bonyl isothiocyanate and simple aromatic or heteroaromatic compounds or alkylmagnesium halides.[1,4] It is noteworthy that in contrast to most common synthetic approaches to the same heterocyclic systems,[5] the present method circumvents the use of carboxylic acids or their derivatives as starting materials.

Experimental Section[6]

***N*-Ethoxycarbonylthioamides (1)** were prepared as previously described.[1,4]

General Procedure for Preparation of Compounds 4–9. A solution of 0.010 mol of 1 and 0.012 mol of dinucleophilic reagent in 10 ml of tetrahydrofuran (or 0.010 mol of 1 and 0.020 mol of reagent in 20 ml of ethanol) was refluxed until evolution of H_2S had stopped (2–48 h). Following removal of the solvent by distillation under reduced pressure, the residue was treated as indicated in Tables I and II.

Isolation of Ethyl Carbamate. The residue from the reaction of *N*-ethoxycarbonyl-2-pyrrolethioamide with 2-aminoethanol was treated with water and the resulting mixture was filtered. Extraction with ether of the acidified aqueous filtrate followed by evaporation of the ethereal solution (charcoal, $MgSO_4$) yielded a solid the IR and NMR spectra of which were superimposable on those of authentic ethyl carbamate.

Acknowledgments. Financial support by the Research Corporation, the Research Allocations Committee of the University of new Mexico, and the Department of Chemistry of the University of New Mexico is gratefully acknowledged.

Registry No.—1 (R = $PhCH_2$), 60705-35-3; 1 (R = MeC_6H_4), 57774-66-0; 1 (R = $MeOC_6H_4$), 57774-72-8; 1 (R = 2-pyrrolyl), 37488-43-0; 1 (R = 2-thienyl), 51774-59-5; 1 (R = Et), 59812-12-3; $H_2NCH_2CH_2NH_2$, 107-15-3; $H_2NCH_2CH_2OH$, 141-43-5; $H_2NCH_2CH_2SH$, 60-23-1; *o*-$H_2NC_6N_4NH_2$, 95-54-5; *o*-$H_2NC_6H_4OH$, 95-55-6; *o*-$H_2NC_6H_4SH$, 137-07-5.

Supplementary Material Available. NMR data for all compounds in tables (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) B. George and E. P. Papadopoulos, *J. Org. Chem.*, **41**, 3233 (1976).
(2) P. R. Atkins, S. E. J. Glue, and I. T. Kay, *J. Chem. Soc., Perkin Trans. 1*, 2644 (1973).
(3) (a) G. Forssel, *Chem. Ber.*, **24**, 1846 (1891); **25**, 2132 (1892); (b) H. Lehr and H. Erlenmeyer, *Helv. Chim. Acta*, **27**, 489 (1944).
(4) E. P. Papadopoulos, *J. Org. Chem.*, **41**, 962 (1976).
(5) R. C. Elderfield, Ed., "Heterocyclic Compounds", Vol. 5, Wiley, New York, N.Y., 1957, pp 239, 274, 377, 420, 507, 679.
(6) Melting points were determined in a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer using mineral oil mulls. NMR spectra were obtained on a Varian EM 360 spectrophotometer using solutions in hexadeuteriodimethyl sulfoxide with tetramethylsilane as internal standard.

Thermolysis and Photolysis of Various *N*-Imidolyliminopyridinium Ylides

Akikazu Kakehi,* Suketaka Ito, Kenji Uchiyama, Yoshiaki Konno, and Kenji Kondo

Department of Industrial Chemistry, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380, Japan

Received July 27, 1976

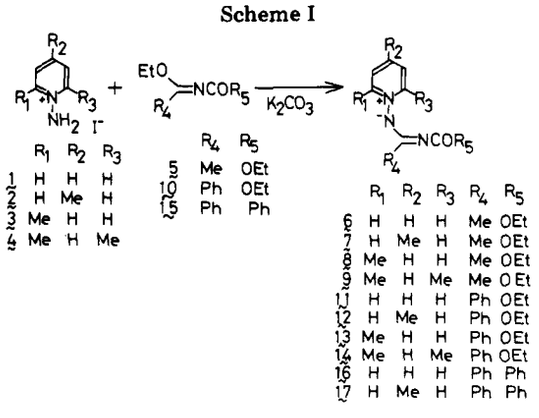
The reactions of pyridinium *N*-imines with some imidates **5**, **10**, and **15** gave the corresponding *N*-imidoyliminopyridinium ylides **6–9**, **11–14**, **16**, and **17** in very good yields. Thermolyses of these *N*-ylides **6–9** and **11–14** in refluxing xylene afforded *s*-triazolo[1,5-*a*]pyridines **18–20**, **23**, **25**, and **27**, pyrazolo[1,5-*a*]pyridines **21**, **22**, **28**, and **29**, and mesoionic compounds **24** and **26**, while thermolyses of *N*-ylides **16** and **17** and photolyses of *N*-ylides **16**, **17**, **11**, and **12** gave the corresponding 1,2,4-oxadiazoles **30** and **31** together with pyridine derivatives in considerable yields. Structural elucidation of these compounds was accomplished mainly by physical and spectral means and partially by their independent syntheses. The formation of pyrazolopyridine derivatives **21**, **22**, **28**, and **29** was confirmed to proceed via isocyanate intermediates.

Pyridinium *N*-ylide acting as an extended dipole is an intriguing molecule in heterocyclic chemistry, and we are especially interested in its reaction leading to polyazabicyclic compounds.[1-3] Recently, a novel 1,6 cyclization has been found in the photolysis of *N*-vinyliminopyridinium ylide.[4] We sought to generalize the 1,6 cyclization, but no such type of reaction could be found in other pyridinium *N*-ylides reported already by us and many investigators.[5-8] Hence, we focused our attention on synthesis of a new class of pyridinium *N*-ylides and we found the 1,6 cyclization in the case of the thermolysis of *N*-imidoyliminopyridinium ylides.[9] In this paper, we wish to report the first synthesis of some *N*-imidoyliminopyridinium ylides and their thermal and photochemical behavior involving the 1,6 cyclization.

