUZO KATO[a]

Pharmaceutical Institute, Tohoku University,[a] Aobayama, Sendai 980, Japan
Central Research Institute and Kantoishi Pharmaceutical Co., Ltd.,[b] 1780 Kitano, Tokorozawa 359, Japan

(Received February 3, 1983)

The reaction of dichloroketene with ethyl *N*-(2-pyridyl)formimidates (**1**) gave ethyl 2,2-dichloro-3-ethoxy-3-(2-pyridylamino)propionates (**3**) and 3-chloro-2-ethoxypyrido[1,2-*a*]pyrimidin-4(4*H*)-ones (**4**), together with 3,3-dichloro-4-ethoxy-1-(2-pyridyl)-2-azetidinone (**2**). Compound **3b**, on standing at room temperature, was transformed into ethyl 2-ethoxy-8-methylimidazo[1,2-*a*]pyridine-3-carboxylate (**6**).

Keywords——dichloroketene; ethyl *N*-(2-pyridyl)formimidate; 1,2-cycloaddition; 1,4-cycloaddition; 2-azetidinone; ethyl 2,2-dichloro-3-ethoxy-3-(2-pyridylamino)propionate; pyrido-[1,2-*a*]pyrimidine; imidazo[1,2-*a*]pyridine; 2-dichloroacetamidopyridine

Reports concerned with dichloroketene have mostly dealt with the cycloaddition to unsaturated bonds, and only a few studies on the reaction with compounds having C=N bonds have been reported.[2] The most typical reaction of dichloroketene with C=N bonds is the cycloaddition to imines to give 2-azetidinones.[3-5] However, the reaction with compounds bearing a conjugated C=N bond gives [2+4] cycloadducts.[3,6]

Previously, we have reported that dichloroketene reacted with aromatic amine *N*-oxides to give 2- or 4-dichloromethyl derivatives.[7] In connection with our continuing interest in the reaction of dichloroketene with compounds having C=N bonds we now wish to report the reaction of dichloroketene with ethyl *N*-(2-pyridyl)formimidates, which have a C=N bond conjugated with a pyridine ring C=N bond.

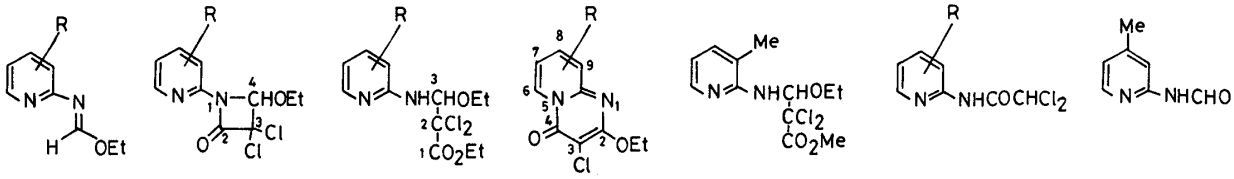
When ethyl *N*-(2-pyridyl)formimidate (**1a**) was allowed to react with dichloroketene[8] in ether, 3,3-dichloro-4-ethoxy-1-(2-pyridyl)-2-azetidinone (**2a**), ethyl 2,2-dichloro-3-ethoxy-3-(2-pyridylamino)propionate (**3a**), and 3-chloro-2-ethoxypyrido[1,2-*a*]pyrimidin-4(4*H*)-one (**4a**) were obtained in 7, 22, and 45% yields, respectively. Similarly, reaction of dichloroketene with the imidate **1d** gave the 2-azetidinone **2d**, ester **3d**, and pyridopyrimidine **4d** in 7, 11, and 36% yields, respectively. Similar reaction of dichloroketene with ethyl *N*-(3-methyl-2-pyridyl)formimidate (**1b**) did not give the 2-azetidinone, but gave the ester **3b** and pyridopyrimidine **4b** in 51 and 47% yields, respectively. The reaction in the presence of excess triethylamine gave exclusively the pyridopyrimidine **4b** in 80% yield.

