Anal. Calcd for $C_{14}H_{16}N_6OS$: C, 55.79; H, 5.05; N, 23.24. Found: C, 55.84; H, 5.04; N, 23.20.

Registry No.—**3**, 30855-40-4; **3** HCl, 30855-41-5; **4** HCl, 30855-42-6; **5**, 30855-43-7; **8**, 30855-44-8; **9**, 30855-45-9; **11**, 30855-46-0; **12**, 30855-47-1; **13**, 30855-48-2; **14**, 30855-49-3; **15**, 30936-92-6; **16**, 30855-50-6; **17**, 30855-51-7; **18**, 30855-52-8; **19**, 30855-53-9; **20**, 30855-54-0; **20** (R_1 = CH_2Br), 30855-55-1; **21**, 30855-56-2; **22**, 30855-57-3; **25**, 30855-58-4; **26**, 30855-59-5; **28**, 30855-60-8; **29**, 30855-61-9; **30**, 30855-62-0.

Acknowledgments.—The authors are indebted to Dr. W. C. Coburn, Jr., and members of the Molecular Spectroscopy Section of Southern Research Institute, who performed most of the microanalytical and spectral determinations reported.

The Facile Isomerization in the 1,3-Dipolar Addition Reactions of Substituted 1-Alkoxycarbonyliminopyridinium Ylides with Dimethyl Acetylenedicarboxylate[1]

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The 1,3-dipolar cycloaddition of substituted 1-alkoxycarbonyliminopyridinium ylides (**1**, **2**, **6**, **7**, **10–14**, and **32–34**) with dimethyl acetylenedicarboxylate in the absence and the presence of tetracyanoethylene produced pyrazolo[1,5-*a*]pyridines (**3–5**, **8**, **9**, and **39**), dihydropyrazolo[1,5-*a*]pyridines (**15–19**), vinylpyridines (**20–24** **35–37**), and cycloadducts (**25**, **26**, and **29–31**). The dihydro compounds **22** and **23** were easily transformed into the vinylpyridines **41** and **42**. Structural elucidation of the cycloadducts and the rearranged products was accomplished by spectral means, while the structures of **45** and **46** were established by chemical degradation. Some mechanisms for the rearranged products are also discussed.

Although 1,3-dipolar cycloaddition reactions of zwitterionic ylides have been extensively studied,[2] the addition of 1-alkoxycarbonyliminopyridinium ylides (pyridinium *N*-betaines) to dipolarophiles have not yet been reported. Okamoto, *et al.*,[3] observed that *N*-iminopyridinium ylides reacted with nucleophilic reagents, but the reactions of *N*-methylimino- and *N*-acetyliminopyridinium ylides with a dipolarophile such as acetonitrile did not afford 1,3-dipolar cycloadducts; the contrasting reactivity of these compounds was attributed to the difference in basicity. The mechanism of 1,3-dipolar cycloaddition reactions of the heteroaromatic nitrogen ylides with dipolarophiles has been discussed,[3] but information concerning the detailed mechanisms and, in particular, convincing evidence for dihydro-type intermediates have not been presented. In continuation of work in this area,[4] this paper deals with the 1,3-dipolar cycloaddition of substituted 1-alkoxycarbonyliminopyridinium ylides with dimethyl acetylenedicarboxylate (DAC) in the presence and the absence of tetracyanoethylene (TCNE).

Results and Discussion

Several ring-substituted 1-alkoxycarbonyliminopyridinium ylides **1**, **2**, **6**, **10–14**, and **32–34** were prepared by the modified Gösl method.[4] The ylide **7**[5] was obtained by the modified Hafner method described by Snieckus, *et al.*, and the yield was increased to 40%.

1,3-Dipolar Cycloaddition of Substituted Pyridinium Ylides with DAC.—The 1,3-dipolar cycloaddition reactions of the 1-alkoxycarbonyliminopyridinium ylides with dimethyl acetylenedicarboxylate (DAC) were carried out both in the absence and the presence of tetracyanoethylene (TCNE) in benzene or acetonitrile. These results are summarized in Tables I and II.

TABLE I

1,3-DIPOLAR CYCLOADDITION OF THE YLIDES AND DAC IN THE ABSENCE OF TCNE

	Yields of reaction products[a]					
	Dihydropyrazolopyridine derivatives		Vinylpyridine derivatives		Pyrazolopyridine derivatives	
Ylide	Yield, %	Compd no.	Yield, %	Compd no.	Yield, %	Compd no.
1					*Ca.* 1	3
2					Trace	4 + 5
6					27	8
7					28	9
10	12	15	22	20		
11	11	16	24	21		
12	80	17	3	22		
13	68	18	17	23		
14	56	19	44	24		
32			43	35		
33			27	36		
34			5	37		

[a] C, H, and N analyses within ±0.35% for all products: Ed.

