chloride–pentane afforded 14 (0.644 g, 67%), identical to the material isolated from the reaction of 2 with 3 in methylene chloride.

C. Reactions with Dipropylcyclopropenone 24 in Methanol. A solution of pyridinium *N*-imine salt (2.5 mmol), triethylamine (0.75 mL, 5 mmol), and cyclopropenone **24** (0.276 g, 2 mmol) in 50 mL of dry methanol was heated under reflux until the IR spectrum of an aliquot no longer demonstrated the presence of cyclopropenone. The residue of the workup as in A was separated by column chromatography on silica gel using benzene–ether as an eluent. The results are summarized in Table II.

Sodium Borohydride Reduction of 2-Methyl-4-phenyl-3*H*-pyrido[1,2-*b*]pyridazin-3-one (14). Sodium borohydride (80 mg, 2.1 mmol) was added to a solution of 14 (118 mg, 0.5 mmol) in 15 mL of absolute ethanol. After 17 days at room temperature (additional 80-mg portions of sodium borohydride were added on the 6th and 14th days), the solvent was evaporated and the resulting white solid was treated with 10% aqueous ammonium chloride (30 mL). An ether extract (100 mL) was dried over $MgSO_4$, filtered, and evaporated to give a yellow oil which was separated by column chromatography on silica gel using benzene–ether as an eluent to afford 73 mg (61%) of a white solid: mp 164–166 °C; mass spectrum *m/e* (rel intensity) 240 (65, M^+), 239 [100, $(M-1)^+$], 212 [13, $(M-CO)^+$]; IR (KBr) 1605, 1580 cm^{-1}; NMR ($CDCl_3$) δ 1.10–2.20 (4 H, multiplet), 2.36 (3 H, singlet), 2.63 (2 H, triplet, J = 6.0 Hz), 4.15 (2 H, triplet, J = 6.0 Hz), 7.05–7.45 (5 H, multiplet). Anal. Calcd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.97; H, 6.78; N, 11.83.

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Registry No.—**4**, 36012-28-9; **10**, 66213-64-7; **11**, 66213-65-8; **22**, 66213-66-9; **29**, 60047-73-6.

References and Notes

(1) Y. Tamura, Y. Sumida, Y. Miki, and M. Ikeda, *J. Chem. Soc., Perkin Trans. 1*, 406 (1975), and references therein.
(2) V. Boekelheide and K. Fahrenholtz, *J. Am. Chem. Soc.*, **83**, 458 (1961).
(3) T. Eicher and A. Hansen, *Tetrahedron Lett.*, 1169 (1967).
(4) T. Sasaki, K. Kanematsu, and A. Kakehi, *J. Org. Chem.*, **36**, 2451 (1971).
(5) A. Kascheres and D. Marchi, Jr., *J. Org. Chem.*, **40**, 2985 (1975).
(6) A. Kascheres and D. Marchi, Jr., *Chem. Commun.*, 275 (1976).
(7) K. Matsumoto and Y. Koni, *Chem. Commun.*, 1045 (1976).
(8) Reaction of **2** with **9** in the presence of triethylamine resulted in immediate darkening of the solution and low yields of products.
(9) A. Kakehi, S. Ito, T. Manabe, H. Amano, and Y. Shimaoka, *J. Org. Chem.*, **41**, 2739 (1976).
(10) A. Kascheres, C. Kascheres, J. A. R. Rodrigues, and A. A. Santana, *J. Org. Chem.*, **41**, 3546 (1976).
(11) T. Sasaki, K. Kanematsu, and A. Kakehi, *J. Org. Chem.*, **37**, 3106 (1972).
(12) R. Breslow and R. Peterson, *J. Am. Chem. Soc.*, **82**, 4426 (1960).
(13) E. V. Dehmlow, *Tetrahedron Lett.*, 5177 (1967).
(14) Examination of the NMR spectra of the crude products from shorter reaction times failed to reveal the presence of possible *cis*-4,4a-dihydro intermediates.
(15) R. Gösl and A. Neuwsen, *Org. Synth.*, **43**, 1 (1963).
(16) Y. Tamura, J. Minamikawa, Y. Miki, S. Matsugashita, and M. Ikeda, *Tetrahedron Lett.*, 4133 (1972).
(17) A. Krebs and J. Breckwoldt, *Tetrahedron Lett.*, 3797 (1969).
(18) R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, and I. Murata, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1326 (1965).
(19) H. B. Kagan and Y. Heng Suen, *Bull. Soc. Chim. Fr.*, 1819 (1966).

