Synthesis and Characterization of *N*-Vinyliminopyridinium Ylides.[1] Evidences for 1,5-Dipolar Cyclizations

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N-Vinyliminopyridinium ylides (**13–22**) were prepared from pyridinium *N*-imine hydriodides (**3–12**) and dimethyl 1-chlorofumarate or -maleate in the presence of potassium carbonate. The N ylides cyclized in various solvents at room temperature to afford primary dihydro-type cycloadducts (**23–34**) in moderate yields. The dihydro-type cycloadducts (**23–33**) were stable in the crystalline state but aromatized readily with dehydrogenating agents to give the corresponding pyrazolo[1,5-*a*]pyridine derivatives (**35–45**) in good yields. Structural elucidation of the N ylides, dihydro cycloadducts, and the pyrazolo[1,5-*a*]pyridine derivatives was accomplished by physical and spectral means. The structures of the pyrazolo[1,5-*a*]pyridine derivatives were also established by independent syntheses. Orientations and modes of these cycloadducts are also discussed.

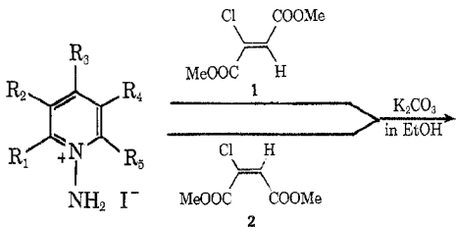
Although intermolecular cycloaddition reactions of pyridinium ylides with various reagents have been extensively studied,[2] intramolecular cyclizations of *N*-vinyliminopyridinium ylides have not been well investigated.

Recently, Tamura and coworkers[3] have reported the cyclization reactions of *N*-(1-oxocyclohexen-2-yl)iminopyridinium ylides and the reactions of pyridinium *N*-imines with ethyl β-chloroisocrotonate in the presence of potassium carbonate to give the corresponding pyrazolopyridine derivatives. In particular, they have suggested that the latter reactions might proceed *via* 1,3-dipolar cycloaddition rather than 1,5-dipolar cyclization, since attempts to obtain the possible intermediates of *N*-vinyliminopyridinium ylides were unsuccessful. In this paper, we wish to report the isolation of *N*-vinyliminopyridinium ylides and their cyclization products.

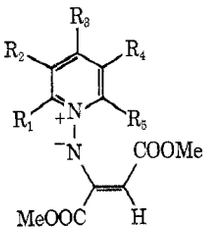
Results and Discussion

Isolations of the *N*-Vinyliminopyridinium Ylides.—A mixture of pyridinium *N*-imine hydriodides, **3–12**, prepared by the Gösl method,[2] and dimethyl 1-chlorofumarate (**1**) were treated with an excess potassium carbonate in ethanol at room temperature within 1 hr to afford the corresponding *N*-vinyliminopyridinium ylides, **13–22**, in over 75% yields. Interestingly, similar reactions of the N imines with dimethyl 1-chloromaleate (**2**) gave the same N ylides. These results are shown in Scheme I.

SCHEME I



3, $R_1=R_2=R_3=R_4=R_5=H$
4, $R_1=H$; $R_2=Me$; $R_3=R_4=R_5=H$
5, $R_1=R_2=H$; $R_3=Me$; $R_4=R_5=H$
6, $R_1=H$; $R_2=R_3=Me$; $R_4=R_5=H$
7, $R_1=H$; $R_2=R_4=Me$; $R_3=R_5=H$
8, $R_1=Me$; $R_2=R_3=R_4=R_5=H$
9, $R_1=R_2=Me$; $R_3=R_4=R_5=H$
10, $R_1=R_3=Me$; $R_2=R_4=R_5=H$
11, $R_1=R_4=Me$; $R_2=R_3=R_5=H$
12, $R_1=R_5=Me$; $R_2=R_3=R_4=H$



13, $R_1=R_2=R_3=R_4=R_5=H$
14, $R_1=H$; $R_2=Me$; $R_3=R_4=R_5=H$
15, $R_1=R_2=H$; $R_3=Me$, $R_4=R_5=H$
16, $R_1=H$; $R_2=R_3=Me$; $R_4=R_5=H$
17, $R_1=R_3=R_5=H$; $R_2=R_4=Me$
18, $R_1=Me$; $R_2=R_3=R_4=R_5=H$
19, $R_1=R_2=Me$; $R_3=R_4=R_5=H$
20, $R_1=R_3=Me$; $R_2=R_4=R_5=H$
21, $R_1=R_4=Me$; $R_2=R_3=R_5=H$
22, $R_1=R_5=Me$; $R_2=R_3=R_4=H$

Isomerization of the N Ylides.—The N ylides, **13–22**, were comparatively stable in the crystalline state but in solvent such as chloroform, methylene chloride and carbon tetrachloride they isomerized intramolecularly to afford the corresponding cycloadducts, **23–34.** These cyclizations were influenced by the substituents on the pyridine ring: (a) α-unsubstituted N ylides **13–17** cyclized quantitatively in chloroform at room temperature within 24 hr to yield the cycloadducts **23–29**, respectively (Scheme II); (b) with unsymmetrical substituted N ylides **14** and **16**, cyclization was observed to take place at two sites, and the cyclization of the more sterically hindered site on a pyridine ring was always predominant to the alternate less substituted site [the ratio of **24** to **25** (or **27** to **28**) as determined by nmr spectroscopy was 1:12 (or 1:8), respectively]; and (c) in α-substituted N ylides **18–22** similar isomerizations were observed, but the rates were slower than those of α-unsubstituted N ylides (below 30% after 24 hr), and in these cases only cyclization to the less hindered α′ position was observed (Scheme III).