Results and Discussion

Preparation of *N*-Imidoyliminopyridinium Ylides 6–9, 11–14, 16 and 17. The title compounds, *N*-imidoyliminopyridinium ylides **6–9**, **11–14**, **16**, and **17**, were synthesized in very good yields by the reactions of 1-aminopyridinium iodides **1–4** with ethyl *N*-ethoxycarbonylacetimidate (**5**), ethyl *N*-ethoxycarbonylbenzimidate (**10**), and ethyl *N*-benzoylbenzimidate (**15**) in the presence of base (Scheme I). All of the *N*-ylides are stable, crystalline compounds and were not apt to cyclize intramolecularly at ordinary conditions. The structures assigned to these *N*-imidoyliminopyridinium ylides

Scheme I

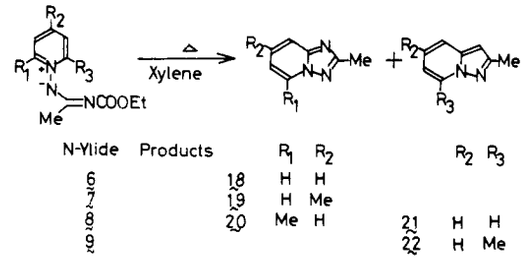


	R_1	R_2	R_3
1	H	H	H
2	H	Me	H
3	Me	H	H
4	Me	H	Me

	R_4	R_5
5	Me	OEt
10	Ph	OEt
15	Ph	Ph

	R_1	R_2	R_3	R_4	R_5
6	H	H	H	Me	OEt
7	H	Me	H	Me	OEt
8	Me	H	H	Me	OEt
9	Me	H	Me	Me	OEt
11	H	H	H	Ph	OEt
12	H	Me	H	Ph	OEt
13	Me	H	H	Ph	OEt
14	Me	H	Me	Ph	OEt
16	H	H	H	Ph	Ph
17	H	Me	H	Ph	Ph

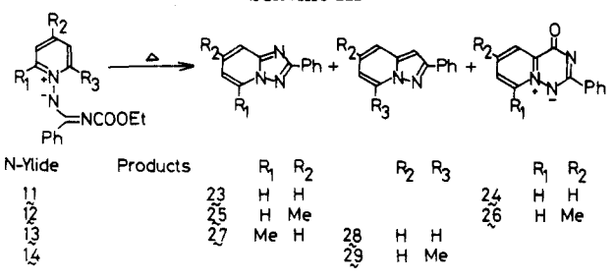
Scheme II



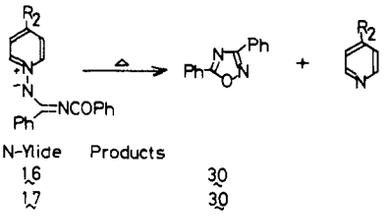
6–9, **11–14**, **16**, and **17** are consistent with the spectroscopic data. For example, they showed a characteristic carbonyl absorption at 1628–1663 cm^{-1} (**6–9** and **11–14**) or at near 1490 cm^{-1} (**16** and **17**) in the IR spectra, and, in the NMR spectra, signals due to protons on the pyridine ring appeared in the range of δ 7.3–9.0, whose values coincide well with those of other substituted *N*-iminopyridinium ylides.[5,6,9]

Thermolyses and Photolyses of *N*-Imidoyliminopyridinium Ylides. In contrast with *N*-vinyliminopyridinium ylides[5,11] and pyridinium *N*-allylides,[7,8,12] these *N*-imidoyliminopyridinium ylides **6–9**, **11–14**, **16**, and **17** did not exhibit 1,5-dipolar cyclization at room temperature at all, but they were thermolyzed in refluxing xylene. Thermolyses of *N*-ylides **6–9** gave the corresponding compounds **18** (60%), **19** (54%), **20** and **21** (total yield ca. 60%), and **22** (75%) together with considerable amounts of polymeric substances. The ratio of product **20** to **21** is 2:3, which was determined by NMR. Similarly, thermolyses of *N*-ylides **11–14** afforded the products **23** (36%) and **24** (58%), **25** (38%) and **26** (51%), **27** and **28** (product ratio **27**/**28** ⅓, total yield 81%), and **29** (87%), respectively, and those of *N*-ylides **16** and **17** gave the same compound **30** in 79 and 80% yields together with pyridine and 4-picoline.

Scheme III



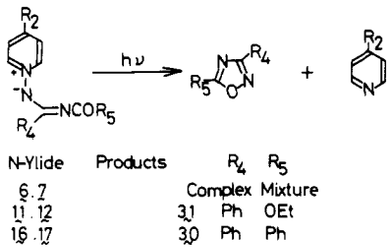
Scheme IV



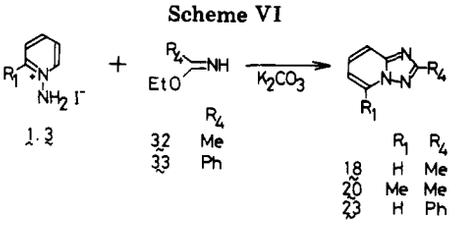
On the other hand, irradiations of *N*-ylides **11** and **12** in benzene (or acetone) using a high-pressure mercury lamp afforded the same compound **31** in 58 (64) and 59% (60%) yields, together with considerable amounts of pyridine and 4-picoline (detected by TLC). Similarly, photolyses of *N*-ylides **16** and **17** in benzene gave compound **30**, quantitatively, which was the same product as that prepared by the thermolyses of the same *N*-ylides **16** and **17**. However, irradiations of *N*-ylides **6** and **7** gave only complex mixtures, and the isolation of any significant product was unsuccessful. These results are shown in Scheme V.