Synthesis Using Allylidenedihydropyridines. 3.[1] Synthesis and Thermolysis of Functionalized 2-Allylidene-1,2-dihydropyridines

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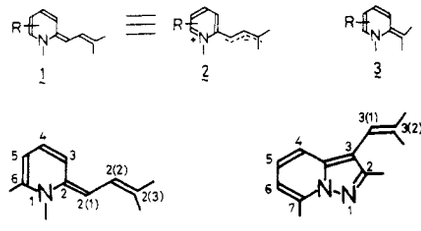
Some 2-allylidene-1,2-dihydropyridines (**19–24**) possessing an electrophilic center in the 1-substituent were prepared by the reactions of pyridinium salts **10, 13,** and **14** with ethoxymethylene compounds **17** and **18** in the presence of alkali, and they were converted in high yields to the corresponding 3-ethenylpyrazolo[1,5-*a*]pyridines **25, 26,** and **29–32** with elimination of ethyl *N*-methylcarbamate **38** by heating in refluxing xylene. On the other hand, the reactions of pyridinium salts **11** + **12** and **15** with the same reagents, **17** and **18,** did not give the corresponding allylidenedihydropyridines, but directly afforded pyrazolopyridines **27, 28, 33,** and **34** in comparatively high yields.

Although 2-allylidene-1,2-dihydropyridine **1** is a vinylog of 2-methylene-1,2-dihydropyridine **3** which is one of the most important precursors in the indolizine synthesis,[2] its versatility as a source of heterocycles has not been investigated at all. Since this molecule **1** has also the contribution of the ionic



structure **2**, in which the negative charge delocalizes on the 2-allylidene group, its nucleophilic reaction due to this structure **2** would be expected.

Recently, we have reported a simple and widely applicable preparative method for allylidenedihydropyridines[3] and the formation of functionalized 2-allylidene-1,2-dihydropyridines[4] using this route. This paper describes the preparations of some 2-allylidene-1,2-dihydropyridines possessing an electrophilic center and their conversions to 3-ethenylpyrazolo[1,5-*a*]-pyridines.

Results and Discussion

Preparations of Pyridinium Salts 10–16. Pyridinium salts possessing an electrophilic center in the 1-substituent were prepared by the alkylation of various 2-picolinium *N*-ylides which can act not only as 1,3-dipoles but also as 1,5-dipoles:[5] treatment of 1-imidoylimino- (**4–7**),[5h] 1-vinylimino- (**8**), and 1-ethoxycarbonyliminopyridinium ylide (**9**)[5a] with methyl iodide at room temperature afforded the corresponding pyridinium salts **10, 11** + **12,** and **13–16** in quantitative yields, respectively (Scheme I).

Since the formations of various types of pyridinium salts might be possible via the alkylation, the structures of the resulting pyridinium salts **10–16** were indicated by their NMR spectra (Table I) and the thermal behavior of the corresponding allylidenedihydropyridines derived from the pyri-

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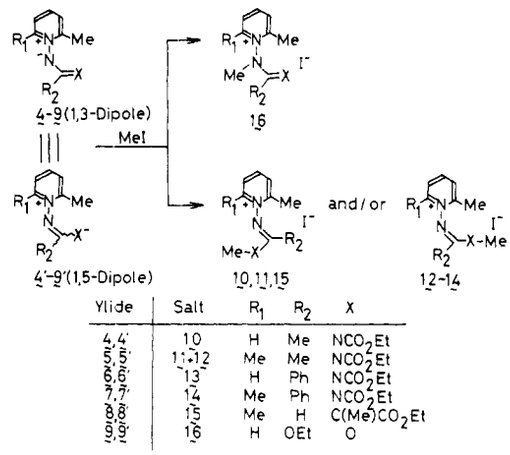
Table I. NMR Data of Pyridinium Salts

compd no.	registry no.	C-2	C-3	C-4	C-5	C-6	NMe	R_2	X
10	66270-14-2	2.21 s	8.43 br d	8.69 br t	8.27 br t	9.24 d	3.54 s	2.39, s	4.38 q, 1.40 t
		$J_{3,4} = J_{4,5} = 7.5$, $J_{5,6} = 6.5$, $J_{Et} = 7.0$ Hz							
11	66270-15-3	2.70 s	8.18 d	8.35 t	8.18 d	2.70 s	3.60 s	2.27 s	4.38 q, 1.40 t
		$J_{3,4} = J_{4,5} = 7.5$, $J_{Et} = 7.0$ Hz							
12	66270-16-4	2.77 s	8.02 d	8.44 t	8.02 d	2.77 s	3.28 s	2.27 s	3.99 q, 1.12 t
		$J_{3,4} = J_{4,5} = 7.5$, $J_{Et} = 7.0$ Hz							
13	66270-17-5	2.80 s	*a*	8.42 br t	*a*	9.49 d	3.28 s	7.5–8.2 m	3.98 q, 1.07 t
		$J_{3,4} = J_{4,5} = 7.5$, $J_{5,6} = 6.5$, $J_{Et} = 7.0$ Hz							
14	66270-18-6	2.81 s	8.15 d	8.42 q	8.15 d	2.81 s	3.07 s	7.5–8.0 m	4.03 q, 1.05 t
		$J_{3,4} = 7.5$, $J_{4,5} = 7.0$, $J_{Et} = 7.0$ Hz							
15	66270-19-7	2.80 s	8.17 d	8.53 q	8.17 d	2.80 s	1.67[b] s	7.74 s	4.35 q, 1.33 t
		$J_{3,4} = 7.5$, $J_{4,5} = 7.0$, $J_{Et} = 7.0$ Hz							
16	66270-20-0	2.91 s	8.36 br d	8.77 br t	8.23 br t	9.66 d	3.82 s		4.34 q, 1.32 t
		$J_{3,4} = J_{4,5} = 7.5$, $J_{5,6} = 6.5$, $J_{Et} = 7.0$ Hz							