Photochemical Behavior of the N Ylides.—With a view to obtaining mechanistic information on the

(1) Studies of Heteroaromaticity. Part LXII. Part LXI of this series: T. Sasaki, K. Kanematsu, and M. Murata, *Tetrahedron*, **28**, 2383 (1972).

(2) T. Sasaki, K. Kanematsu, and A. Kakehi, *J. Org. Chem.*, **36**, 2978 (1971).

(3) (a) Y. Tamura, N. Tsujimoto, and M. Ikeda, *Chem. Commun.*, 310 (1971); (b) Y. Tamura, A. Yamagami, and M. Ikeda, *Yakugaku Zasshi*, **91**, 1154 (1971).

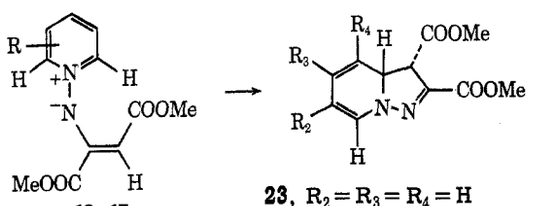
TABLE I

NMR SPECTRA OF N YLIDES IN $CDCl_3$ (τ VALUE)[a]

Compd	R_1	R_2	R_3	R_4	R_5	Vinyl H	$COOCH_3$	Coupling constant (J, Hz)
13	1.51 (br d)		1.9–2.4 (m)		1.51 (br d)	6.34 (s)	6.10 (s), 6.51 (s)	$J_{1,2} = J_{4,5} = 6.0$
14	1.73 (s)	7.42 (s)	2.11 (br d)	2.33 (q)	1.68 (br d)	6.46 (s)	7.12 (s), 6.53 (s)	$J_{3,4} = 7.5$, $J_{4,5} = 6.0$
15	1.63 (d)	2.43 (d)	7.40 (s)	2.43 (d)	1.69 (d)	7.43 (s)	6.09 (s), 6.50 (s)	$J_{1,2} = J_{4,5} = 7.0$
16	1.92 (s)	7.47 (s)	7.57 (s)	2.51 (d)	1.88 (d)	6.47 (s)	6.09 (s), 6.50 (s)	$J_{4,5} = 7.0$
17	1.95 (s)	7.53 (s)	2.30 (br s)	7.53 (s)	1.95 (s)	6.46 (s)	6.10 (s), 6.50 (s)	
18	7.30 (s)	2.29 (br d)	2.00 (m)	2.35 (m)	1.60 (d d)	6.75 (s)	6.09 (s), 6.51 (s)	$J_{4,5} = 6.5$, $J_{3,5} = 2.0$, $J_{2,3} = 6.5$
19	7.38 (s)	8.48 (s)	2.14 (br d)	2.52 (q)	1.73 (br d)	6.76 (s)	6.07 (s), 6.49 (s)	$J_{3,4} = 7.5$, $J_{4,5} = 6.5$
20	7.37 (s)	2.60 (s)	7.43 (s)	2.65 (d)	1.92 (d)	6.77 (s)	6.11 (s), 6.53 (s)	$J_{4,5} = 6.0$
21	7.34 (s)	2.38 (d)	2.16 (d)	7.53 (s)	1.80 (br s)	6.75 (s)	6.09 (s), 6.49 (s)	$J_{2,3} = 9.0$, $J_{3,5} = 2.0$
22	7.28 (s)	2.50 (d)	2.13 (q)	2.52 (d)	7.28 (s)	6.81 (s)	6.06 (s), 6.49 (s)	$J_{2,3} = 6.5$, $J_{3,4} = 9.0$

[a] Multiplicity is indicated as follows: s, singlet; d, doublet; q, quartet; br, broad.