On the other hand, when absolute methanol was added to the reaction mixture, the corresponding methyl ester **5** was obtained in 65% yield, together with a 25% yield of **4b**. When the esters **3b** and **5** were allowed to stand at room temperature, they cyclized to ethyl 2-ethoxy-8-methylimidazo[1,2-*a*]pyridine-3-carboxylate (**6**) and methyl 2-ethoxy-8-methylimidazo[1,2-*a*]pyridine-3-carboxylate (**7**), respectively. Compound **7** was also obtained by treatment of **5** with triethylamine. Structural assignments for compounds **6** and **7** were made on the basis of elemental analyses and spectral data as described in the experimental section.

Reaction of ethyl *N*-(4-methyl-2-pyridyl)formimidate (**1c**) with dichloroketene under

NII-Electronic Library Service

TABLE I. Reaction of Dichloroketene ($Cl_2C=C=O$) with Ethyl *N*-(2-Pyridyl)formimidates (**1a—e**)



1a—e **2a, d** **3a, b, d, e** **4a—e** **5** **8c, e** **9**

	Starting imidates (**1a—e**)	Yields of products (%) **2**	**3**	**4**	**5**	**8**	**9**
1a	R=H	7	22	45			
1b	R=3-Me		51	47			
	$+Et_3N$			80			
	+abs. MeOH			25	65		
1c	R=4-Me			21		9	9
1d	R=5-Me	7	11	36			
1e	R=6-Me		11	43		2	