The reactions of **1** and **2** with DAC in the presence of TCNE gave the pyrazolopyridine derivative **3**[2] and an isomeric mixture of **4** and **5** (on the basis of the nmr inspection), respectively, in very low yields. In the reactions in the absence of TCNE, the pyrazolopyridine derivatives were formed in only trace amounts. On similar treatment of γ-substituted pyridinium ylides

(1) Part LI: Studies of Heteroaromaticity. For part L of this series, see T. Sasaki, T. Yoshioka, and Y. Suzuki, *J. Syn. Org. Chem. Jap.*, **28**, 1054 (1970).

(2) For leading references, see (a) R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, Chapter 11, p 739; (b) V. Boekelheide and N. A. Fedoruk, *J. Org. Chem.*, **33**, 2062 (1968).

(3) T. Okamoto, M. Hirobe, Y. Tamai, and E. Yabe, *Chem. Pharm. Bull.*, **14**, 506 (1966).

(4) (a) T. Sasaki, K. Kanematsu, and Y. Yukimoto, *J. Chem. Soc. C*, 481 (1970); (b) T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, **35**, 426 (1970).

(5) This ylide could not be synthesized by the Gösl method. Although 4-ethoxycarbonyl-1-ethoxycarbonyliminopyridinium ylide was prepared by the Hafner method, the yield was reported as only 1%; see A. Balasubramanian, J. M. McItosh, and V. Snieckus, *ibid.*, **35**, 433 (1970).

TABLE II

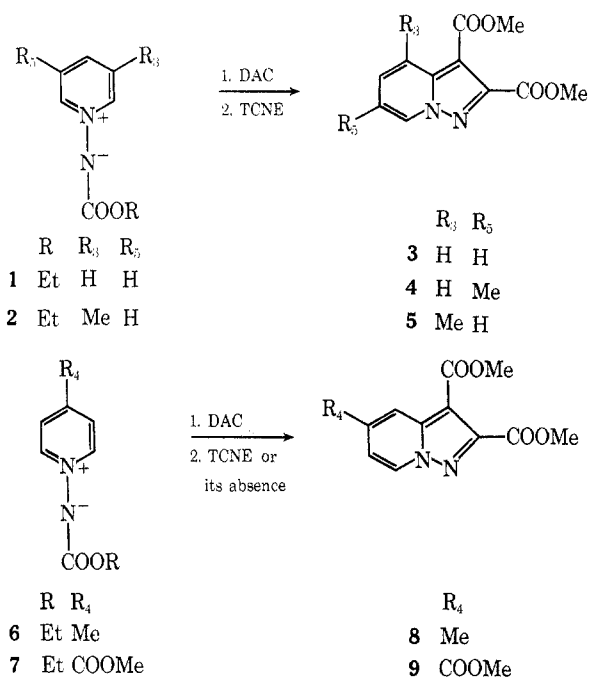
1,3-DIPOLAR CYCLOADDITION OF THE YLIDES AND DAC IN THE PRESENCE OF TCNE

	Yields of reaction products[a]			
	Diels–Alder adduct		Pyrazolopyridine derivatives	
Ylide	Yield, %	Compd no.	Yield, %	Compd no.
1	0		5	3
2	0		1	4 + 5
6	0		44	8
7			45	9
10	12	25	40	28
11	15	26	51	28
12	75	29		
13	62	30		
14	67	31		
32	0		0	(38)
33	0		46	39
34	0		0	(40)

[a] C, H, and N analyses within ±0.35% for all products: Ed.

6 and 7 with DAC in the presence or the absence of TCNE, the products were characterized by nmr spectral data as the corresponding pyrazolopyridine derivatives 8 and 9, the normal products as suggested by Huisgen and others,[2] as shown in Scheme I. The structures of 3–5, 8, and 9 were elucidated by the unequivocal independent synthesis (see Experimental Section). These nmr data are shown in Table III. The formation of these pyrazolopyridines involves aromatization of the initial unstable adducts with loss of the ethoxycarbonyl group and hydrogen. TCNE has been found to function as a dehydrogenating agent in analogous reactions,[6] although in the present case a less common elimination by loss of alkyl formate is observed.[7]