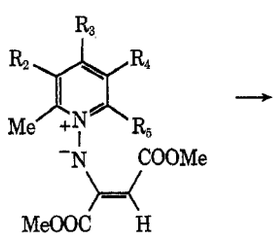
SCHEME II



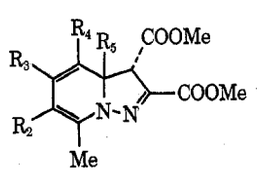
13–17

23, $R_2 = R_3 = R_4 = H$
24, $R_2 = Me$, $R_3 = R_4 = H$
25, $R_2 = R_3 = H$; $R_4 = Me$
26, $R_2 = H$; $R_3 = Me$; $R_4 = H$
27, $R_2 = R_3 = Me$; $R_4 = H$
28, $R_2 = H$; $R_3 = R_4 = Me$
29, $R_2 = R_4 = Me$; $R_3 = H$

SCHEME III



18, $R_2 = R_3 = R_4 = R_5 = H$
19, $R_2 = Me$; $R_3 = R_4 = R_5 = H$
20, $R_2 = H$; $R_3 = Me$; $R_4 = R_5 = H$
21, $R_2 = R_3 = H$; $R_4 = Me$; $R_5 = H$
22, $R_2 = R_3 = R_4 = H$; $R_5 = Me$



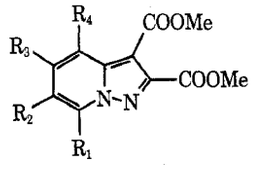
30, $R_2 = R_3 = R_4 = R_5 = H$
(**31**, $R_2 = Me$; $R_3 = R_4 = R_5 = H$)
32, $R_2 = H$; $R_3 = Me$; $R_4 = R_5 = H$
33, $R_2 = R_3 = H$; $R_4 = Me$; $R_5 = H$
34, $R_2 = R_3 = R_4 = H$; $R_5 = Me$

above-mentioned reactions, the photochemical reactions of unsubstituted and α,α'-disubstituted *N*-vinyliminopyridinium ylides were investigated, since the photochemical intramolecular 1,3-dipolar cyclization of substituted 1-ethoxycarbonyliminopyridinium ylides produced 1*H*,1,2-diazepines.[4]

(4) T. Sasaki, K. Kanematsu, A. Kakehi, K. Hayakawa, and I. Ichikawa, *J. Org. Chem.*, **35**, 426 (1970).

Irradiation of **13** in acetone at 0° for 45 min gave a 60% yield of a mixture of **23** and **35** (2,3-dimethoxycarbonylpyrazolo[1,5-*a*]pyridine) in the ratio of 1:1 (by nmr analysis) instead of the seven-membered product. The same reaction at 25° for 2 hr gave only **35** in 50% yield. Isolated **23** was converted rapidly on irradiation to **35** in 80% yield. These results appear to involve a photoinduced process, since the formation of **23** and **35** occurs thermally to the extent of only few per cent. Compound **22**, whose α and α' positions of the pyridine ring were occupied, was irradiated in acetone at room temperature to give the bicyclic product **34** in 20% yield, and no isomeric dihydro compound could be detected.

Dehydrogenation of the Cycloadducts.—The cycloadducts **23–34** are generally stable in the crystalline state. The dehydrogenation reactions of these adducts (**23–33**) except **34** were carried out by treating them with dehydrogenation agents such as palladium on carbon or tetracyanoethylene to afford the corresponding pyrazolopyridine derivatives, **35–45**, in high yields. The dehydrogenation was also observed under irradiation of the cycloadduct as described above. Compounds **27–33**, in particular, were dehydrogenated smoothly without such reagents even at room temperature. Compound **34** which has a methyl substituent on a bridged carbon was too stable in carbon tetrachloride even at 100° in a sealed tube to be aromatized to **42** with a loss of methane.



35, $R_1 = R_2 = R_3 = R_4 = H$
36, $R_2 = Me$; $R_1 = R_3 = R_4 = H$
37, $R_4 = Me$; $R_1 = R_2 = R_3 = H$
38, $R_3 = Me$; $R_1 = R_2 = R_4 = H$
39, $R_2 = R_3 = Me$; $R_1 = R_4 = H$
40, $R_3 = R_4 = Me$; $R_1 = R_2 = H$
41, $R_2 = R_4 = Me$; $R_1 = R_3 = H$
42, $R_1 = Me$; $R_2 = R_3 = R_4 = H$
43, $R_1 = R_2 = Me$; $R_3 = R_4 = H$
44, $R_1 = R_3 = Me$; $R_2 = R_4 = H$
45, $R_1 = R_4 = Me$; $R_2 = R_3 = H$

Structural Elucidation of the N Ylides.—The structures of N ylides **13–22** were determined by elemental and spectral analyses (Table I) and by chemical re-