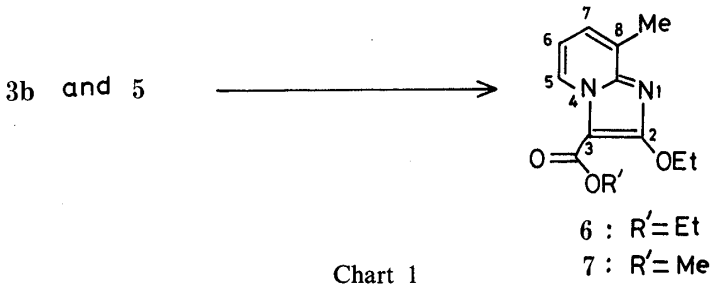


Chart 1

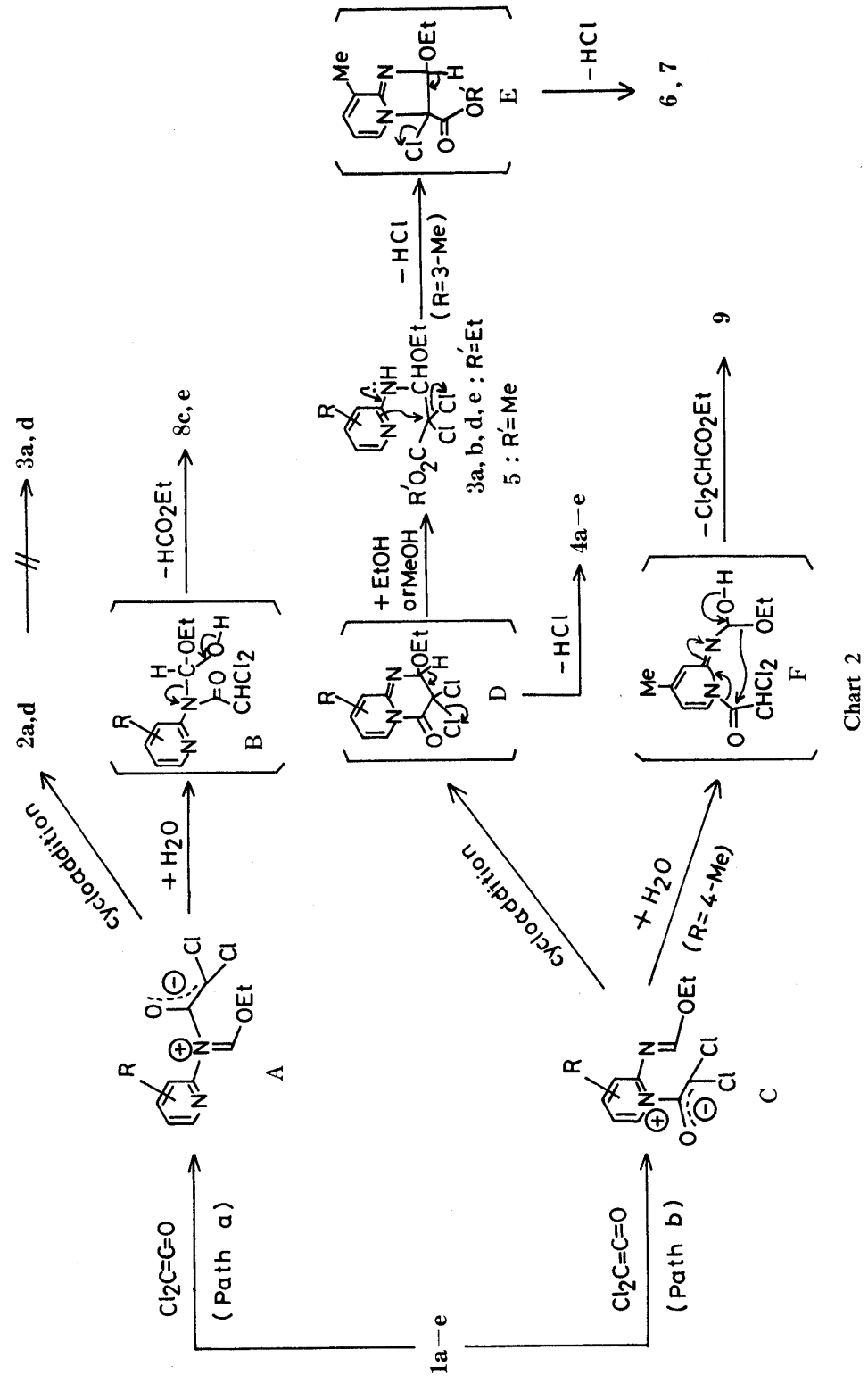
TABLE II. Spectral Data for Compounds **3a, b, d, e**

Compd. No.	IR ($CHCl_3$) cm^{-1} N–H	C=O	^{1}H-NMR ($CDCl_3$) δ NH	N–CH=	Pyridyl 6-H	MS *m/e* (M^+-OEt)
3a	3450	1750	5.27 (d)	6.23 (d)	8.13 (d)	261
3b	3450	1760	5.12 (d)	6.53 (d)	8.05 (d)	275
3d	3400	1760	5.18 (d)	6.27 (d)	7.95 (s)	275
3e	3450	1760	5.12 (d)	6.15 (d)	—	275

TABLE III. Melting Points and Spectral Data for Pyrido[1,2-*a*]pyrimidines (**4a—e**)

Compd. No.	mp (°C) (Recryst. solvent)	IR ($CHCl_3$) cm^{-1}	^{1}H-NMR ($CDCl_3$) δ OCH_2CH_3	OCH_2CH_3	6-H
4a	159—160 (Ether)	1675 1640	1.47 (3H, t)	4.60 (2H, q)	9.00 (1H, dd)
4b	165—166 (Benzene)	1675 1635	1.50 (3H, t)	4.60 (2H, q)	8.97 (1H, dd)
4c	150—151 (Ether)	1680 1650	1.45 (3H, t)	4.55 (2H, q)	8.93 (1H, d)
4d	178—179 (Ether)	1675 1645	1.45 (3H, t)	4.53 (2H, q)	8.79 (1H, s)
4e	121—122 (Ether)	1670 1635	1.43 (3H, t)	4.53 (2H, q)	—

NII-Electronic Library Service



NII-Electronic Library Service

similar conditions gave the pyridopyrimidine **4c**, 2-dichloroacetamido-4-methylpyridine (**8c**), and 2-formamido-4-methylpyridine (**9**) in 9, 9, and 21% yields, respectively. Lastly, the reaction of ethyl *N*-(6-methyl-2-pyridyl)formimidate (**1e**) with dichloroketene was also carried out to give the ester **3e**, pyridopyrimidine **4e**, and 2-dichloroacetamido-6-methylpyridine (**8e**) in 11, 43, and 2% yields, respectively.