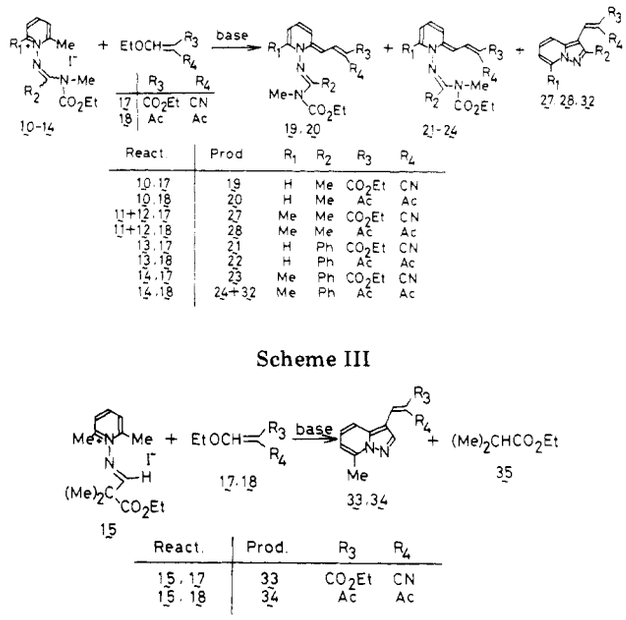
[a] Overlapped with the phenyl signals at δ 7.5–8.2. [b] C-methyl proton.

Scheme I



Ylide	Salt	R_1	R_2	X
4,4'	10	H	Me	NCO_2Et
5,5'	11+12	Me	Me	NCO_2Et
6,6'	13	H	Ph	NCO_2Et
7,7'	14	Me	Ph	NCO_2Et
8,8'	15	Me	H	$C(Me)CO_2Et$
9,9'	16	H	OEt	O

Scheme II



React.	Prod	R_1	R_2	R_3	R_4
10,17	19	H	Me	CO_2Et	CN
10,18	20	H	Me	Ac	Ac
11+12,17	27	Me	Me	CO_2Et	CN
11+12,18	28	Me	Me	Ac	Ac
13,17	21	H	Ph	CO_2Et	CN
13,18	22	H	Ph	Ac	Ac
14,17	23	Me	Ph	CO_2Et	CN
14,18	24+32	Me	Ph	Ac	Ac

Scheme III

React.	Prod.	R_3	R_4
15,17	33	CO_2Et	CN
15,18	34	Ac	Ac

dinium salts. Inspection of the structures using Dreiding models indicated that free rotation about the nitrogen–nitrogen single bond is strongly restricted by the 2- (or 2,6-) methyl group in the 1-pyridyl moiety and, hence, in molecules such as salts **12–14** the influence of the diamagnetic ring current due to the 1-pyridyl group is seen on the *N*-ethoxycarbonyl and the *N*-methyl groups. The NMR spectrum of the salt mixture **11** + **12** obtained from *N*-ylide **5** and methyl iodide, for example, showed each pair of proton signals at δ 1.12 and 1.40 (each 3 H, t, J = 7.0 Hz) and 3.99 and 4.38 (each 2 H, q, J = 7.0 Hz) due to the *N*-ethoxycarbonyl groups, and at δ 3.28 and 3.60 (each 3 H, s) due to the *N*-methyl groups. The signals at δ 1.12, 3.99, and 3.28, at higher magnetic field, should correspond to those of salt **12**, only in which the shielding effect due to the 1-pyridyl group can be expected. The ratio of salt **11** to **12** was determined to be about 2:1 by the integrations of the proton peaks of each *N*-methyl group. Furthermore, the NMR spectrum of salt **15** derived from ylide **8** exhibited proton signals at δ 1.33 (3 H, t, J = 7.0 Hz) and 4.35 (2 H, q, J = 7.0 Hz) due to the ethoxycarbonyl group and at δ 1.67 (6 H, s) and 7.74 (1 H, s) due to the two methyl and the imino methine groups, together with signals at δ 2.80 (6 H, s), 8.17 (2 H, almost d, J = 7.5 and 8.5 Hz), and 8.53 (1 H, q, J = 7.5 and 8.5 Hz) attributable to the 2,6-lutidine moiety. The chemical shift (δ 1.67) of the methyl group from the alkylating agent indicated clearly that salt **15** is not the N-methylated product but the C-methylated one, and those (δ 1.33 and 4.35) of the ethoxycarbonyl group indicated also that a shielding effect upon this group is not apparent. The structures of other salts **10, 13, 14,** and **16** were determined similarly.