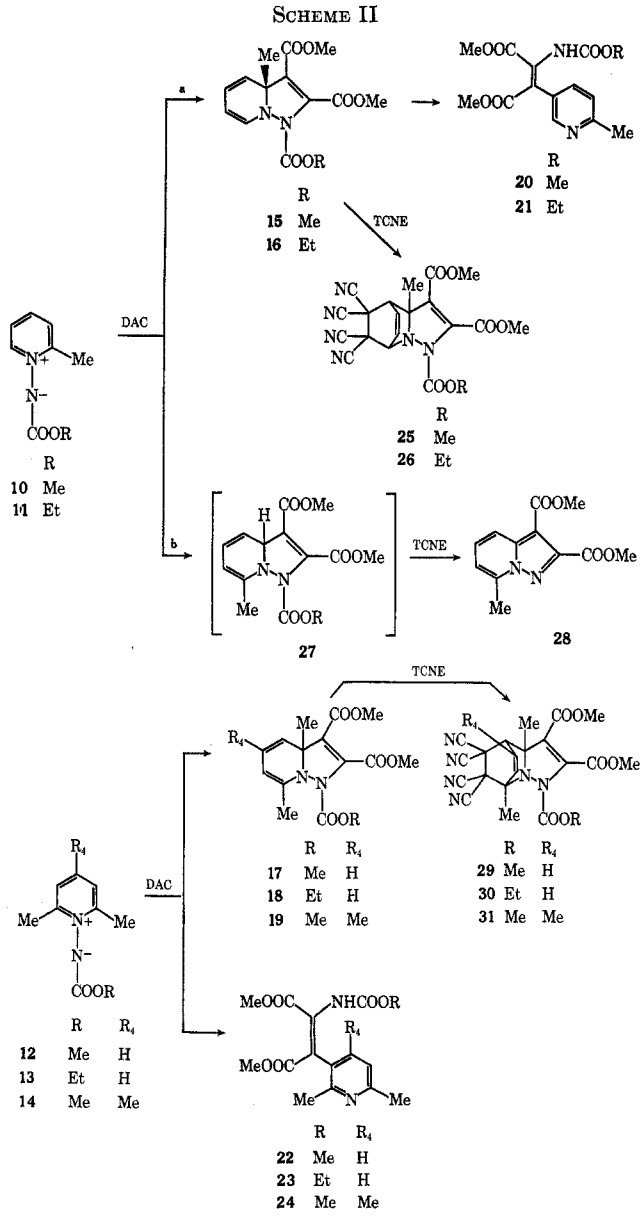
SCHEME I



1 Et H H
2 Et Me H
3 H H
4 H Me
5 Me H
6 Et Me
7 Et COOMe
8 Me
9 COOMe

On the other hand, the reactions of the ylides 10–14 and DAC proceeded rapidly even at room temperature, as detected by immediate disappearance of the deep color of the solution, to give the relatively unstable 1:1 adducts 15–19, together with the corresponding stable products 20–24, respectively. Since the ethoxycarbonyl ylides are colorless, the deep color is probably associated with a charge-transfer complex of DAC plus ylide. This point should be noted, because the N-unsubstituted imine itself is blue.[2b] Intractable tarry material always accompanied these products. When the former oily, unstable products were allowed to stand at room temperature, they were easily transformed after 3 days into the latter crystalline stable products. The unstable 1:1 adducts 15 and 16 reacted readily with TCNE in benzene even at room temperature to give the crystalline Diels–Alder adducts 25 and 26, respectively, in *ca.* 70% yields. When an equimolar amount of TCNE was added to the reaction solution of the ylides 10 and 11 with DAC after disappearance of the deep blue color, compound 28, together with the corresponding cycloadducts 25 and 26, was isolated alternatively. In the reactions of 12, 13, and 14 with DAC in the presence of TCNE, the cycloadducts 29, 30, and 31 were obtained in 62–75% yields, but pyrazolopyridine derivatives could not be detected. These results are summarized in Scheme II.

SCHEME II



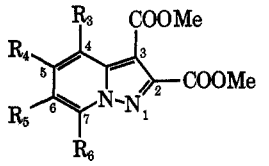
10 Me
11 Et
15 Me
16 Et
20 Me
21 Et
25 Me
26 Et
27
28
12 Me H
13 Et H
14 Me Me
17 Me H
18 Et H
19 Me Me
29 Me H
30 Et H
31 Me Me
22 Me H
23 Et H
24 Me Me

(6) V. Boekelheide and N. A. Fedoruk, *J. Amer. Chem. Soc.*, **90**, 3830 (1968).

(7) T. Sasaki, K. Kanematsu, Y. Yukimoto, and S. Ochiai, *J. Org. Chem.*, **36**, 813 (1971).