Although the details of the mechanism of formation of these products are unclear at present, likely pathways are shown in Chart 2. Namely, electrophilic attack of dichloroketene at the imidoyl nitrogen forms a zwitter-ionic intermediate A,[6,12] which undergoes cycloaddition to give 2-azetidinones **2a** and **2d**. Addition of water to A (formation of the intermediate B), followed by elimination of ethyl formate gives 2-dichloroacetamides **8c** and **8e** (path a).

On the other hand, dichloroketene attacks at the pyridine ring nitrogen to give an intermediate C. The intramolecular cycloaddition of C would give an intermediate D, which reacts with ethanol, presumably contained within the ethyl acetate used for column chromatography (or chloroform used for extraction), or methanol to give esters **3a**, **b**, **d**, **e** or **5**. Although the azetidinone **2** is also a possible intermediate for **3** or **5**, it should be ruled out because **2a** is not transformed into **3a** by heating with ethanol even in the presence of an acidic catalyst.

Elimination of hydrogen chloride from D forms **4a**—**e**, whereas **3** or **5** eliminates 2 molar eq of hydrogen chloride to give **6** or **7** *via* an intermediate E. In contrast, addition of water to C would give rise to an intermediate F, which eliminates ethyl dichloroacetate to give **9** (path b). Such a pathway was also observed in the reaction of ketene with ethyl *N*-(2-pyridyl)-formimidates.[9]

Experimental

Melting points are uncorrected. Infrared (IR) spectra were taken with a JASCO A-102 spectrophotometer. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a JEOL JNM PMX-60 spectrometer using tetramethylsilane as an internal standard.

Reaction of Dichloroketene with Ethyl *N*-(2-Pyridyl)formimidate (1a)[10]——A solution of dichloroacetyl chloride (5.3 g, 0.036 mol) in dry ether (15 ml) was added dropwise to a solution of **1a** (4.5 g, 0.03 mol) and triethylamine (4.6 g, 0.045 mol) in dry ether (45 ml) with stirring at −15——10 °C. The mixture was stirred for 1 h at room temperature. The precipitated triethylamine hydrochloride was filtered off, and the filtrate was concentrated *in vacuo* to give a residue (6.6 g), which was subjected to silica gel (200 g) column chromatography. Elution with hexane–ethyl acetate (10 : 1) gave 3,3-dichloro-4-ethoxy-1-(2-pyridyl)-2-azetidinone (**2a**) as pale yellow needles. mp 76—77 °C (from hexane). Yield, 0.54 g (7%). *Anal.* Calcd for $C_{10}H_{10}Cl_2N_2O_2 \cdot 1/6H_2O$: C, 45.47; H, 3.94; N, 10.61. Found: C, 45.57; H, 3.75; N, 10.66. IR ($CHCl_3$): 1795 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.37 (3H, t, J=7 Hz, $-CH_2\underline{CH_3}$), 4.10 (2H, m, $-\underline{CH_2}CH_3$), 5.73 (1H, s, 4-H), 7.0—8.5 (4H, m, pyridyl protons). MS *m/e*: 260 (M^+). Subsequent elution with hexane–ethyl acetate (5 : 1) gave ethyl 2,2-dichloro-3-ethoxy-3-(2-pyridylamino)propionate (**3a**) as a pale yellow oil. Yield, 2.0 g (22%). Further elution with hexane–ethyl acetate (3 : 1) gave 3-chloro-2-ethoxypyrido[1,2-*a*]pyrimidin-4(4*H*)-one (**4a**) as pale yellow needles. Yield, 3.0 g (45%).