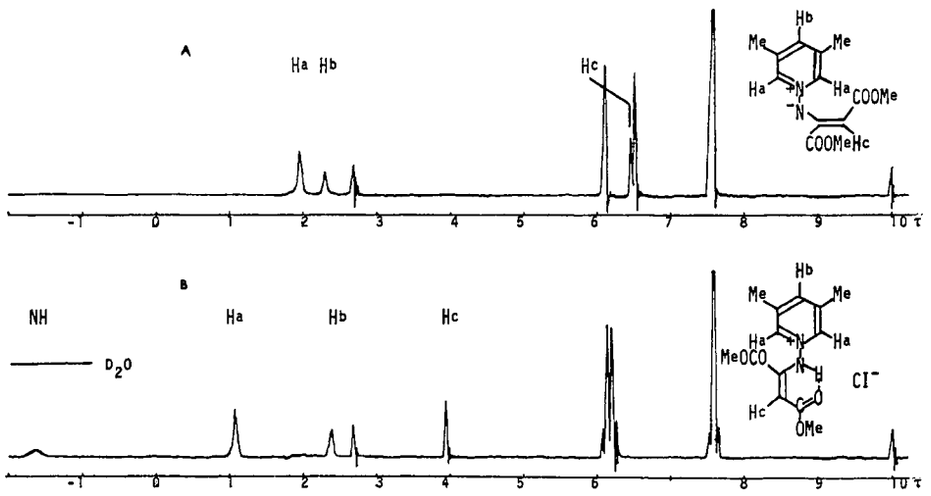


Figure 1.—A, observed nmr spectrum of 17 in $CDCl_3$; B, nmr spectra of 17 added HCl in $CDCl_3$.

actions. The elemental analyses were in good accord with the proposed structures. The configuration of the *N*-vinylimino group in all the N ylides was assigned as trans. This was based on the nmr inspection of the salt of the N ylide. In the nmr spectra, they show each singlet at higher region due to the vinyl proton (τ 6.34–6.81) suggesting strongly the delocalization of the vinyl proton with ester carbonyl group. Interestingly, the nmr of hydrochloride of the N ylide was considerable changed. For example, when the nmr of **17** was taken in deuteriochloroform at room temperature, the signals appeared at τ 1.95 (H_a), 2.30 (H_b), and 6.46 (H_c). By contrast, when **17** was added with a small amount of hydrochloric acid in deuteriochloroform, the signals were exhibited at τ −1.63 (NH, exchanged by D_2O), 1.07 (H_a), 2.40 (H_b), and 3.96 (H_c). The signal of τ −1.63 indicated obviously the presence of a hydrogen bonding with carbonyl group, which was possible only in the trans configuration as shown in Figure 1.

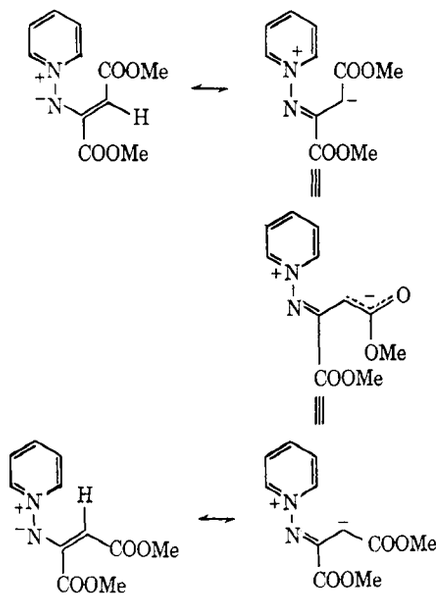
Further deviation of chemical shifts between the vinyl proton in α-unsubstituted N ylides **13–17** (τ 6.34–6.47) and α-substituted N ylides **18–22** (τ 6.75–6.81) (Table I) might be caused from the effect of the diamagnetic ring current on the pyridine ring, since the steric hindrance of free rotation of the N substituent by the α-methyl group could favor a conformation in which the vinyl proton is less influenced by the pyridine ring than in the α-unsubstituted N ylides. As observed experimentally, such an effect obviously leads to retardation of the isomerization of α-substituted N ylides **18–22** to the corresponding cycloadducts, **30–34**.

Formation of the same N ylides from both **1** and **2** indicates rapid cis–trans isomerization of the vinyl moiety as indicated in Scheme IV.

Structural Elucidation of the Cycloadducts.—Based mainly on nmr analysis, these cycloadducts, **23–30** and **32–34,** were assigned as the cis rather than the trans configurations at the C-3 and C-3a positions. The nmr spectral patterns of the cycloadducts are grossly similar to each other, as shown in Table II.

The nmr signals of **23** at τ 3.14, 4.00, 4.54, 4.78, and 5.35 with the relative intensities of 1:1:1:1:1 are attributable to five protons of the six-membered ring, at 6.03 to one proton of C-3 position, and at 6.24 to two methyl protons. In particular, signals at τ 5.35 and 6.03 coupling each other with the coupling constant of

SCHEME IV

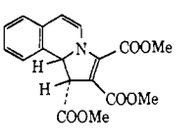


17.0 Hz[5] attributable to the protons attached at C-3a and C-3 positions indicate clearly its cis configuration[6] which is supported by Dreiding models of these structures. Similarly, the singlet signal (1 H) at τ 6.30 of compound **34** is assigned to the C-3 position.

Structural Elucidation of the Aromatics.—Structures of the aromatics, **35–45,** were determined as pyrazolo-

(5) The 100-MHz nmr spectrum of **23** taken in CCl_4 shows the same coupling constant: τ 3.06 (br, d, $J_{1,2}$ = 7.0 Hz, H_1), 4.71 (br t, $J_{1,2}$ = 7.0, $J_{2,3}$ = 6.0 Hz, H_2), 3.93 (m, H_3), 4.45 (br d, $J_{3,4}$ = 9.0 Hz, H_4), 5.29 (br d, $J_{5,6}$ = 17.0 Hz, H_5), 5.96 (d, $J_{6,5}$ = 17.0 Hz, H_6).