TABLE III

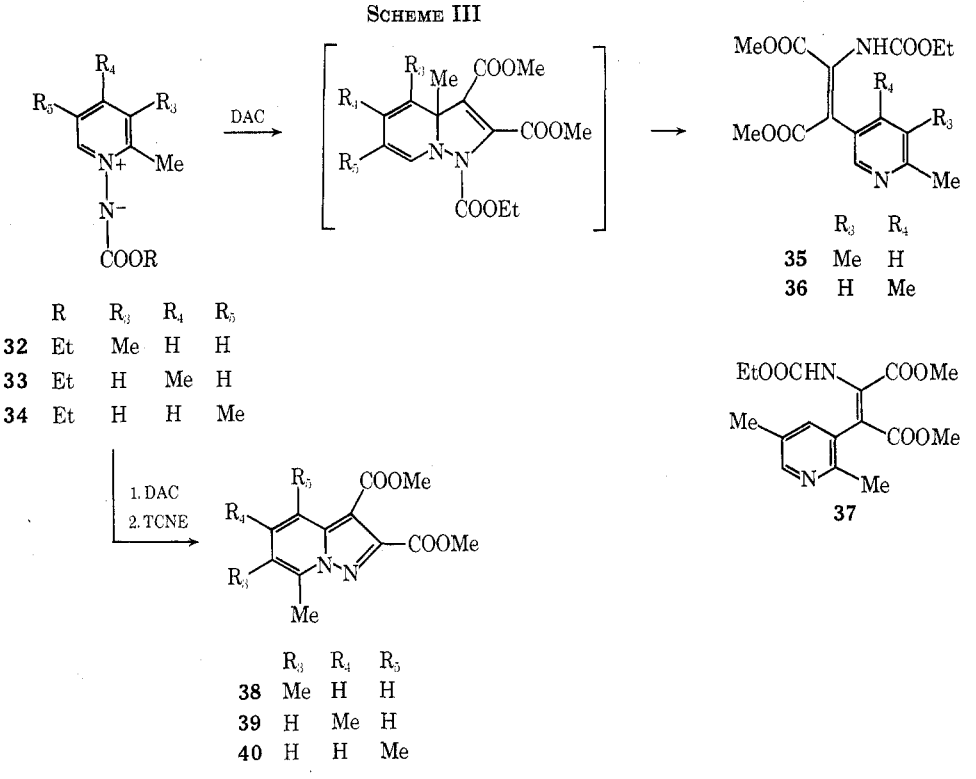
NMR DATA OF PYRAZOLO[1,5-*a*]PYRIDINE DERIVATIVES[a]



Compd no.	Ring protons and ring methyl protons				Coupling constant, Hz
	R_3	R_4	R_5	R_6	
3	1.82 (dd, 1 H)	2.55 (br t, 1 H)	2.97 (dt, 1 H)	1.44 (dd, 1 H)	$J_{4,5} = 9.0$, $J_{5,6} = 7.0$, $J_{6,7} = 7.0$
4	1.93 (d, 1 H)	2.70 (dd, 1 H)	7.63 (s, 3 H)	1.67 (br s, 1 H)	$J_{4,5} = 9.0$, $J_{5,7} = 1.5$
5	7.43 (s, 1 H)	2.96 (br d, 1 H)	3.19 (t, 1 H)	1.62 (dd, 1 H)	$J_{5,6} = 7.0$, $J_{5,7} = 1.0$, $J_{6,7} = 7.0$
8	2.15 (br s, 1 H)	7.55 (s, 3 H)	3.17 (br d, 1 H)	1.66 (d, 1 H)	$J_{4,5} = 1.5$, $J_{6,7} = 7.0$
9	1.17 (br s, 1 H)	6.02 (s, 3 H)	2.43 (dd, 1 H)	1.45 (dd, 1 H)	$J_{4,6} = 2.0$, $J_{6,7} = 7.5$
28	1.97 (br d, 1 H)	2.67 (q, 1 H)	3.17 (br d, 1 H)	7.24 (s, 3 H)	$J_{4,5} = 9.0$, $J_{5,6} = 7.0$
39	2.20 (br s, 1 H)	7.57 (s, 3 H)	3.33 (br s, 1 H)	7.27 (s, 3 H)	

[a] The methyl protons of 2,3-dimethoxycarbonyl groups appear at τ 5.97–6.14 as each singlet.

SCHEME III



	R	R_3	R_4	R_5
32	Et	Me	H	H
33	Et	H	Me	H
34	Et	H	H	Me

	R_3	R_4
35	Me	H
36	H	Me

37

	R_3	R_4	R_5
38	Me	H	H
39	H	Me	H
40	H	H	Me

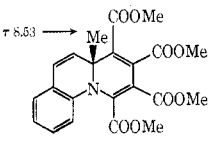
In the similar reactions of **32**, **33**, and **34**, with DAC, only the corresponding stable products **35** (43%), **36** (27%), and **37** (5%) were produced, respectively, suggesting the intermediacy of the dihydropyrazolopyridine derivatives which rapidly rearranged into the stable compounds. However, in the presence of TCNE, only **39** was obtained in 46% yield together with considerable amounts of intractable tarry compounds, and neither Diels–Alder adducts nor pyrazolopyridine derivatives such as **38** and **40** could be detected. These are summarized in Scheme III.

Structural Elucidation of 1,3-Dipolar Cycloadducts.— Structural elucidation of 1,3-dipolar cycloadducts **15–19** was accomplished by their nmr spectral analysis. The spectral patterns of these products are grossly similar to each other, as shown in Table IV.