Reaction of Dichloroketene with Ethyl *N*-(5-Methyl-2-pyridyl)formimidate (1d)[11]——A soltion of dichloroacetyl chloride (1.77 g, 0.012 mol) in dry 1,2-dimethoxyethane (DME) (5 ml) was added dropwise to a solution of **1d** (1.64 g, 0.01 mol) and triethylamine (1.52 g, 0.015 mol) in dry DME (15 ml) with stirring at −15——10 °C. The mixture was stirred for 4 h at room temperature. Removal of the solvent *in vacuo* gave a residue, which was dissolved in chloroform (100 ml). The chloroform solution was washed with water (100 ml × 3), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The residue (5.3 g) was subjected to silica gel (100 g) column chromatography. Elution with hexane–ethyl acetate (10 : 1) gave 3,3-dichloro-4-ethoxy-1-(5-methyl-2-pyridyl)-2-azetidinone (**2d**) as a pale yellow oil. Yield, 0.19 g (7%). *Anal.* Calcd for $C_{11}H_{12}Cl_2N_2O_2$: C, 48.02; H, 4.40; N, 10.18. Found: C, 48.13; H, 4.58; N, 9.91. IR ($CHCl_3$): 1790 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.37 (3H, t, J=7 Hz, $-OCH_2\underline{CH_3}$), 2.33 (3H, s, ring-CH_3), 4.11 (2H, m, $-O\underline{CH_2}CH_3$), 5.70 (1H, s, 4-H), 7.56 (2H, s, pyridyl 3,4-H), 8.18 (1H, s, pyridyl 6-H). MS *m/e*: 274 (M^+). Subsequent elution with hexane–ethyl acetate (5 : 1) gave ethyl 2,2-dichloro-3-ethoxy-3-(5-methyl-2-pyridyl-amino)propionate (**3d**) as a pale yellow oil. Yield, 0.34 g (11%). Further elution with hexane–ethyl acetate (3 : 1) gave 3-chloro-2-ethoxy-7-methylpyrido[1,2-*a*]pyrimidin-4(4*H*)-one (**4d**) as colorless needles. Yield, 0.86 g (36%).

Reaction of Dichloroketene with Ethyl *N*-(3-Methyl-2-pyridyl)formimidate (1b)[10]——1) A solution of dichloroacetyl chloride (1.77 g, 0.012 mol) in dry DME (5 ml) was added dropwise to a solution of **1b** (1.64 g,

NII-Electronic Library Service

0.01 mol) and triethylamine (1.52 g, 0.015 mol) in dry DME (15 ml) with stirring at −15—−10 °C. The mixture was stirred for 5 h at room temperature. The reaction mixture was concentrated *in vacuo* to give a residue, which was dissolved in chloroform (100 ml). The chloroform solution was washed with water (100 ml × 3), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The residue (4.0 g) was subjected to silica gel (100 g) column chromatography. Elution with hexane–ethyl acetate (5 : 1) gave 2,2-dichloro-3-ethoxy-3-(3-methyl-2-pyridylamino)-propionate (**3b**) as a pale yellow oil. Yield, 1.63 g (51%). Further elution with hexane–ethyl acetate (3 : 1) gave 3-chloro-2-ethoxy-9-methylpyrido[1,2-*a*]pyrimidin-4(4*H*)-one (**4b**). Yield, 1.11 g (47%).

2) A solution of dichloroacetyl chloride (3.54 g, 0.024 mol) in dry DME (10 ml) was added dropwise to a solution of **1b** (3.28 g, 0.02 mol) and triethylamine (4.85 g, 0.048 mol) in dry DME (40 ml) with stirring at −15—−10 °C. The mixture was stirred for 5 h at room temperature. Removal of the solvent *in vacuo* gave a residue, which was dissolved in dichloromethane (100 ml). The dichloromethane solution was washed with water (100 ml × 3), dried over sodium sulfate, and concentrated *in vacuo*. The residue (5.0 g) was subjected to silica gel (150 g) column chromatography. Elution with hexane–ethyl acetate (2 : 1) gave **4b**. Yield, 3.85 g (80%).