(6) In general, such a large coupling constant is not assignable to trans, since, so far, vicinal trans coupling constants are usually smaller than cis, and cis coupling constants are 13.0–14.0 Hz in a similar compound (shown below) as reported by Kobayashi, *et al.*; see Y. Kobayashi, T. Kuzuma, Y. Sekine, and K. Fujiyama, Abstracts of Papers in Symposium of the Chemistry of Heteroaromatic Compounds, p 93, 1970, Tokyo.



τ 4.67 (d)
τ 5.51 (d)
J = 13.3 Hz

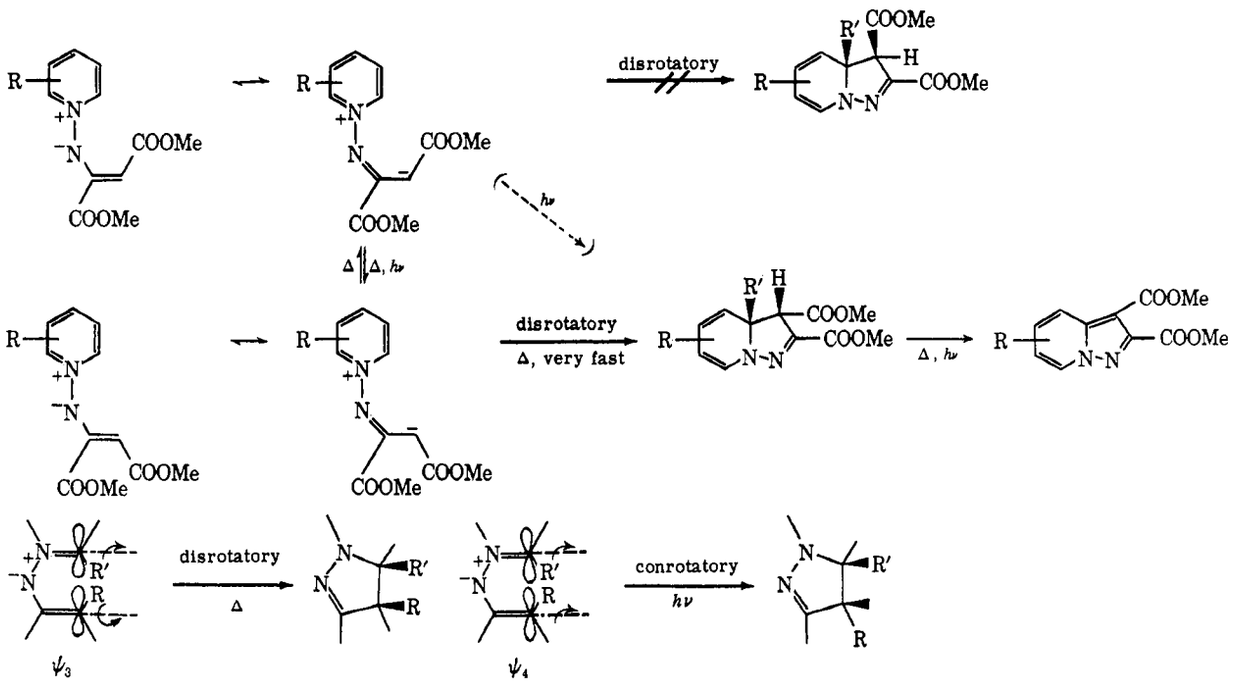
TABLE II

NMR SPECTRA OF DIHYDROPYRAZOLOPYRIDINES IN CCl_4 (τ VALUE)

Compd[a]	R_1	R_2	R_3	R_4	R_5	C_3H	Coupling constant (J, Hz)
23	3.14 (br d)	4.78 (br t)	4.00 (m)	4.54 (br d)	5.35 (br d)	6.03 (d)	$J_{1,2} = 7.0$, $J_{2,3} = 7.0$, $J_{3,4} = 9.0$, $J_{5,C_3H} = 17.0$
25[b]	3.29 (br d)	4.91 (q)	4.33 (br d)	8.15 (d)	5.10 (br d)	5.82 (d)	$J_{1,2} = 7.0$, $J_{2,3} = 6.0$, $J_{3,4} = 1.5$, $J_{5,C_3H} = 17.0$
26	3.16 (d)	4.90 (d d)	8.21 (t)	4.76 (m)	5.38 (br d)	6.07 (d)	$J_{1,2} = 7.5$, $J_{2,4} = 1.5$, $J_{5,C_3H} = 17.0$
28[c]	3.33 (d)	4.96 (d)	8.24[d] (m, 2 H)		5.13 (br d)	5.83 (d)	$J_{1,2} = 7.5$, $J_{5,C_3H} = 17.0$
29	3.46	8.22	4.40	8.14	5.15	5.85	$J_{1,2} = 1.0$, $J_{4,5} = 1.5$, $J_{5,C_3H} = 17.0$
31	7.85 (s)	4.95 (br d)	4.08 (m)	4.55 (br d)	5.45 (br d)	6.08 (d)	$J_{2,3} = 6.0$, $J_{3,4} = 9.0$, $J_{5,C_3H} = 17.0$
32	7.90 (s)	5.06 (br s)	8.25 (d)	4.80 (br s)	5.44 (br d)	6.11 (d)	$J_{5,C_3H} = 17.0$
33	7.95 (s)	5.13 (br s)	4.46 (br d)	8.21 (s)	5.29 (br d)	5.90 (d)	$J_{2,3} = 6.0$, $J_{5,C_3H} = 17.0$
34	7.83 (s)	5.05 (br s)	6.15 (q)	4.68 (br d)	8.88 (s)	6.30 (s)	$J_{2,3} = 6.0$, $J_{3,4} = 9.0$