The methylated position in salts **10–15** was also confirmed by the elimination of ethyl isobutyrate or ethyl *N*-methylcarbamate from the corresponding allylidenedihydropyridines (see below).

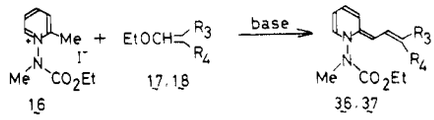
Reactions of Pyridinium Salts 10–16 with Ethoxymethylene Compounds 17 and 18. The reactions of pyridinium salts **10, 13,** and **14** with activated ethoxymethylene compounds such as ethyl ethoxymethylenecyanoacetate (**17**) and 3-ethoxymethylenepentane-2,4-dione (**18**) in the presence of alkali gave the expected 2-allylidene-1,2-dihydropyridine derivatives **19–24** as reddish crystals in yields of 50–87%, while those of salts **11** + **12** and **15** with the same reagents did not afford such allylidenedihydropyridines but gave the corresponding 3-ethenylpyrazolo[1,5-*a*]pyridine derivatives **27, 28, 33,** and **34** as yellow or pale yellow crystals in yields of 56–72%. In the reaction of salt **14** with **18** pyrazolopyridine **32** was also isolated in 24% yield together with allylidenedihydropyridine **24** (50%). In the reactions of **15** with **17** and **18,** the formation of ethyl isobutyrate **35** was detected by GLC of the reaction mixtures. Similarly, the reactions of salt **16** with **17** and **18** gave the corresponding allylidenedihydropyridines **36** and **37** in 63 and 88% yields. These results are shown in Schemes II–IV.

Table II. NMR Data of Allylidenedihydropyridines

compd no.	registry no.	C-3	C-4	C-5	C-6	2(1)	2(2)	NMe	R_2	Et		$R_{3,4}$	
19	66270-21-1	7.66 br d	7.39 br t	6.51 br t	7.24 br d	5.56 d	8.32 d	3.56 s	2.25 s	4.38 q	4.31 q	1.37 t	1.30 t
		$J_{3,4}$ = 8.0, $J_{4,5}$ = $J_{5,6}$ = 7.5, $J_{2(1),2(2)}$ = 13.0, J_{Et} = 7.0 Hz											
20	66270-22-2	7.4 br d	7.39 br t	6.57 br t	7.25 d	6.98 d	8.06 d	3.66 s	2.26 s	4.36 q	1.37 t	2.43[a] s	
		$J_{3,4}$ = 8.0, $J_{4,5}$ = $J_{5,6}$ = 7.5, $J_{2(1),2(2)}$ = 13.5, J_{Et} = 7.0 Hz											
21	66270-23-3	*b*	*b*	6.51 br t	*b*	5.77 d	8.37 d	2.98 s	7.2–8.1 m	4.14 q	1.02 t	4.29 q	1.30 t
		$J_{4,5}$ = $J_{5,6}$ = 7.5, $J_{2(1),2(2)}$ = 13.0, J_{Et} = 7.0 Hz											
22	66270-24-4	*b*	*b*	6.52 br t	*b*	6.94 d	8.09 d	3.00 s	7.2–8.1 m	4.13 q	1.03 t	2.38[a] s	
		$J_{4,5}$ = $J_{5,6}$ = 7.5, $J_{2(1),2(2)}$ = 13.5, J_{Et} = 7.0 Hz											
23	66270-25-5	*c*	*c*	6.52 br d	2.42 s	5.63 d	8.30 d	3.02 s	7.1–8.1 m	4.08 q	1.06 t	4.27 q	1.29 t
		$J_{4,5}$ = 7.5, $J_{2(1),2(2)}$ = 13.0, J_{Et} = 7.0 Hz											
24	66270-26-6	*d*	*d*	6.49 br d	2.41 s	7.13 d	7.97 d	2.93 s	7.2–8.0 m	4.02 q	1.08 t	2.38[a] s	
		$J_{4,5}$ = 7.0, $J_{2(1),2(2)}$ = 13.0, J_{Et} = 7.0 Hz											
36	66270-27-7	7.54 br d	7.17 br t	6.34 br t	7.21 br d	5.57 d	8.35 d	3.39 s		4.37 q	4.34 q	1.31 t	1.30 t
		$J_{3,4}$ = 8.0, $J_{4,5}$ = $J_{5,6}$ = 7.5, $J_{2(1),2(2)}$ = 13.0, J_{Et} = 7.0 Hz											
37	66270-28-8	7.55 br d	7.17 br t	6.29 br t	7.20 br d	6.48 br d	8.00 d	3.39 s		4.37 q	1.28 t	2.44 s	2.42 s
		$J_{3,4}$ = 8.0, $J_{4,5}$ = $J_{5,6}$ = 7.0, $J_{2(1),2(2)}$ = 13.5, J_{Et} = 7.0 Hz											