3) A solution of dichloroacetyl chloride (3.54 g, 0.024 mol) in dry DME (10 ml) was added dropwise to a solution of **1b** (3.28 g, 0.02 mol) and triethylamine (3.03 g, 0.03 mol) in dry DME (40 ml) with stirring at −15—−10 °C. The reaction temperature was raised gradually to room temperature. Abs. methanol (20 ml) was added to the mixture. The resulting mixture was stirred for 2 h, then allowed to stand for 15 h. The reaction mixture was concentrated *in vacuo*, and the residue was dissolved in dichloromethane (100 ml). The dichloromethane solution was washed with water (100 ml × 3), and dried over anhydrous sodium sulfate. Removal of the solvent *in vacuo* gave a residue (7.2 g), which was subjected to silica gel (150 g) column chromatography. Elution with hexane–ethyl acetate (5 : 1) gave methyl 2,2-dichloro-3-ethoxy-3-(3-methyl-2-pyridylamino)propionate (**5**) as a pale yellow oil. Yield, 3.96 g (65%). *Anal.* Calcd for $C_{12}H_{16}Cl_2N_2O_3$: C, 46.92; H, 5.25; N, 9.12. Found: C, 46.72; H, 5.31; N, 8.83. IR ($CHCl_3$): 3450, 1760 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.18 (3H, t, J=7 Hz, $-OCH_2C\underline{H}_3$), 2.18 (3H, s, pyridyl-CH_3), 3.77 (3H, q, J=7 Hz, $-OC\underline{H}_2CH_3$), 3.87 (3H, s, OCH_3), 5.10 (1H, d, J=10 Hz, NH), 6.50 (1H, d, J=10 Hz, N–CH=), 6.63 (1H, dd, J=7, 5 Hz, pyridyl 5-H), 7.32 (1H, dd, J=7, 2 Hz, pyridyl 4-H), 8.03 (1H, dd, J=5, 2 Hz, pyridyl 6-H). MS *m/e*: 306 (M^+), 275 ($M^+ - OMe$). Further elution with hexane–ethyl acetate (2 : 1) gave **4b**. Yield, 1.17 g (25%).

Ethyl 2-Ethoxy-8-methylimidazo[1,2-*a*]pyridine-3-carboxylate (6)——Compound **3b** (0.5 g) was allowed to stand without solvent for 6 d at room temperature. The mixture was subjected to silica gel column chromatography. Elution with hexane–ethyl acetate (5 : 1) gave **3b**. Further elution with hexane–ethyl acetate (3 : 1) afforded **6** as colorless needles, mp 86—87 °C (from hexane). Yield, 0.03 g (8%). *Anal.* Calcd for $C_{13}H_{16}N_2O_3$: C, 62.89; H, 6.50; N, 11.28. Found: C, 62.59; H, 6.56; N, 11.18. IR ($CHCl_3$): 1670 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.10—1.67 (6H, m, $-OCH_2C\underline{H}_3 \times 2$), 2.57 (3H, s, 8-$CH_3$), 4.10—4.83 (4H, m, $OC\underline{H}_2CH_3 \times 2$), 6.80—7.30 (2H, m, 6,7-H), 9.10 (1H, d, J=6 Hz, 5-H).

Methyl 2-Ethoxy-8-methylimidazo[1,2-*a*]pyridine-3-carboxylate (7)——1) Following the procedure given for **6**, compound **5** (3.96 g) was allowed to stand for 6 d at room temperature to give **5** and **7** (0.2 g, 7%) as colorless needles, mp 103—104 °C (from hexane). *Anal.* Calcd for $C_{12}H_{14}N_2O_3$: C, 61.52; H, 6.02; N, 11.96. Found: C, 61.45; H, 6.04; N, 11.89. IR ($CHCl_3$): 1675 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.50 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.55 (3H, s, 8-CH_3), 3.95 (3H, s, OCH_3), 4.65 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 6.70—7.30 (2H, m, 6,7-H), 9.17 (1H, d, J=6 Hz, 5-H).