Structures of these products **18–31** were determined mainly by their physical and spectral inspections and partially by comparisons with authentic samples. Compounds **18–20**, **23**, **25**, and **27** were assigned to be 2-substituted *s*-triazolo[1,5-*a*]pyridine derivatives, because no carbonyl absorption was exhibited in their IR spectra and the chemical shifts (see Table I) of the ring protons were grossly similar to those of bicyclic 10π heteroaromatics such as pyrazolo[1,5-*a*]pyridine[5,6] and indolizine.[7,8,10] Furthermore, compounds **18**, **20**, and **23** were completely in accord with the triazolopyridines prepared by the reactions of pyridinium *N*-imines with imidates **32** and **33** (Scheme VI).

Scheme V



Scheme VI



Structures of compounds **21**, **22**, **28**, and **29** were concluded to be 3-unsubstituted pyrazolo[1,5-*a*]pyridine derivatives from NMR and by comparison with the known pyrazolopyridine **28** reported by Bower and Ramage.[13] The NMR spectra of compounds **21**, **22**, **28**, and **29**, in particular, showed a characteristic singlet signal at δ 6.08–6.60 attributable to a methine proton at the 3 position on the pyrazolopyridine skeleton and the absence of the signal due to one methyl group on the pyridine ring derived from *N*-ylides **8**, **9**, **13**, and **14**. The melting point (107–108 °C) of compound **28** was also in accord with that (109 °C) of 2-phenylpyrazolo[1,5-*a*]pyridine.[13]

Compounds **24** and **26** were determined to be mesoionic pyrido[2,1-*f*]-*as*-triazine derivatives by the elemental and spectral analyses and by comparison with similar mesoionic pyrido[1,2-*b*]pyridazine reported recently by us.[4] For example, the NMR spectrum of compound **24** exhibited signals at δ 7.50 (3 H, m, meta, meta′, and para protons of phenyl), 7.88 (1 H, br t, J = 8.0, 7.0 Hz, 7-H), 8.13 (1 H, br t, J = 8.0, 7.5 Hz, 6-H), 8.42 (2 H, m, ortho and ortho′ protons of phenyl), 8.72 (1 H, dd, J = 7.5, 2.0 Hz, 5-H), and 8.82 (1 H, dd, J = 7.0, 1.0 Hz, 8-H), and the UV spectrum of **24** in ethanol showed two maxima at 253 (log ϵ 4.43) and 343 nm (log ϵ 4.15). The spectral pattern in the UV spectrum of compound **24** is similar to those [251 (log ϵ 4.22) and 338 nm (log ϵ 3.37)] of parent *N*-ylide **11** and those of mesoionic pyridopyridazine.[4] In particular, the enhanced extinction coefficients of product **24** in comparison with *N*-ylide **11** may be due to the increased coplanarity of the ylidic chromophore.

Compounds **30** and **31** were assigned to be 3,5-diphenyl- and 5-ethoxy-3-phenyl-1,2,4-oxadiazole by mechanistic consideration and by comparisons with authentic samples. Since the generation of pyridine derivatives in the reactions was always observed, it is clear that compounds **30** and **31** were formed by the ylidic bond fissions of the corresponding *N*-ylides **16**, **17**, **11**, and **12**. The melting points of **30** and **31** were in accord with those of samples reported in the literature.[14,15]

Mechanisms. Possible mechanisms for the formations of triazolopyridines **18–20**, **23**, **25**, and **27** and pyrazolopyridines

Table I. NMR Data of Triazolopyridines and Pyrazolopyridines

Registry no.	Compd	Solvent	C-5	C-6	C-7	C-8	C-2
768-19-4	18	CCl_4	8.37 d	6.73 br t	7.24 br t	7.47 dd	2.48 s
				$J_{5,6}$ = 7.0, $J_{6,7}$ = 7.5, $J_{7,8}$ = 9.0, $J_{6,8}$ = 1.0			
4931-22-0	19	CCl_4	8.19 d	6.55 dd	2.38 d	7.20 br s	2.43 s
				$J_{5,6}$ = 7.0, $J_{6,8}$ = 1.5, $J_{7,8}$ = 1.5			
4931-28-6	20	CCl_4	2.65 s	6.58 dd	7.21 q	7.40 dd	2.55 s
				$J_{6,7}$ = 7.0, $J_{7,8}$ = 9.0, $J_{6,8}$ = 1.0			
779-24-8	23	$CDCl_3$	8.58 dd	6.94 br t	*a*	7.75 d	7.4–7.6 and 8.2–8.5 m — m
				$J_{5,6}$ = $J_{6,7}$ = 7.0, $J_{7,8}$ = 8.0, $J_{5,7}$ = 1.0			
4931-23-1	25	$CDCl_3$	8.48 d	6.81 dd	2.46 s	*b*	7.4–7.7 and 8.2–8.4 m m
					$J_{5,6}$ = 7.0, $J_{6,8}$ = 1.5		
4931-29-7	27	CCl_4	2.67 s	6.53 d	7.16 q	*c*	7.2–7.5 and 8.1–8.4 m m
					$J_{6,7}$ = 7.0, $J_{7,8}$ = 8.0		