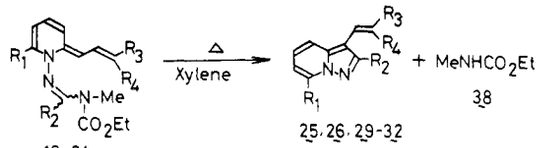
[a] 6 H of the two acetyl groups. [b] Overlapped with the phenyl signals at δ 7.2–8.1. [c] Overlapped with the phenyl signals at δ 7.1–8.1. [d] Overlapped with the phenyl signals at δ 7.2–8.0.

Scheme IV



React.	Prod.	R_3	R_4
16, 17	36	CO_2Et	CN
16, 18	37	Ac	Ac

Scheme V



React.	Prod.	R_1	R_2	R_3	R_4
19	25	H	Me	CO_2Et	CN
20	26	H	Me	Ac	Ac
21	29	H	Ph	CO_2Et	CN
22	30	H	Ph	Ac	Ac
23	31	Me	Ph	CO_2Et	CN
24	32	Me	Ph	Ac	Ac

These allylidenedihydropyridines **19–22, 36,** and **37** were comparatively stable under ordinary conditions but **23** and **24** were unstable and decomposed gradually even at room temperature.[6]

The structures of allylidenedihydropyridines **19–24, 36,** and **37** were determined by the analyses of their physical and spectral data and by the comparisons of their NMR spectra (Table II) with those of other allylidenedihydropyridines prepared earlier by us[3] and other investigators.[7] The stereochemistry of the 1-substituent in compounds **19–24** was also assigned by similar inspection of their NMR spectra as described in pyridinium salts **10–15,** and that of the 2-allylidene group in **19–24, 36,** and **37** was determined by the analyses of the chemical shifts of each 2(2) proton and by the recent literature.[7c] For example, the *N*-methyl signals appeared at near δ 3.6 (**19** and **20**) or 3.0 (**21–24**) and the *N*-ethoxycarbonyl signals at near δ 4.4 and 1.4 (**19** and **20**) or 4.1 and 1.1 (**21–24**) in the NMR spectra. Of course, the signals (near δ 3.0, 4.1, and 1.1) appearing at a higher region must be those of the *N*-ethoxycarbonyl-*N*-methylamino group cis to the 1-(2-allylidene-1,2-dihydropyridyl) group as proposed for the structures of **21–24** (see Scheme II). On the other hand, the *N*-methyl signals of **36** and **37** both appeared at δ 3.39.

The stereochemistry of the ethoxycarbonyl and the cyano groups in the 2-allylidene moiety of **19, 21, 23,** and **36** was determined by the comparison of their chemical shifts (near δ 8.3) of the 2(2) protons with those (near δ 8.0) of diacetyl derivatives **20, 22, 24,** and **37,** because the extent of diamagnetic anisotropy in such circumstance decreases usually in order of ester, acyl, and cyano groups. The other chemical shifts of the allylidene and the dihydropyridine moieties were quite parallel to those of known allylidenedihydropyridines reported recently by us.[3] The other products, 3-ethenylpyrazolo[1,5-*a*]pyridines **27, 28,** and **32–34,** will be discussed in the next section.

Thermolyses of Allylidenedihydropyridines 19–24, 36, and 37. In order to confirm the formation mechanism of 3-ethenylpyrazolo[1,5-*a*]pyridines **27, 28,** and **32–34** and to clarify the reactivity of these functionalized allylidenedihydropyridines we examined the thermolyses of **19–24, 36,** and **37** isolated in the above reactions. When solutions of allylidenedihydropyridines **19–24** and xylene were heated at the reflux temperature for 3–6 h, the red color of the reaction solutions faded gradually and in each case two new spots were