2) A solution of **5** (0.5 g, 0.00163 mol) and triethylamine (0.5 g, 0.005 mol) in dry DME (5 ml) was heated under reflux for 18 h. Removal of the solvent *in vacuo* gave a residue, which was dissolved in chloroform (20 ml). The solution was washed with water (10 ml × 3), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The crystalline residue was recrystallized from hexane to furnish **7** (0.3 g, 79%).

Reaction of Dichloroketene with Ethyl *N*-(4-Methyl-2-pyridyl)formimidate (1c)[10]——A solution of dichloroacetyl chloride (1.77 g, 0.012 mol) in dry DME (5 ml) was added dropwise to a solution of **1c** (1.64 g, 0.01 mol) and triethylamine (1.52 g, 0.015 mol) in dry DME (15 ml) with stirring at −15—−10 °C. The mixture was stirred for 1 h at room temperature. Removal of the solvent *in vacuo* gave a residue, which was dissolved in chloroform (100 ml). The solution was washed with water (100 ml × 3), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The resulting residue (2.9 g) was subjected to silica gel (100 g) column chromatography. Elution with hexane–ethyl acetate (10 : 1) gave 2-dichloroacetamido-4-methylpyridine (**8c**) as yellow needles, mp 136—137 °C (from hexane). Yield, 0.2 g (9%). *Anal.* Calcd for $C_8H_8Cl_2N_2O$: C, 43.86; H, 3.68; N, 12.79. Found: C, 43.79; H, 3.66; N, 12.62. IR ($CHCl_3$): 3400, 1700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.40 (3H, s, 4-CH_3), 6.07 (1H, s, $C\underline{H}Cl_2$), 6.97 (1H, d, J=5 Hz, 5-H), 8.00 (1H, s, 3-H), 8.20 (1H, d, J=5 Hz, 6-H), 8.6—9.3 (1H, br s, NH). MS *m/e*: 218 (M^+). Further elution with hexane–ethyl acetate (3 : 1) gave 2-formamido-4-methylpyridine (**9**) (0.12 g, 9%) as yellow needles, mp 85—87 °C (from hexane), and **4c** (0.51 g, 21%) as orange leaves. *Anal.* Calcd for $C_7H_8N_2O$ (**9**): C, 61.75; H, 5.92; N, 20.58. Found: C, 61.85; H, 5.86; N, 20.70. IR ($CHCl_3$): 3400, 1690 cm^{-1}.

Reaction of Dichloroketene with Ethyl *N*-(6-Methyl-2-pyridyl)formimidate (1e)[10]——A solution of dichloroacetyl chloride (5.31 g, 0.036 mol) in dry ether (15 ml) was added dropwise to a solution of **1e** (4.93 g, 0.03 mol) and triethylamine (4.55 g, 0.045 mol) in dry ether (45 ml) with stirring at −15—−10 °C. The mixture was stirred for 1 h at room temperature. The precipitate ($Et_3N \cdot HCl$) was filtered off, and the filtrate was concentrated *in vacuo* to give a residue (8.58 g), which was subjected to silica gel (200 g) column chromatography. Elution with hexane–ethyl