The spectrum of **17** exhibits signals at τ 4.21, 4.53, and 5.08 with relative intensities of 1:1:1 attributable to the ring protons and at τ 6.10, 6.15, 6.24, 8.13, and 8.54 with relative intensities of each three protons. In particular, a singlet at τ 8.54 clearly arises from a methyl group at C-3a, since methyl protons attached to a fully substituted carbon atom should appear further upfield, as given in a literature.[8]

For further structural elucidation, the spectral data of the TCNE adducts **25**, **26**, and **29–31** were analyzed; spectral assignments were derived by comparison with those of ethoxycarbonylazepine–,[9] ethoxycarbonyldi-

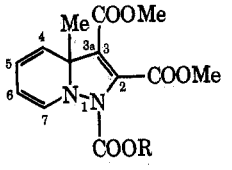
(8) A. Crabtree, L. M. Jackman, and A. W. Johnson, *J. Chem. Soc.*, 4417 (1962); *for example*



(9) T. Sasaki, K. Kanematsu, and A. Kakehi, *Bull. Chem. Soc. Jap.*, **43**, 2893 (1970), and references cited therein.

TABLE IV

NMR DATA[a] OF COMPOUNDS 15–19[b]



Compd no.	Ring protons and ring methyl protons, τ (CCl_4)
15	3.97 (br d, 1 H, H_7, $J_{7,6}$ = 7.5 Hz), 4.35 (m, 2 H, H_4 and H_5), 5.10 (m, 1 H, H_6), 8.57 (s, 3 H, C_{3a}-CH_3)
16	3.86 (br d, 1 H, H_7, $J_{7,6}$ = 8.0 Hz), 4.31 (m, 2 H, H_4 and H_5), 4.98 (m, 1 H, H_6), 8.56 (s, 3 H, C_{3a}-CH_3)
17	4.21 (q, 1 H, H_5, $J_{5,4}$ = 10 Hz, $J_{5,6}$ = 5.0 Hz), 4.53 (br d, 1 H, $J_{4,5}$ 10 Hz), 5.08 (br d, 1 H, H_6, $J_{6,5}$ = 5.0 Hz), 8.13 (br s, 3 H, C_7-CH_3), 8.54 (s, 3 H, C_{3a}-CH_3)
18	4.26 (q, 1 H, H_5, $J_{5,4}$ = 10, $J_{5,6}$ = 5.0 Hz), 4.60 (br d, 1 H, $J_{5,4}$ = 10 Hz), 5.17 (br d, 1 H, H_6, $J_{6,5}$ = 5.0 Hz), 8.15 (br s, 3 H, C_6-CH_3), 8.57 (s, 3 H, C_{3a}-CH_3)
19	5.01 (br s, 1 H, H_4), 5.41 (br s, 1 H, H_6), 8.21 (s, 3 H, C_7-CH_3), 8.39 (d, 3 H, C_5-CH_3, J = 1.5 Hz), 8.65 (s, 3 H, C_{3a}-CH_3)

[a] Multiplicity is indicated as follows: s, singlet; d, doublet; dd, double doublet; m, multiplet; t, triplet; q, quartet; br, broad. [b] The methyl proton signals of the 2,3-dimethoxycarbonyl and 1-methoxycarbonyl groups appear at τ 6.10 ~ 6.36 as each singlet, and the proton signals of the 1-ethoxycarbonyl group at τ 5.75 (q, J = 7.0 Hz) and 8.70 (t, J = 7.0 Hz), respectively.

azepine–,[4b] and ethoxycarbonyl-2,3,-homoazepine–TCNE adducts.[10] Each adduct displayed characteristic ir bands for C=O (1700–1770 cm^{-1}), C≡N (2280 cm^{-1}), and C=C (1620–1650 cm^{-1}).

The nmr spectral patterns of the adducts are grossly similar as seen in Table V. From these data, the structures of the adducts were concluded to be normal $_{\pi}4_s + _{\pi}2_s$ cycloadducts, having 1-alkoxycarbonyl-2,3-dimethoxycarbonyl-3a-methyl-1,3a(1*H*)-dihydropyrazolo-[1,5-*a*]pyridine structures **25**, **26**, and **29–31**.

Structural Elucidation of the Rearranged Products by Spectra.—Structural elucidation of the rearranged products **20–24** and **35–37** was based on the spectra, since attempted hydrogenation and oxidation with ozone or potassium permanganate of the rearranged products were unsuccessful. The assignments of the methyl and ring proton signals could be correlated with those of the corresponding α-, β-, and γ-substituted pyridine derivatives;[11] the methyl protons appear at τ 7.44–7.57 (attached to C_2), 7.70–7.73 (to C_3), 7.85 (to C_4), and 7.65–7.68 (to C_6) as each singlet with relative intensity of three, respectively. The spectra of compounds **15–19** changed after 3 days standing at room temperature, and the methyl proton signals were shifted to lower field regions, arising from the protons attached to the pyridine skeleton. These spectral patterns are completely identical with those of compounds **20–24** and **35–37** (Table VI).