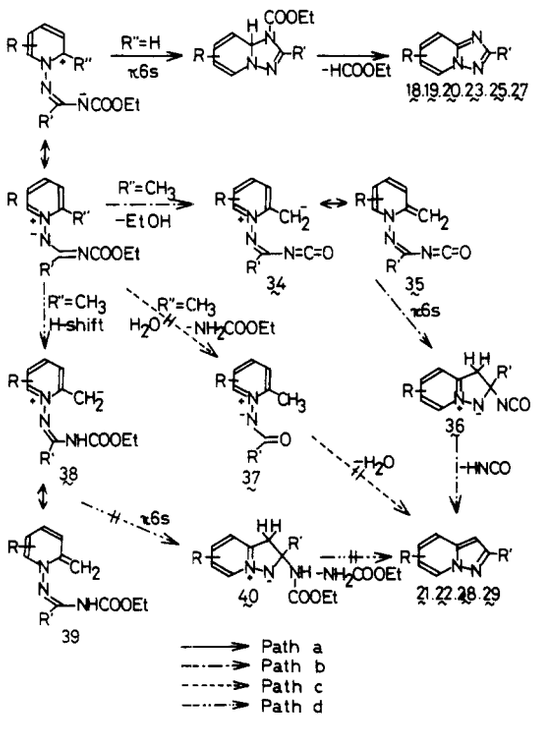
	Compd	Solvent	C-3	C-4	C-5	C-6	C-7	C-2
34760-58-2	21	CCl_4	6.08 s	7.23 d	6.86 br t	6.55 br t	8.22 d	2.40 s
						$J_{4,5}$ = 8.0, $J_{5,6}$ = $J_{6,7}$ = 7.0		
60705-36-4	22	CCl_4	6.09 s	7.12 d	6.76 q	6.28 d	2.61 s	2.42 s
						$J_{4,5}$ = 8.0, $J_{5,6}$ = 7.0		
56983-95-0	28	CCl_4	6.59 s	*d*	6.87 br t	6.49 br t	8.34 d	7.0–7.5 and 7.7–8.0 m m
						$J_{4,5}$ = 8.0, $J_{5,6}$ = $J_{6,7}$ = 7.0		
60705-37-5	29	CCl_4	6.60 s	*e*	6.77 q	6.33 br d	2.67 s	7.0–7.4 and 7.7–8.0 m m
						$J_{4,5}$ = 8.0, $J_{5,6}$ = 7.0		

[a] Overlapped with signals at δ 7.4–7.6. [b] Overlapped with signals at δ 7.4–7.7. [c] Overlapped with signals at δ 7.2–7.5. [d] Overlapped with signals at δ 7.0–7.5. [e] Overlapped with signals at δ 7.0–7.4.

21, **22**, **28**, and **29** are summarized in Scheme VII.

Triazolopyridines **18–20**, **23**, **25**, and **27** must be formed via 1,5-dipolar cyclizations of *N*-imidoyliminopyridinium ylides

Scheme VII



6–8 and **11–13**, followed by aromatizations of primary dihydrotriazolopyridines (path a). Such cyclizations of the corresponding 1,5-dipoles such as *N*-vinyliminopyridinium ylides[5,11] and pyridinium *N*-allylides[7,8,10,12] have been documented recently by many authors. On the other hand, there are three possible routes for the formations of pyrazolopyridines **21**, **22**, **28**, and **29**: path b, 1,5 cyclization of the isocyanate intermediate **34** or **35** formed by the elimination of 1 mol of ethanol from the corresponding *N*-ylide, followed by aromatization of the resulting 2-isocyanato-2,3-dihydropyrazolopyridine **36** with elimination of isocyanic acid; path c, hydrolysis of the *N*-ylide, followed by dehydration between the 2-methyl group and the carbonyl group in the resulting *N*-acyliminopyridinium ylide **37**; path d, 1,5 cyclization of the rearranged intermediate **38** or **39** formed by sigmatropic shift of a hydrogen on the 2-methyl group in the *N*-ylide, followed by aromatization of the resulting 2-ethoxycarbonylamino-2,3-dihydropyrazolopyridine **40** with elimination of urethan.

Analogous routes to paths c and d were proposed in the reactions of 2-picolinium *N*-phenacylides[16] and in the thermolyses of 2-picolinium *N*-allylides,[8] respectively. Paths c and d, however, can be neglected in this reaction, since no urethan could be detected from the reaction mixture by gas chromatographic examination, and dehydration of *N*-acetyliminopyridinium ylide[17] synthesized independently was unsuccessful under the reaction condition employed here. Further informative evidence was obtained by a trapping experiment, in which gaseous isocyanic acid evolved in the thermolysis of *N*-ylide **14** was introduced into ethanol and the resulting urethane was actually isolated (see Experimental Section).

Table II. Some Data of *N*-Imidoyliminopyridinium Ylides

Registry no.	*N*-Ylide[a]	Reactants: *N*-Imine	Reactants: Imidate	Yield, %	Mp, °C	ν^{KBr} (C=O), cm^{-1}
60705-38-6	**6**	**1**[b]	**5**[f]	89	138–140	1640
60705-39-7	**7**	**2**[c]	**5**	71	124–126	1660
60705-40-0	**8**	**3**[d]	**5**	91	102	1638
60705-41-1	**9**	**4**[e]	**5**	79	167–170	1645
60072-17-5	**11**	**1**	**10**[g]	74	132–133	1660
60072-18-6	**12**	**2**	**10**	88	128–130	1663
60705-42-2	**13**	**3**	**10**	78	163–165	1631
60705-43-3	**14**	**4**	**10**	67	163–164	1628
60705-44-4	**16**	**1**	**15**[h]	79	179–181	1490
60705-45-5	**17**	**2**	**15**	69	166–168	1488