NII-Electronic Library Service

TABLE IV. Analytical Data for Compounds **3** and **4**

Compd. No.	Formula	Analysis (%)					
		Calcd			Found		
		C	H	N	C	H	N
3a	$C_{12}H_{16}Cl_2N_3O_3 \cdot 5/4H_2O$	43.71	5.66	8.50	43.53	5.71	8.68
3b	$C_{13}H_{18}Cl_2N_2O_3 \cdot 1/6H_2O$	48.16	5.70	8.64	48.29	5.56	8.38
3d	$C_{13}H_{18}Cl_2N_2O_3$	48.61	5.65	8.72	48.39	5.42	8.65
3e	$C_{13}H_{18}Cl_2N_2O_3 \cdot 5/4H_2O$	45.42	6.01	8.15	45.33	6.05	8.19
4a	$C_{10}H_9ClN_2O_2$	53.46	4.04	12.47	53.74	3.89	12.49
4b	$C_{11}H_{11}ClN_2O_2$	55.35	4.65	11.74	55.36	4.60	11.71
4c	$C_{11}H_{11}ClN_2O_2$	55.35	4.65	11.74	55.33	4.64	11.70
4d	$C_{11}H_{11}ClN_2O_2$	55.35	4.65	11.74	55.24	4.61	11.62
4e	$C_{11}H_{11}ClN_2O_2$	55.35	4.65	11.74	55.06	4.59	11.69

acetate (10:1) gave 2-dichloroacetamido-6-methylpyridine (**8e**) as yellow needles, mp 119—121 °C (from hexane). Yield, 0.15 g (2%). *Anal.* Calcd for $C_8H_8Cl_2N_2O$: C, 43.86; H, 3.68; N, 12.79. Found: C, 43.97; H, 3.63; N, 12.96. IR ($CHCl_3$): 3400, 1710 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.50 (3H, s, 6-CH_3), 6.07 (1H, s, C<u>H</u>Cl_2), 6.80—8.10 (3H, m, 3,4,5-H), 8.9—9.9 (1H, br, NH). MS *m/e*: 218 (M^+). Subsequent elution with hexane–ethyl acetate (5:1) gave ethyl 2,2-dichloro-3-ethoxy-3-(6-methyl-2-pyridylamino)propionate (**3e**) as a pale yellow oil. Yield, 1.03 g (11%). Further elution with hexane–ethyl acetate (3:1) gave 3-chloro-2-ethoxy-6-methylpyrido[1,2-*a*]pyrimidin-4(4*H*)-one (**4e**) as pale yellow needles. Yield, 3.11 g (43%).

Acknowledgement A part of the expense of this work was defrayed by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan. Thanks are also due to the staff of the Central Analyses Room of this institute for spectral measurements and elemental analyses.

References and Notes

1) Part CXVI: T. Chiba, M. Okada, and T. Kato, *Chem. Pharm. Bull.*, **31**, 2669 (1983).
2) W. T. Brady, *Tetrahedron*, **37**, 2949 (1981).
3) F. Duran and L. Ghosez, *Tetrahedron Lett.*, **1970**, 245.
4) D. A. Nelson, *Tetrahedron Lett.*, **1971**, 2543.
5) J. P. Luttringer and J. Streigh, *Tetrahedron Lett.*, **1973**, 4163.
6) A. O. Fitton, J. R. Frost, P. G. Houghton, and H. Suschitzky, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 1450.
7) N. Katagiri, R. Niwa, Y. Furuya, and T. Kato, *Chem. Pharm. Bull.*, **31**, 1833 (1983).
8) Dichloroketene was generated by the reaction of dichloroacetyl chloride with triethylamine.
9) N. Katagiri, R. Niwa, and T. Kato, *Heterocycles*, **20**, 597 (1983).
10) B. Pal and L. Pallos, *J. Prakt. Chem.*, **313**, 179 (1971).
11) The methyl analog **1d** was prepared from ethyl orthoformate and 2-amino-5-methylpyridine according to ref. 10). **1d**: bp 66—67 °C (0.3 mmHg). *Anal.* Calcd for $C_9H_{12}N_2O \cdot 1/5H_2O$; C, 64.41; H, 7.45; N, 16.70. Found: C, 64.52; H, 7.39; N, 16.84.
12) W. T. Brady and E. D. Dorsey, *J. Org. Chem.*, **35**, 2732 (1970).

NII-Electronic Library Service