Interestingly, when the nmr of **17** was taken in carbon tetrachloride at 68 and 100°, the signals appeared at τ 2.73 (d, 1 H, J = 7.5 Hz) and 3.07 (d, 1 H, J = 7.5 Hz), indicating obviously the presence of the trisubstituted pyridine ring, and τ 3.50 (br s, 1 H, NH, exchanged by D_2O) and 7.55 and 7.75 as each singlet with relative intensities of 3:3 attributable to methyl protons attached to pyridine ring (*cf.* Figure 1). From the results, it was concluded that **17** rearranged to the vinylpyridine derivative **22**. In addition, heating of **22** and **23** without solvent at 120° in a sealed tube afforded **41** and **42**, respectively, in quantitative yields. The nmr spectra of **41** and **42** exhibit signals at τ −0.50 ~ −0.55 (br s, exchanged by D_2O) due to a hydrogen bonding amino group as shown in Figure 1, suggesting that the thermal cis–trans isomerization has occurred (Scheme IV).

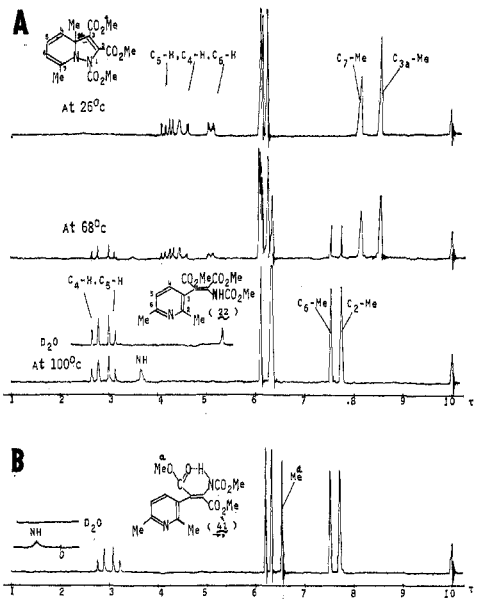
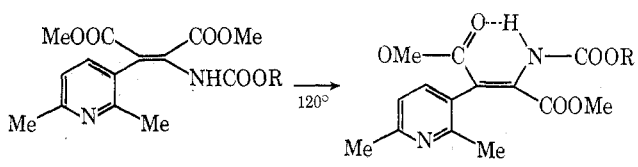


Figure 1.—A, observed nmr spectra of **17** in carbon tetrachloride at 26, 68, and 100°; B, nmr spectrum of isomerization product **41** in CCl_4.

SCHEME IV



	R		R
22	Me	**41**	Me
23	Et	**42**	Et

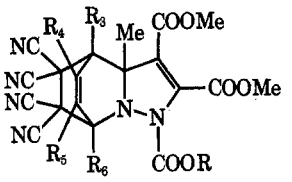
On the basis of the nmr assignments, it appears that the migration group attacked on the pyridine ring at the R_5 position to give **20–24**, **35**, and **36**, respectively, with the exception of **37**. Since the R_5 position in **37** is occupied with methyl group, the migration group (ethoxycarbonylethenyl diester group) is forced to attack at R_3 position, although the yield was quite low. The facts that the rearrangement products **20–24**, **35**, and **36** were obtained by the cycloaddition reactions of the ylides, whose α, α,α', α,β, and α,γ positions are occupied with methyl groups, with DAC would give more information of the reaction mechanism. Whereas, mechanistic speculation for the rearranged products also leads to consideration of the alternate pathway by either a concerted 1,4- or stepwise two 1,2-methyl migrations rather than that of the alkoxycarbonylethenyl diester group. With one exception, iden-

(10) T. Sasaki, K. Kanematsu, and A. Kakehi, *Chem. Commun.*, 1030 (1970).

(11) *Cf.* F. A. Bovey, "Nmr Data for Organic Compounds," Vol. 1, Interscience, New York, N. Y., 1967.

TABLE V

NMR DATA OF THE DIELS–ALDER ADDUCTS[a]

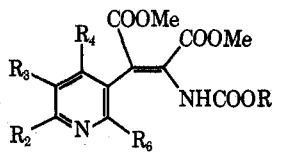


Adduct	Ring protons and ring methyl protons, τ (CDCl3)				
	R_3	R_4	R_5	R_6	Me
25	5.83 (m, 1 H)	3.23 (m, 2 H)		4.83 (m, 1 H)	8.52 (s, 3 H)
26	5.81 (m, 1 H)	3.21 (m, 2 H)		4.75 (m, 1 H)	8.52 (s, 3 H)
29	5.83 (dd, 1 H)	3.16 (q, 1 H, J = 8.0, J = 6.5)	3.46 (dd, 1 H, J = 8.0, J = 1.5)	7.89 (s, 3 H)	8.53 (s, 3 H)
30	5.82 (dd, 1 H, J = 6.5, J = 1.5)	3.16 (q, 1 H, J = 8.0, J = 6.5)	3.46 (dd, 1 H, J = 8.0, J = 1.5)	7.99 (s, 3 H)	8.53 (s, 3 H)
31	6.13 (1 H, overlapping with methyl protons of methoxycarbonyl group)	7.83 (d, 3 H, J = 1.5)	3.94 (br s, 1 H)	8.06 (s, 3 H)	8.56 (s, 3 H)

[a] Coupling constant J given in hertz.