[a] Chemical shifts to the methyl protons of dimethoxycarbonyl groups appeared in the regions of τ 6.06–6.53 as each a singlet. [b] Chemical shifts of isomeric product **24** appeared at τ 8.18 (R_2) and 4.80 (R_4). [c] Chemical shifts of isomeric product **27** appeared at τ 3.34 (br s, R_1), 4.63 (br s, R_4), and 5.68 (d, C_3H). [d] Overlapping with 2 H.

SCHEME V



[1,5-*a*]pyridine derivatives by physical and spectral comparison with authentic samples prepared by independent syntheses.[2]

Reaction Mechanism.—From the above results, it is concluded that the pyrazolo[1,5-*a*]pyridine derivatives are produced by 1,5-dipolar cyclization of the *N*-vinyliminopyridinium ylides. However, as described above, the isolated trans N ylides **13–22** seem not to be precursors of the corresponding cycloadducts, **23–34**. Thermal intramolecular concerted electrocyclic reactions of the N ylides should give rise to the trans cycloadducts but the disrotatory cyclization of the trans N ylide is unfavorable owing to steric hindrance of the substituents. Actually, the cycloadducts were obtained as cis isomers, suggesting that such precursors are cis N ylides and not trans isomers. Thus thermal or photochemical trans–cis isomerization of the N ylide must occur prior to ring closure, followed by thermal cyclization and dehydrogenation. The photochemical preparation of **23** or **34** from N ylide **13** or **22** is seen as a result of photochemical trans–cis isomerization, followed by the thermal disrotatory cyclization[7] rather than photochemical conrotatory process as shown in Scheme V.

(7) For an analogous disrotatory ring closure in a heterocyclic reaction, see J. Elguero, *Bull. Soc. Chim. Fr.*, 1925 (1971).

Experimental Section[8]

Reaction of N Imine and Olefin.—A mixture of dimethyl 1-chlorofumarate (**1**) or -maleate (**2**) (0.36 g, 2 mmol) and a small excess of pyridinium *N*-imine hydriodide in ethanol was stirred with excess potassium carbonate (~6 g) at room temperature for 0.5–1 hr. The insoluble substances were removed by filtration. The filtrate was evaporated *in vacuo*. The results are summarized in Table III.

Isomerizations of N Ylides 13–22 and Aromatizations of Their Cycloadducts, 23–33. General Procedure.—A mixture of N ylide (0.2–0.4 g) and chloroform (50 ml) was kept at room temperature for 1 day and then the solvent was removed *in*

(8) Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. Microanalyses were performed on a Perkin-Elmer 240 elemental analyzer. The uv spectra were determined with a JASCO Model ORD/UV-5 recorder. The nmr spectra were taken with a Japan Electric Optics, Model C-60-XL, nmr spectrometer and with a Varian A-60 recording spectrometer with tetramethylsilane as an internal standard. Chemical shifts are expressed in τ values. The ir spectra were taken with a JASCO Model IR-S spectrophotometer. The glpc was done isothermally on a Hitachi K-23 gas chromatograph with a 3-ft, 5 wt % SE-30 (Chromosorb G-NAW) column (flame-isomerization detector). A Varian Aerograph Model 7000 (hydrogen flame-ionization detector, nitrogen carrier gas, fitted with a 5 ft × 1/8 in. column containing 12% Dow Corning silicone oil 550 on 80–100 Chromosorb W) was used for preparative separation.