[a] **6**. Anal. Calcd for $C_{10}H_{13}N_3O_2$: C, 57.96; H, 6.32; N, 20.28. Found: C, 57.86; H, 6.33; N, 20.14. **7**. Calcd for $C_{11}H_{15}N_3O_2$: C, 59.71; H, 6.83; N, 18.99. Found: 59.51; H, 6.85; N, 18.73. **8**. Calcd for $C_{11}H_{15}N_3O_2$: C, 59.71; H, 6.83; N, 18.99. Found: C, 59.91; H, 6.86; N, 18.83. **9**. Calcd for $C_{12}H_{17}N_3O_2$: C, 61.25; H, 7.28; N, 17.86. Found: C, 61.32; H, 7.23; N, 18.03. **11**. Calcd for $C_{15}H_{15}N_3O_2$: C, 66.90; H, 5.61; N, 15.61. Found: C, 66.99; H, 5.73; N, 15.32. λ_{max} (EtOH) 251 nm (log ϵ 4.22) and 338 (3.37). **12**. Calcd for $C_{16}H_{17}N_3O_2$: C, 67.82; H, 6.05; N, 14.83. Found: C, 68.01; H, 6.03; N, 14.72. λ_{max} (EtOH) 249 nm (log ϵ 4.24) and 330 (3.40). **13**. Calcd for $C_{16}H_{17}N_3O_2$: C, 67.82; H, 6.05; N, 14.83. Found: C, 67.73; H, 5.98; N, 14.71. **14**. Calcd for $C_{17}H_{19}N_3O_2$: C, 68.66; H, 6.44; N, 14.13. Found: C, 68.41; H, 6.45; N, 14.02. **16**. Calcd for $C_{19}H_{15}N_3O$: C, 75.73; H, 5.02; N, 13.95. Found: C, 75.68; H, 4.91; N, 14.13. **17**. Calcd for $C_{20}H_{17}N_3O$: C, 76.17; H, 5.43; N, 13.33. Found: C, 75.88; H, 5.26; N, 13.18. [b] Registry no., 6295-87-0. [c] Registry no., 7583-92-8. [d] Registry no., 7583-90-6. [e] Registry no., 36012-28-9. [f] Registry no., 31084-70-5. [g] Registry no., 33243-90-2. [h] Registry no., 19344-10-6.

Table III. NMR Data of *N*-Imidoyliminopyridinium Ylides

Compd[a]	Chemical shifts (coupling constants, Hz)
6[b]	2.38 (3 H, s, 2′-CH_3), 7.62 (2 H, br t, J = 6.0, 7.0, 3-H and 5-H), 7.92 (1 H, br t, J = 7.0, 7.0, 4-H), 8.47 (2 H, d, J = 6.0, 2-H and 6-H)
7[b]	2.35 (3 H, s, 2′-CH_3), 2.50 (3 H, s, 4-CH_3), 7.39 (2 H, d, J = 7.0, 3-H and 5-H), 8.29 (2 H, d, J = 7.0, 2-H and 6-H)
8[b]	2.41 (3 H, s, 2′-CH_3), 2.63 (3 H, s, 2-CH_3), 4.78 (1 H, br t, J = 6.0, 7.0, 5-H), 7.53 (1 H, d, J = 7.0, 3-H), 7.83 (1 H, t, J = 7.0, 7.0, 4-H), 8.30 (1 H, d, J = 6.0, 6-H)
9[b]	2.40 (3 H, s, 2′-CH_3), 2.58 (6 H, s, 2-CH_3 and 6-CH_3), 7.33 (2 H, br d, J = 7.0, 3-H and 5-H), 7.67 (1 H, t, J = 7.0, 7.0, 4-H)
11[b]	7.4–8.2 (8 H, m, 2′-Ph, 3-H, 4-H, and 5-H), 8.80 (2 H, br d, J = 7.5, 2-H and 6-H)
12[b]	2.54 (3 H, s, 4-CH_3), 7.4–7.9 (7 H, m, 2′-Ph, 3-H, and 5-H), 8.62 (2 H, d, J = 7.5, 2-H and 6-H)
13[b]	2.77 (3 H, s, 2-CH_3), 7.4–8.0 (8 H, m, 2′-Ph, 3-H, 4-H, and 5-H), 8.62 (1 H, d, J = 7.0, 6-H)
14[b]	2.74 (6 H, s, 2-CH_3 and 6-CH_3), 7.4–8.0 (8 H, m, 2′-Ph, 3-H, 4-H, and 5-H)
16	7.2–7.4 (8 H, m, Ph, 3-H, and 5-H), 7.52 (1 H, t, J = 7.5, 7.5, 4-H), 7.7–8.0 (4 H, m, pH), 8.66 (2 H, br d, J = 7.5, 2-H and 6-H)
17	2.41 (3 H, s, 4-CH_3), 7.1–7.4 (8 H, m, Ph, 3-H, and 5-H), 7.8–8.0 (4 H, m, Ph), 8.46 (2 H, d, J = 7.5, 2-H and 6-H)

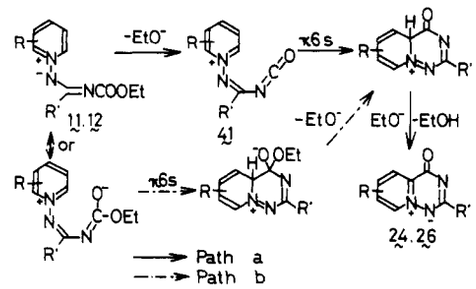
[a] These NMR spectra were measured in deuteriochloroform. [b] The ethyl signals appeared at near δ 1.00 (3 H, t, J = 7.5 Hz) and at near δ 4.00 (2 H, q, J = 7.5 Hz).

Since urethan was not decomposed under such condition, these facts strongly supported path b involving an isocyanate intermediate.

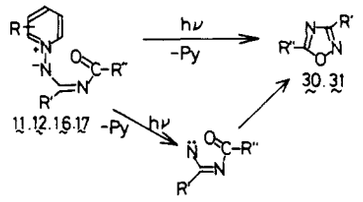
Mechanisms for the formation of mesoionic pyridotriazines **24** and **26** are similar to those given for mesoionic pyridopyridazine (Scheme VIII).[4] The facility of elimination of the ethoxide ion from the *N*-ylide in the formations of pyrazolopyridine derivatives may result in preference of path a involving isocyanate intermediate **41** rather than path b.