Table III. NMR Data of 3-Ethenylpyrazolo[1,5-*a*]pyridines

compd no.	registry no.	C-4	C-5	C-6	C-7	3(1)	R_2	R_3[a] and R_4	
25	66270-04-0	8.47 d	7.58 br t	7.16 br t	8.66 d	8.52 s	2.63 s	4.47 q	1.42 t
		$J_{4,5}$ = 8.0, $J_{5,6}$ = 7.5, $J_{6,7}$ = 7.0 Hz							
26	66270-05-1	7.48 m	7.48 m	7.02 m	8.61 d	8.00 s	2.55 s	2.46 s	2.30 s
		$J_{4,5}$ = 0, $J_{6,7}$ = 7.5 Hz							
27	66270-06-2	8.17 d	7.44 q	6.87 d	2.78 s	8.35 s	2.61 s	4.41 q	1.39 t
		$J_{4,5}$ = 8.0, $J_{5,6}$ = 7.5 Hz							
28	66270-07-3	7.26 d	7.26 d	6.74 t	2.76 s	7.87 s	2.53 s	2.41 s	2.25 s
		$J_{4,5}$ = 0, $J_{4,6}$ = $J_{5,6}$ = 4.0 Hz							
29	66270-08-4	8.42 d	*b*	7.26 br t	8.86 d	8.57 s	7.5–7.8 m	4.46 q	1.37 t
		$J_{4,5}$ = 9.0, $J_{5,6}$ = 7.5, $J_{6,7}$ = 7.0 Hz							
30	66270-09-5	*c*	7.27 br t	6.89 br t	8.49 d	7.81 s	7.4–7.8 m	2.38 s	2.22 s
		$J_{4,5}$ = 9.0, $J_{5,6}$ = 7.5, $J_{6,7}$ = 7.0 Hz							
31	66270-10-8	8.33 d	*d*	7.08 br d	2.91 s	8.60 s	7.5–7.9 m	4.46 q	1.39 t
		$J_{4,5}$ = 9.0, $J_{5,6}$ = 7.5 Hz							
32	66270-11-9	*e*	*e*	6.84 br d	2.83 s	7.92 s	7.3–7.9 m	2.38 s	2.21 s
		$J_{5,6}$ = 7.5 Hz							
33	66270-12-0	7.72 dd	7.44 q	6.90 br d	2.95 s	8.39 s	9.07 s	4.43 q	1.51 t
		$J_{4,5}$ = 9.0, $J_{5,6}$ = 7.5, $J_{4,6}$ = 1.5 Hz							
34	66270-13-1	7.64 d	7.36 q	6.84 br d	2.79 s	7.64 s	8.17 s	2.45[f] s	
		$J_{4,5}$ = 9.0, $J_{5,6}$ = 7.0 Hz							

[a] When R_3 = CO_2Et, J_{Et} = 7.0 Hz. [b] Overlapped with the phenyl signals at δ 7.5–7.8. [c] Overlapped with the phenyl signals at δ 7.4–7.8. [d] Overlapped with the phenyl signals at δ 7.5–7.9. [e] Overlapped with the phenyl signals at δ 7.3–7.9. [f] 6 H of the two acetyl groups.

Table IV. Some Data of the Reactions of Salts with Ethylenes

materials no.		prod. no. (%)[a]	appearance	mp, °C	ν_{CO} (KBr)	ν_{CN} (KBr)
10	**17**	**19** (87)	red prisms	96–98 dec	1729, 1669	2215
10	**18**	**20** (78)	red prisms	117–119 dec	1734	
11 + 12	**17**	**27** (72)	yellow needles	114–116	1717	2240
11 + 12	**18**	**28** (72)	yellow needles	120–122	1696, 1644	
13	**17**	**21** (84)	red prisms	130–132 dec	1731, 1680	2220
13	**18**	**22** (74)	red prisms	136–138 dec	1726	
14	**17**	**23** (77)	red prisms	110–112 dec	1726, 1672	2220
14	**18**	**24** (50)[b]	red prisms		1726	
		32 (24)	yellow needles	102–104	1675	
15	**17**	**33** (47)	pale yellow needles	150–153	1711	2235
15	**18**	**34** (56)	pale yellow needles	159–161	1701	
16	**17**	**36** (63)	red prisms	170–171	1707	2230
16	**18**	**37**(88)	red prisms	158–160	1713	

[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all compounds except **24**. [b] Recrystallization of **24** was unsuccessful because of its unstability.

observed by TLC. From the reaction mixtures the corresponding 3-ethenylpyrazolo[1,5-*a*]pyridine derivatives **25, 26,** and **29–32** were isolated in 82–96% yields, and ethyl *N*-methylcarbamate **38** was also detected (by GLC). On the other hand, the thermolyses of **36** and **37** did not give the expected pyrazolopyridinone derivatives but afforded only intractable tarry substances (Scheme V).