TABLE III

N Imine	Olefin	N Ylide[a]	Yield, %	Mp, °C	Ir (KBr), cm^{-1} (C=O)	Uv λ_{max} (MeOH), nm (ϵ)
3	**1**	**13**	87	103–105	1649, 1732	416 (1.28×10^3)
						280 (1.72×10^4)
3	**2**		85			238 (6.39×10^3)
4	**1**	**14**	88	85–86	1649, 1734	408 (1.93×10^3)
						280 (1.75×10^4)
4	**2**		80			238 (5.68×10^3)
5	**1**	**15**	88	112–113	1652, 1737	400 (1.99×10^3)
						281 (1.75×10^4)
5	**2**		90			238 (8.52×10^3)
6	**1**	**16**	95	113–114	1655, 1721	410 (1.58×10^3)
						281 (1.39×10^4)
						238 (5.35×10^3)
7	**1**	**17**	93	96–98	1650, 1735	410 (1.68×10^3)
						279 (1.68×10^4)
						238 (4.86×10^3)
8	**1**	**18**	78	107–108	1658, 1738	400 (0.78×10^3)
						280 (1.46×10^4)
						236 (3.65×10^3)
9	**1**	**19**	95	160–162	1659, 1730	405 (1.22×10^3)
						278 (2.23×10^4)
						234 (7.39×10^3)
10	**1**	**20**	91	119–122	1645, 1743	390 (0.66×10^3)
						282 (1.53×10^3)
						236 (5.45×10^3)
11	**1**	**21**	87	113–115	1651, 1733	404 (0.99×10^3)
						283 (2.04×10^4)
						236 (5.50×10^3)
12	**1**	**22**	95	130–133	1660, 1731	400 (1.32×10^3)
						279 (2.15×10^4)
						235 (5.90×10^3)

[a] Satisfactory analytical data (±0.2% for C, H, N) were reported for ylides **13–22**: Ed.

vacuo without heating. When unreacted N ylide still remained, the cycloadduct was separated by column chromatography (alumina) using ether as eluent. Furthermore, these phenomena were observed in time-interval measurements of its uv and nmr spectra. The cycloadducts in benzene were aromatized by heating or treatment with palladium on carbon or tetracyanoethylene to give the corresponding 2,3-dimethoxycarbonylpyrazolo[1,5-a]pyridine derivatives (**35–45**) in high yields.

Isomerization of 13.—From **13** (0.20 g) in chloroform (50 ml) 2,3-dimethoxycarbonyl-*cis*-3,3a-dihydropyrazolo[1,5-*a*]pyridine (**23**) was obtained in quantitative yield as orange needles (from *n*-hexane): mp 83–86°; ν (KBr) 1685, 1725 cm^{-1} (C=O); λ_{max} (MeOH) 379 nm (ϵ 8.68×10^3), 305 (sh), 252 (5.73×10^3).

Anal. Calcd for $C_{11}H_{12}N_2O_4$: C, 55.93; H, 5.12; N, 11.86. Found: C, 55.97; H, 5.11; N, 11.81.

A solution of **23** (0.20 g) in dry benzene (30 ml) was treated with palladium on carbon (0.20 g) at 60–80° for 6 hr to give **35** (0.16 g, 80%) as pale yellow needles (from *n*-hexane), mp 71–73°, identical with an authentic sample.[2]

Isomerization of 14.—From **14** (0.3 g) in chloroform (50 ml) **25** and **24** were obtained in quantitative yield as orange needles (from *n*-hexane).

Anal. Calcd for $C_{12}H_{14}N_2O_4$ (a mixture of **24** and **25**): C, 57.59; H, 5.64; N, 11.20. Found: C, 57.77; H, 5.58; N, 11.30.

The isomer ratio of **24** to **25** was 1:12 by nmr inspection (Table II). A mixture of **24** and **25** (0.20 g) was treated with palladium on carbon (0.20 g) in benzene (30 ml) at 60–80° for 6 hr to give **37** and **36** (0.17 g, 85%) as colorless needles (from methanol), identical nmr with that of authentic samples.[2]

Isomerization of 15.—From **15** (0.20 g) in chloroform (50 ml) there was obtained **26** in quantitative yield as orange needles (from ether–*n*-hexane): mp 86–89°; ν (KBr) 1690, 1728 cm^{-1} (C=O), λ_{max} (MeOH) 379 nm (ϵ 1.00×10^4), 310 (sh), 259 (7.15×10^3).

Anal. Calcd for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.65; H, 5.68; N, 11.16.

Cycloadduct **26** (0.20 g) was treated with palladium on carbon (0.20 g) in benzene (30 ml) at room temperature overnight to give **38** (0.18 g, 90%) as colorless needles (from methanol), mp 119–121°, identical with an authentic sample.[2]

Isomerization of 16.—From **16** (0.30 g) in chloroform (50 ml) there was obtained **28** and **27** in quantitative yield as orange needles (from *n*-hexane). The ratio of **27** to **28** was 1:8 by nmr (Table II). The mixture (0.2 g) was heated at reflux benzene for 8 hr to give a mixture of **40** and **39** (0.16 g, 80%) as colorless needles (from methanol), identical with authentic samples (by nmr inspection).[2]

Isomerization of 17.—From **17** (0.20 g) in chloroform (50 ml) there was obtained **29** in quantitative yield as orange needles (from ether–*n*-hexane): mp 95–100°; ν (KBr) 1683, 1730 cm^{-1} (C=O); λ_{max} (MeOH) 398 nm (ϵ 9.42×10^3), 320 (sh), 252 (6.78×10^3).