The formation of 1,2,4-oxaziazoles **30** and **31** resulted obviously from ylidic bond fissions of the corresponding *N*-ylides, and its possible mechanism is a concerted elimination–cyclization or its stopwise route (Scheme IX). In view of similar reaction examples of some pyridinium ylides reported by Tamura et al.,[18] the most probable route must be a concerted one.

Scheme VIII



Scheme IX



The formation of different products in the thermolyses of *N*-acetimidoyl- **6** and **7** and *N*-benzimidoyliminopyridinium ylides **11** and **12** may be caused by the difference of steric and stabilization effects between the methyl and the phenyl groups, since the introduction of a bulky substituent such as a phenyl group at the 2′ position in the *N*-ylide makes the isocyanate intermediate prefer the configuration fitted in with 1,6 cyclization and the suppression of the formation of polymeric substances in the thermolyses of the latter *N*-ylides **11** and **12** may be attributable to the stabilization effect of the phenyl group.

Experimental Section

Melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed on a Perkin-Elmer 240 elemental analyzer. The NMR spectra were determined with a JEOL JNM-4H-100 spectrometer in deuter-

Table IV. Some Data on the Thermolyses of *N*-Imidoyliminopyridinium Ylides

N-Ylide	Products (%)[a]	Mp, °C	ν^{KBr}, cm^{-1}	λ_{max} (EtOH), nm (log ϵ)
6	18 (60)[21,c]	178–179[b]	1598[b]	
7	19 (54)[d]	186–189[b]	1595[b]	
8	20 + 21 (60)		Mixture (20/21 = 2/3)	
9	22 (75)	Oil	1639 (neat)	
11	23 (36)[21]	135–137	1631	
	24 (58)[e]	232–234	1603 1404	253 (4.43), 343 (4.15)
12	25 (38)	140–142	1629	
	26 (51)[f]	245 dec	1610 1388	252 (4.43), 344 (4.21)
13	27 + 28 (81)		Mixture (27/28 = 1/6)	
	(28)[13]	107–108	1625)	
14	29 (87)	Oil	1630 (neat)	
16	30 (79)[g]	106–108		
17	30 (80)			

[a] **19**. Anal. Calcd for $C_{14}H_{12}N_6O_7$ (its picrate): C, 44.68; H, 3.21; N, 22.34. Found: C, 44.77; H, 3.19; N, 22.22. **24**. Calcd for $C_{13}H_9N_3O$: C, 69.94; H, 4.06; N, 18.83. Found: C, 69.75; H, 4.28; N, 18.62. **25**. Calcd for $C_{13}H_{11}N_3$: C, 74.62; H, 5.30; N, 20.08. Found: C, 74.84; H, 5.41; N, 19.88. **26**. Calcd for $C_{14}H_{11}N_3O$: C, 70.87; H, 4.67; N, 17.71. Found: C, 70.72; H, 4.70; N, 17.58. δ ($CDCl_3$) 2.63 (3 H, s, 6-CH_3), 7.50 (3 H, m, meta, meta′, and para protons of phenyl), 7.65 (1 H, dd, J = 7.0, 2.5 Hz, 7-H), 8.50 (3 H, m, ortho and ortho′ protons of phenyl and 5-H), and 8.70 (1 H, d, J = 7.0 Hz, 8-H). **28**. Calcd for $C_{13}H_{10}N_2$: C, 80.38; H, 5.19; N, 14.42. Found: C, 80.28; H, 5.29; N, 14.55. Compounds **22** and **29** are unstable oils and preparations of pure samples for analyses were unsuccessful. [b] Its picrate. [c] Registry no. (picrate), 7170-11-8. [d] Registry no. (picrate), 60705-46-6. [e] Registry no., 60072-19-7. [f] Registry no., 60111-74-2. [g] Registry no., 888-71-1.

iochloroform or carbon tetrachloride with tetramethylsilane as an internal standard. The chemical shifts are expressed in δ values. The IR and UV spectra were taken with a JASCO DS-301 and a Hitachi EPS-2A spectrophotometer.

Materials. 1-Aminopyridinium iodides **1–4** were prepared by Gösl's method[19] and *N*-acylimidates **5**, **10**, and **15** by the N-acylations of ethyl acetimidate (**32**) and ethyl benzimidate (**33**)[20] with ethyl chlorocarbonate and benzoyl chloride in ether or chloroform in the presence of potassium carbonate. Ethyl *N*-ethoxycarbonylacetimidate (**5**), colorless oil, bp 75–81 °C (14 mm). Ethyl *N*-ethoxycarbonylbenzimidate (**10**), colorless oil, bp 150–160 °C (27 mm). Ethyl *N*-benzoylbenzimidate (**15**), colorless crystals, mp 64–65 °C.

Preparations of *N*-Imidoyliminopyridinium Ylides 6–9, 11–14, 16, and 17. General Method. An equimolar mixture of 1-aminopyridinium iodide (2 mmol) and imidate (2 mmol) in ethanol (50 ml) was stirred in the presence of potassium carbonate (5 g) at room temperature for 1–2 days, and then the reaction mixture was filtered to remove insoluble inorganic substances. The filtrate was concentrated under reduced pressure and the residue was separated by column chromatography (alumina) using chloroform as an eluent. Recrystallization from chloroform–ether gave pure *N*-imidoyliminopyridinium ylide as colorless or pale yellow crystals. Some physical and spectral data of the *N*-ylides **6–9**, **11–14**, **16**, and **17** are summarized in Tables II and III.

Thermolyses of the *N*-Ylides 6–9, 11–14, 16, and 17. General Method. *N*-Ylide (1 mmol) was refluxed in xylene (50 ml) until the disappearance of the *N*-ylide was observed by its TLC (ca. 12–24 h). The reaction mixture was then concentrated under reduced pressure and the residue was separated by the usual manner.