The structural assignments of 3-ethenylpyrazolo[1,5-*a*]-pyridine derivatives **25–34,** which were prepared from allylidenedihydropyridines **19–24** and directly from the reactions of pyridinium salts **11 + 12** and **15** with ethoxymethylene compounds **17** and **18,** were based upon their physical and spectral properties and by mechanistic consideration of these reactions. The elementary analyses were in good accord with the compositions for the proposed structures, and the NMR spectra (Table III) exhibited aromatic proton signals at δ 6.84–8.86 due to the pyridine moiety and singlet signals at δ 7.64–8.60 due to the vinyl protons. Interestingly, no coupling between the 4 and 5 protons was observed in the NMR spectra of compounds **26** and **28.** Furthermore, the fact that these 3-ethenylpyrazolopyridines **25–34** were formed with the elimination of ethyl isobutyrate **35** or ethyl *N*-methylcarbamate **38** is good evidence for the proposed structures.

Reaction Mechanism. Since allylidenedihydropyridines **19–24** were actually converted to the corresponding 3-ethenylpyrazolopyridines **25, 26,** and **29–32,** the intermediacy of the corresponding allylidenedihydropyridines in the formations of other pyrazolopyridines **27, 28,** and **32–34** is certain. Perhaps, these 3-ethenylpyrazolopyridines **25–34** must be formed by the intramolecular cyclization–eliminations of the corresponding allylidenedihydropyridines.

On the other hand, the failure to isolate the corresponding allylidenedihydropyridines derived from salts **11 + 12** and **15** and the instability of the 6-methyl isomers **23** and **24** seem to indicate acceleration of these cyclizations due to the increase (R_1 = Me) of steric hindrance, and in the case from **15** its decrease (R_2 = H) may also accelerate such cyclization.

Experimental Section

Melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were carried out on a Perkin-Elmer 240 Elemental Analyzer. The NMR spectra were determined with a JEOL JNM-100 spectrometer in deuteriochloroform with tetramethylsilane as an internal standard. The chemical shifts are expressed in δ values. The IR spectra were taken with a JASCO DS-301 spectrophotometer.

Preparations of Pyridinium Salts 10–16. Pyridinium salts **10–16**

Table V. Preparations and Some Data of Pyrazolopyridines

material no.	prod. no. (%)[a]	appearance	mp, °C	ν_{CO} (KBr)	ν_{CN} (KBr)
19	**25** (96)	yellow needles	102–103	1716	2240
20	**26** (93)	yellow needles	91–93	1675	
21	**29** (96)	yellow needles	190–192	1716	2240
22	**30** (92)[b]	yellow amorph		1685[c]	
23	**31** (96)	yellow needles	159–162	1713	2240
24	**32** (82)	yellow needles	102–104	1675	
36	(0)	no reaction			
37	(0)	decomposition			

[a] Satisfactory analyses were reported for compounds **25, 26, 29** and **31.** [b] Crystallization of **30** was unsuccessful. [c] Neat.

were prepared in quantitative yields by the reactions of pyridinium *N*-ylides **4–9**[5a,h,8] with methyl iodide in chloroform or without solvent at room temperature. These salts **10–16** were used for the next reactions without further purification because of the difficulty of their crystallization. The NMR data of salts **10–16** are listed in Table I.

Reactions of Pyridinium Salts 10–16 with Ethoxymethylene Compounds 17 and 18. General method: A solution of pyridinium salt (2.1 mmol) and ethyl ethoxymethylenecyanoacetate **17** (0.34 g, 2 mmol) or 3-ethoxymethylenepentane-2,4-dione **18** (0.31 g, 2 mmol) in chloroform (50 mL) was treated with potassium carbonate (5 g) at room temperature for 3–4 days. The reaction mixture was then filtered to remove insoluble inorganic substances and the filtrate was concentrated in vacuo. The residue was separated by column chromatography (alumina) using ether and then chloroform as eluents. Pyrazolopyridines **27, 28,** and **32–34** were isolated from the ether layer and allylidenedihydropyridines **19–24, 36,** and **37** from the chloroform layer. Recrystallizations of pyrazolopyridines **27, 28,** and **32–34** and allylidenedihydropyridines **19–23, 36,** and **37** were carried out from ether–hexane and chloroform–hexane, respectively. However, the preparation of the analytical sample of **24** was unsuccessful because **24** decomposed gradually even at room temperature to give pyrazolopyridine **32** and ethyl *N*-methylcarbamate **38.** Furthermore, ethyl isobutyrate **35** or ethyl *N*-methylcarbamate **38** was detected by GLC of the reaction solutions. These results and some physical data are shown in Tables II–IV.