TABLE VI

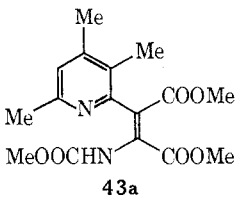
NMR DATA OF THE REARRANGEMENT PRODUCTS[a]



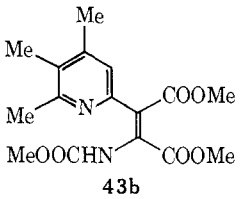
Compd no.	τ (CDCl3)					Coupling constant, Hz
	R_2	R_3	R_4	R_6	NH[b]	
20	7.50 (s, 3 H)	2.80 (br d, 1 H)	2.50 (dd, 1 H)	1.64 (d, 1 H)	2.73 (br s)	$J_{3,4}$ = 8.0 $J_{4,6}$ = 2.0
21	7.45 (s, 3 H)	2.83 (br d, 1 H)	2.54 (dd, 1 H)	1.66 (d, 1 H)	3.25 (br s)	$J_{3,4}$ = 7.5 $J_{4,6}$ = 2.0
22[c]	7.44 (s, 3 H)	2.93 (d, 1 H)	2.60 (d, 1 H)	7.65 (s, 3 H)	3.34 (br s)	$J_{3,4}$ = 7.5
23	7.47 (s, 3 H)	2.96 (d, 1 H)	2.63 (d, 1 H)	7.65 (s, 3 H)	3.50 (br s)	$J_{3,4}$ = 7.5
24	7.50 (s, 3 H)	3.05 (br s, 1 H)	7.85 (s, 3 H)	7.68 (s, 3 H)	3.50 (br s)	
35	7.55 (s, 3 H)	7.73 (s, 3 H)	2.75 (br s, 1 H)	1.84 (d, 1 H)	3.03 (br s)	$J_{4,6}$ = 2.0
36	7.57 (s, 3 H)	3.03 (br s, 1 H)	7.86 (s, 3 H)	1.94 (br s, 1 H)	3.20 (br s)	
37	1.66 (br s, 3 H)	7.70 (s, 3 H)	2.74 (br s, 1 H)	7.66 (s, 3 H)	3.70 (br s)	

[a] The methyl proton signals of the 2,3-dimethoxycarbonyl and 1-methoxycarbonyl groups appear at τ 6.03 ~ 6.35 as each singlet, and the protons of the 1-ethoxycarbonyl group at τ 5.79 ~ 5.90 (q, J = 7.0 Hz) and 8.79 ~ 8.80 (t, J = 7.0 Hz), respectively. [b] Disappeared by shaking with D_2O. [c] In CCl_4, the signals appear at τ 7.55 (s, 3 H), 3.07 (d, J = 7.5 Hz, 1 H), 2.73 (d, J = 7.5 Hz, 1 H), 7.75 (s, 3 H), and 3.50 (br s, NH).

tical mechanisms can be proposed for all other dihydropyrazolo[1,5-*a*]pyridine derivatives and the possible structures resulting from 1,4-methyl migration would have to be considered. The exception involves the transformation of **19** to **43a** or **43b**. In these cases, information available from the nmr spectra of these pyridines is limited to provide a proof of the structures.



43a



43b

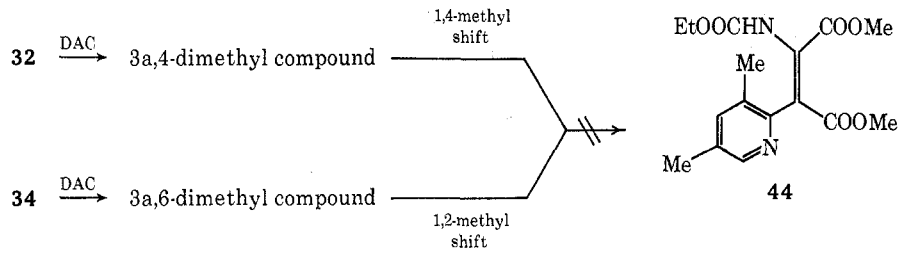
However, in the case of the reactions of **32** or **34** with DAC, the same rearrangement product **44** might be obtained *via* the 1,4- and 1,2-methyl migration process, but actually the rearranged products **35**, mp 144–146°, and **37**, mp 158–161°, were obtained, respectively, as shown in Scheme III. Therefore, **44** can be ruled out as a structural possibility as shown in Scheme V.

Structural Elucidation of the Rearranged Products by Chemical Degradation.—Final structural elucidation of these rearranged compounds was accomplished by chemical degradation.