These results and some properties are summarized in Table IV.

Photolyses of the *N*-Ylides 6, 7, 11, 12, 16, and 17. General Method. A solution of the *N*-ylide (1 or 2 mmol) in benzene (100 ml) or acetone was irradiated with a high-pressure mercury lamp (100 W) for 1–7 h. After the evaporation of the solvent, residual substances were separated by column chromatography or directly recrystallized from aqueous ethanol. However, photolyses of *N*-ylides **6** and **7** gave only unstable products; their isolations were unsuccessful. These results are shown in Table V.

Independent Syntheses of Triazolopyridines 18, 20, and 23. Triazolopyridines **18**, **20**, and **23** were synthesized in 49, 44, and 13% yields by the reactions of 1-aminopyridinium iodides **1** and **3** with ethyl acetimidate (**32**) and ethyl benzimidate (**33**) in the presence of potassium carbonate. These triazolopyridines **18**, **20**, and **23** were also prepared by the reactions of pyridinium *N*-imines with acetonitrile and benzonitrile.[21] The melting points and IR and NMR spectra of the triazolopyridines (or their picrates) **18**, **20**, and **23** were in accord with those of the products prepared by the thermolyses of the *N*-ylides **6**, **8**, and **11**.

2,5-Dimethyl-*s*-triazolo[1,5-*a*]pyridine (**20**), mp (its picrate) 175–178 °C. Anal. Calcd for $C_{14}H_{12}N_6O_7$: C, 44.68; H, 3.21; N, 22.34. Found: C, 44.58; H, 3.23; N, 22.22.

Table V. Some Data on the Photolyses of *N*-Imidoyliminopyridinium Ylides

N-Ylide	1,2,4-Oxadiazole[a]	Irradn time, h	Solvent	Yield, %
11	31	4	Benzene	58
	31	7	Acetone	64
12	31	6	Benzene	59
	31	6	Acetone	60
16	30	1	Acetone	100
17	30	1	Acetone	100

[a] 5-Ethoxy-3-phenyl-1,2,4-oxadiazole (**31**), colorless needles, mp 32–32.5 °C.[14] 3,5-Diphenyl-1,2,4-oxadiazole (**30**), colorless needles, mp 106–108 °C.[15]

Trapping Experiment with Isocyanic Acid. The apparatus consists of a 100-ml two-necked flask equipped with a gas inlet and a condenser. The exit from the condenser was connected to a trapping flask filled with 30 ml of ethanol. In order to pass isocyanic acid (bp 23.5 °C) without condensation, warm water (50–55 °C) was circulated in the condenser. A solution of *N*-ylide **14** (0.30 g, 1 mmol) in dry xylene (50 ml) was placed in the reaction flask and N_2 gas was slowly introduced. The solution was then refluxed for 1 day. Usual workup of the reaction mixture gave 7-methyl-2-phenylpyrazolo[1,5-*a*]pyridine (**29**, 0.14 g, 67%) as the only isolable product, but no urethan could be obtained. On the other hand, evaporation of ethanol in the trapping flask gave urethan (0.01 g, 11%) as white needles.

In the thermolysis of urethan using the apparatus described above, decomposition of urethan to ethanol and isocyanic acid could not be detected.

Others. In the gas chromatographic examinations of the reaction mixtures from the thermolyses of *N*-ylides **8**, **9**, **13**, and **14**, urethan could not be detected.

The thermolysis of *N*-acetylimino-2,6-lutidinium ylide[17] did not give the corresponding pyrazolopyridine **22**.

Registry No.—**20** picrate, 60705-47-7; **32**, 1000-84-6; **33**, 825-60-5; ethyl chlorocarbonate, 541-41-3; benzoyl chloride, 98-88-4; acetonitrile, 75-05-8; benzonitrile, 100-47-0.

References and Notes

(1) A. Kakehi and S. Ito, *J. Org. Chem.*, **39**, 1542 (1974).
(2) A. Kakehi, S. Ito, and T. Manabe, *J. Org. Chem.*, **40**, 544 (1975).
(3) A. Kakehi, S. Ito, T. Manabe, H. Amano, and Y. Shimaoka, *J. Org. Chem.*, **41**, 2739 (1976).
(4) A. Kakehi, S. Ito, T. Funahashi, and Y. Ota, *J. Org. Chem.*, **41**, 1570 (1976).
(5) T. Sasaki, K. Kanematsu, and A. Kakehi, *J. Org. Chem.*, **37**, 3106

(1972).
(6) T. Sasaki, K. Kanematsu, and A. Kakehi, *Tetrahedron Lett.*, 5245 (1972).
(7) Y. Tamura, Y. Sumida, and M. Ikeda, *J. Chem. Soc., Perkin Trans. 1*, 2091 (1973).
(8) Y. Tamura, Y. Sumida, S. Haruki, and M. Ikeda, *J. Chem. Soc., Perkin Trans. 1*, 575 (1975).
(9) A. Kakehi, S. Ito, K. Uchiyama, and Y. Konno, *Chem. Lett.*, 413 (1976).
(10) T. Sasaki, K. Kanematsu, A. Kakehi, and G. Ito, *J. Chem. Soc., Perkin Trans. 1*, 2089 (1973).
(11) Y. Tamura, N. Tsujimoto, Y. Sumida, and M. Ikeda, *Tetrahedron*, **28**, 21 (1972).
(12) T. Sasaki, K. Kanematsu, A. Kakehi, and G. Ito, *Tetrahedron*, **28**, 4947 (1972).
(13) J. D. Bower and G. R. Ramage, *J. Chem. Soc.*, 4506 (1957).
(14) Mp 35–36 °C: Beilstein, Vol. 27, p 607.
(15) Mp 108 °C: E. Beckmann, *Ber.*, **32**, 1589 (1899).
(16) A. E. Tschitschibabin, *Ber.*, **60**, 1607 (1927).
(17) J. Streith, J. P. Luttringer, and M. Nastasi, *J. Org. Chem.*, **36**, 2962 (1971).
(18) Y. Tamura, Y. Miki, Y. Sumida, and M. Ikeda, *J. Chem. Soc., Perkin Trans. 1*, 2580 (1973).
(19) R. Gösl and A. Meuwsen, *Org. Synth.*, **43**, 1 (1963).
(20) S. A. Glickman and A. C. Cope, *J. Am. Chem. Soc.*, **67**, 1017 (1945).
(21) T. Okamoto, M. Hirobe, Y. Tamai, and E. Yabe, *Chem. Pharm. Bull.*, **14**, 506 (1966).