Thermolyses of Allylidenedihydropyridines 19–24, 36, and 37. General method: A solution of 2-allylidenedihydropyridine (1 mmol) in xylene (50 mL) was heated at the reflux temperature until the disappearance of the starting material was observed by TLC (about 3–6 h). The reaction solution was concentrated in vacuo, and the residue was separated in the usual manner. Recrystallization from ether–hexane gave the corresponding 3-ethenylpyrazolopyridines **25, 26,** and **29–32.** The formation of ethyl *N*-methylcarbamate **38** was also confirmed by GLC of the reaction solutions. On the other hand, the thermolyses of allylidenedihydropyridines **36** and **37** did not give the expected pyrazolopyridinones but afforded only tarry substances. These results and some physical data are listed in Tables III and V.

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References and Notes

(1) For part 2 of this series, see A. Kakehi, S. Ito, T. Maeda, R. Takeda, M. Nishimura, and T. Yamaguchi, *Chem. Lett.*, 59 (1978).
(2) See the following recent review for the indolizine synthesis. T. Uchida and K. Matsumoto, *Synthesis*, 209 (1976).
(3) (a) A. Kakehi, S. Ito, T. Funahashi, and N. Ogasawara, *Chem. Lett.*, 919 (1975); (b) A. Kakehi, S. Ito, T. Funahashi, and N. Ogasawara, *Bull. Chem. Soc. Jpn.*, **49,** 2250 (1976).
(4) A. Kakehi, S. Ito, K. Uchiyama, and K. Kondo, *Chem. Lett.*, 545 (1977).
(5) (a) T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, **35,** 426 (1970); (b) T. Sasaki, K. Kanematsu, and A. Kakehi, *ibid.*, **36,** 2978 (1971); (c) Y. Tamura, N. Tsujimoto, and M. Ikeda, *Chem. Commun.*, 310 (1971); (d) T. Sasaki, K. Kanematsu, and A. Kakehi, *J. Org. Chem.*, **37,** 3106 (1972); (e) T. Sasaki, K. Kanematsu, and A. Kakehi, *Tetrahedron Lett.*, 5245 (1972); (f) Y. Tamura, Y. Miki, Y. Sumida, and M. Ikeda, *J. Chem. Soc., Perkin Trans. 1,* 2580 (1973); (g) A. Kakehi, S. Ito, K. Uchiyama, and Y. Konno, *Chem. Lett.*, 413 (1976); (h) A. Kakehi, S. Ito, K. Uchiyama, Y. Konno, and K. Kondo, *J. Org. Chem.*, **42,** 443 (1977).
(6) Compounds **23** and **24** were gradually converted to 3-ethenylpyrazolo[1,5-*a*]pyridines **31** and **32,** respectively.
(7) (a) T. Severin and H.-J. Böhme, *Chem. Ber.*, **101,** 2925 (1968); (b) R. M. Acheson and J. Woollard, *J. Chem. Soc., Perkin Trans. 1,* 744 (1975); (c) J. Kuthan, D. Ilavsky, J. Krechel, and P. Trska, *Tetrahedron Lett.*, 4763 (1976).
(8) *N*-Vinyliminopyridinium ylide **8,** red prisms, mp 131–134 °C, ν(KBr) 1535 cm^{-1} (CO) (Anal. Calcd for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.74; N, 11.96. Found: C, 66.72; H, 7.70; N, 12.11) was prepared in 84% yield by the reaction of 1-aminopyridinium iodide with ethyl β-bromomethacrylate according to the Sasaki's procedure. See ref 5e.

Teleamination of the Imidazo[1,2-*a*]pyridine System

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The reaction of 3-bromoimidazo[1,2-*a*]pyridine (**2**) with strong bases leads to metal–halogen and alkyl–halogen (coupling) exchange at the 3 position of the imidazole ring with CH_3Li, but leads to debromination, coupling via the 5 position (to give the dehydrodimer **11**), and telesubstitution at *all* positions of the pyridinoid ring with metal amides. Which products are obtained depends on the amide used. The formation of the amination products is interpreted to proceed by attack at positions 5 and/or 7, followed by migration to adjacent positions via an aziridine intermediate. Only the first step of the established ANRORC (addition–nucleophilic–ring opening–ring closing) mechanism of other teleamination reactions can be retained for these reactions, subsequent steps including ring opening and ring closing, but in the reverse sequence. A bromination product, the formation of which implicates a positive bromine species, and a Chichibabin amination product are also formed. The coupling product **11** is obtained when the parent imidazo[1,2-*a*]pyridine (**1**) is treated with KNH_2.

Imidazo[1,2-*a*]pyridine (**1**) contains both the π-excessive imidazole and the π-deficient pyridine rings. As such it is expected to undergo reactions of both types of molecules. The anticipated higher electron density in the five-membered ring is confirmed by frontier[1] and CNDO/2[2] calculations and is amply demonstrated by experimental evidence of electrophilic substitution at the 3 position.[3] When this position is blocked, electrophilic substitutions generally fail.[4] Much less is known about the reactivity of imidazo[1,2-*a*]pyridines toward nucleophiles. The parent compound **1** undergoes hydrogen–

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