Anal. Calcd for $C_{13}H_{16}N_2O_4$: C, 59.08; H, 6.10; N, 10.60. Found: C, 59.10; H, 6.12; H, 10.65.

Cycloadduct **29** (0.20 g) was treated in benzene (30 ml) at reflux temperature for 8 hr to give **41** (0.18 g, 90%) as colorless needles (from methanol): mp 95–96°; ν (KBr) 1684, 1727 cm^{-1} (C=O); λ_{max} (EtOH) 300 nm (ϵ 8.5×10^3), 224 (2.85×10^4).

Anal. Calcd for $C_{13}H_{14}N_2O_4$: C, 59.53; H, 5.38; N, 10.68. Found: C, 59.44; H, 5.41; N, 10.88.

Isomerization of 18.—From **18** (0.4 g) in chloroform (50 ml) there was obtained **30** together with the dehydrogenated compound (**42**) in 30% yield as orange crystals. The mixture was heated in benzene (20 ml) to give **42** (80%), identical with an authentic sample.[2]

Isomerization of 19.—From **19** (0.40 g) in chloroform (50 ml) there was obtained **43** (0.02 g, 5%) as colorless needles (from methanol): mp 115–118°; ν (KBr) 1695, 1728 cm^{-1} (C=O); λ_{max} (EtOH) 309 nm (ϵ 9.50×10^3), 225 (2.66×10^4).

Anal. Calcd for $C_{13}H_{14}N_2O_4$: C, 59.53; H, 5.38; N, 10.68. Found: C, 59.53; H, 5.22; N, 10.50.

In this case, **31** was not detected.

Isomerization of 20.—From **20** (0.40 g) in chloroform (50 ml) there was obtained **32** together with **44** in ~10% yield. The mixture was heated in benzene (30 ml) at reflux temperature for 4 hr to give **44** in 85% yield, mp 118–120°, identical with an authentic sample.[2]

Isomerization of 21.—From **21** (0.40 g) in chloroform (50 ml) there was obtained **33** together with **45** in 25% yield as orange crystals. The mixture was heated in benzene (20 ml) at reflux temperature overnight to give **45** in 75% yield as colorless needles: mp 107–110°; ν (KBr) 1703, 1733 cm^{-1} (C=O); λ_{max} (EtOH) 300 nm (ϵ 8.51×10^3), 224 (2.82×10^4).

Anal. Calcd for $C_{13}H_{14}O_4N_2$: C, 59.53; H, 5.38; N, 10.68. Found: C, 59.37; H, 5.53; N, 10.61.

Isomerization of 22.—From **22** (0.40 g) in chloroform (50 ml) there was obtained **34** (0.02 g, 5%) as orange needles (from *n*-hexane): mp 81–83°; ν (KBr) 1717, 1730 cm^{-1} (C=O); λ_{max} (MeOH) 392 nm (ϵ 7.84×10^3), 303 (2.15×10^3).

Anal. Calcd for $C_{13}H_{16}N_2O_4$: C, 59.08; H, 6.10; N, 10.60. Found: C, 59.10; H, 6.17; N, 10.65.

This compound in carbon tetrachloride did not convert to **42** under heating at 100°.

Irradiation of 13.—A mixture of **13** (0.2 g) and acetone (100 ml) was irradiated at 0° for 45 min. Reaction mixture was concentrated *in vacuo*. A mixture of **23** and **35** was obtained in 60% yield in the ratio of 1:1 (by nmr inspection).

When compound **13** was irradiated under above condition for 2 hr at room temperature, only **35** was obtained in 50% yield.

Irradiation of 22.—A mixture of **22** (0.40 g) and acetone (100 ml) was irradiated at room temperature for 1 hr. The solution was concentrated *in vacuo* and the residual oil was separated by column chromatography (silica gel) using benzene. Recrystallization from *n*-hexane gave **34** (0.08 g, 20%).

Irradiation of 23.—A mixture of **23** (0.20 g) and acetone (100 ml) was irradiated at room temperature for 2 hr. Work-up as above gave **35** (0.16 g, 80%).

Compounds **24–33** were also observed to undergo dehydrogenation under irradiation and gave the pyrazolo[1,5-*a*]pyridine derivatives together with considerable amounts of tar.

Registry No.—**13**, 35116-54-2; **14**, 35116-55-3; **15**, 35116-56-4; **16**, 35116-57-5; **17**, 35116-58-6; **18**, 35116-59-7; **19**, 35116-60-0; **20**, 35116-61-1; **21**, 35116-62-2; **22**, 35116-63-3; **23**, 35116-64-4; **24**, 35116-65-5; **25**, 36116-66-6; **26**, 35116-67-7; **27**, 35116-68-8; **28**, 35116-69-9; **29**, 35116-70-2; **30**, 35116-71-3; **32**, 35116-72-4; **33**, 35116-73-5; **34**, 35116-74-6; **38**, 30689-98-6; **41**, 35116-76-8; **43**, 35116-77-9; **44**, 30758-71-5; **45**, 35116-79-1.