Reaction of Ketenimines with an Oxaziridine and Nitrones

Nobuyuki Murai, Mitsuo Komatsu, Yoshiki Ohshiro,* and Toshio Agawa

Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565, Japan

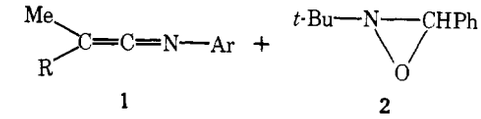
Received July 13, 1976

The reaction of the *N*-arylketenimines **1a–d** with the oxaziridine **2** gave the 1:1 adducts, 1,3-diazolidin-4-ones **3**. In the case of the diphenylketenimine **1e**, the oxindole **9** was isolated instead of **3**. No addition reaction was observed in the reaction of *N*-cyclohexylketenimines. Similar results were obtained in the reactions of **1a,d** with the nitrone **12**, but two oxindoles **9** and **13** were formed in the reaction of **1e**. A substituent effect and the difference between **2** and **12** were observed.

Synthetic application of ketenimines has been less developed than that of other heterocumulenes in the field of heterocyclic chemistry.[1]

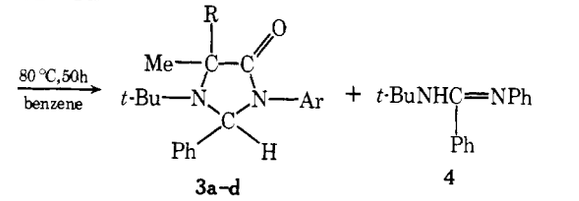
In this paper, the reactions of ketenimines with an oxaziridine and nitrones are described. We reported previously that an isocyanate, a carbodiimide, and an isothiocyanate gave 1:1 adducts in the reactions with 2-*tert*-butyl-3-phenyloxaziridine or *C*-phenyl-*N*-*tert*-butylnitrone, the isomer of the oxaziridine.[2,3] In the reaction with these isomers, on the contrary, a ketene behaved in a different manner from those of the other heterocumulenes.[2,4]

While a ketenimine has one terminal carbon atom like a ketene, the difference between their chemical behavior has been shown in many instances.[1] Most additions to a ketenimine occur on the C=C bond,[1] and Barker and his co-worker reported that *C,N*-diphenylnitrone added to diphenylketene-*N*-*p*-bromophenylimine across the C=C bond.[5] However, our present study revealed that the addition occurs on the C=N bond of ketenimines.



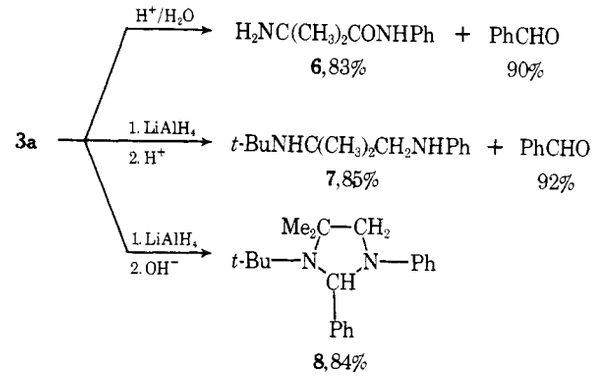
1 **2**

a, R = Me; Ar = Ph
b, R = Me; Ar = *p*-MeC_6H_4
c, R = Me; Ar = *p*-$MeOC_6H_4$
d, R = Ar = Ph



3a–d **4**

+ *t*-BuN=CHPh
5



6, 83% **7**, 85% **8**, 84%

Results and Discussion

Reactions with Oxaziridine. The reaction of dimethylketene-*N*-phenylimine (**1a**) with 2-*tert*-butyl-3-phenyloxaziridine (**2**) gave the 1:1 adduct **3a**, a 1,3-diazolidine derivative, in 40% yield. The dimethylketenimines **1b** and **1c** also gave the 1:1 adducts **3b** and **3c**. In the reaction of phenylmethylketene-*N*-phenylimine (**1d**), however, N^1-*tert*-butyl-N^2-phenylbenzamidine (**4**) and *N*-*tert*-butylbenzaldimine (**5**) were isolated as major products, and the yield of the 1:1 adduct **3d** decreased to 5%.

The adduct **3a** exhibited a strong infrared absorption at 1685 cm^{-1}, which was assigned to the carbonyl group. Furthermore, the following chemical evidences provided conclusive proof for the structure of **3a**. Acidic hydrolysis of **3a** gave the anilide **6** and benzaldehyde.[6] After the reaction with lithium aluminum hydride, the addition of hydrochloric acid afforded the acyclic diamine **7** and benzaldehyde, but the alkaline post-treatment gave the 1,3-diazolidine **8**.

On the other hand, diphenylketene-*N*-*p*-tolylimine (**1e**) gave no 1:1 adduct, but the oxindole **9**,[7] benzaldimine **5**, and benzaldehyde were obtained. Benzaldehyde was presumably formed from **5** by hydrolysis. The oxindole **9** was identical with an authentic sample.[8] Hydrolysis of **9** with perchloric acid gave the oxindole **10**.[9]