The rearranged products **20–24** and **35–37** resisted ozonolysis because of the presence of the bulky tetrasubstituted olefinic moiety. Accordingly, we prepared the trisubstituted rearranged products **45** and **46**, which were synthesized by the reaction of **12** or **13** with ethyl propiolate followed by rearrangement (Scheme VI).

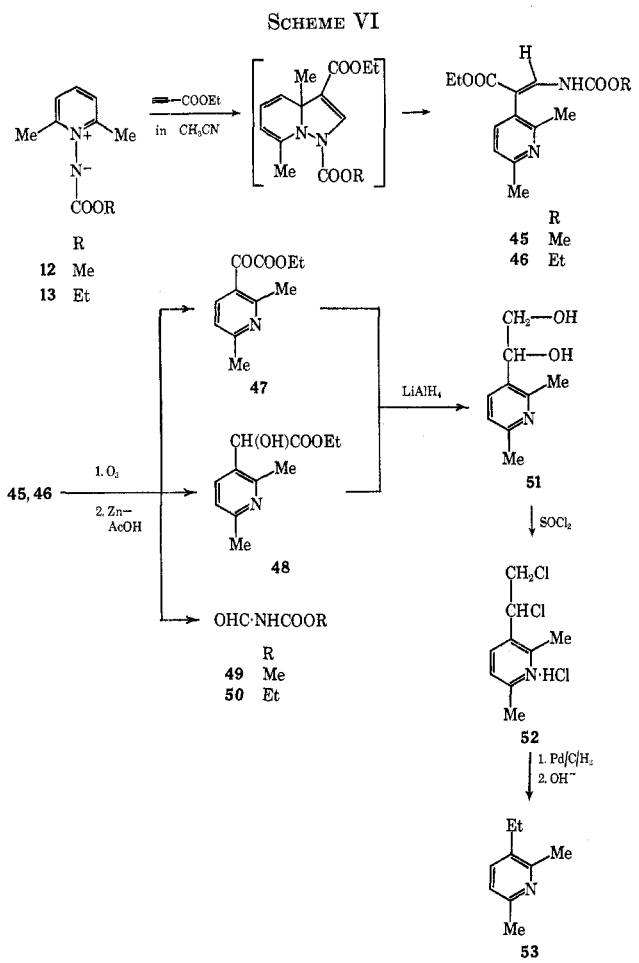
Ozonolysis of **45** or **46** followed by treatment of zinc in acetic acid gave three products, **47–49** (or **50**). Chromatography of the mixture over silica gel afforded an crystalline product **49** (or **50**) and oily products, **47** and **48**. These compounds were elucidated on the basis of the nmr spectral inspection. A mixture of compounds **47** and **48** was reduced by lithium aluminium hydride in tetrahydrofuran under refluxing condition to give a diol (**51**). Treatment of **51** with thionyl chloride followed by catalytic hydrogenation (10% Pd/C) gave **53**, which was found to be identical with the known

SCHEME V



2,6-dimethyl-3-ethylpyridine[12] by mixed glpc and by comparisons of their ir and nmr spectra (see Experimental Section).

SCHEME VI



Mechanisms for the Rearranged Products.—Considering the results, we proposed the reaction mechanisms for the rearranged products **20–24**, **35–37**, **45**, and **46**, as shown in Scheme VII. Thus, the relief of highly strained 3a-methyl-1,3a(1*H*)-dihydropyrazolopyridine ring systems, followed by the migration of the nucleophilic alkoxycarbonylethenyl diester group to give R_5-substituted pyridine derivatives, which involve the initial N–N bonding fission rather than the attack at the sterically hindered R_3 position, might be the driving force for the rearrangement in the facile isomerization of the 1,3-dipolar cycloadducts. In conclusion, when there is no 2 substitution in pyridine ring, the net result of reaction with DAC is dehydrogenation and the intermediate dihydro derivative cannot be isolated. On the other hand, when there is a 2 substituent, the intermediate can be isolated but undergoes facile rearrangement to a vinylpyridine derivative.

(12) T. Omae, H. Yamamoto, T. Motoda, and Y. Yoshie, *Kogyo Kagaku Zasshi*, **65**, 354 (1962).

Experimental Section[13]

4-Methoxycarbonyl-1-ethoxycarbonyliminopyridinium Ylide (7).—Ethyl azidoformate (3.2 g, 0.028 mol) and excess methyl isonicotinate (10 g) were placed in a sealed tube and heated in an oil bath at 90° for 12 hr. The reaction mixture was evaporated *in vacuo*, and the residue was recrystallized from benzene to give pale yellow crystals (2.5 g, 40%), mp 152–154°.

Anal. Calcd for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.39; N, 12.50. Found: C, 53.46; H, 5.30; N, 12.55.

1,3-Dipolar Cycloaddition Reactions of the Ylides with DAC. General Method.—To a benzene or acetonitrile solution of DAC an equimolar amount of the ylides was added under stirring at room temperature. After disappearance (about 5–30 min) of the deep color of the solution, the solvent was removed *in vacuo*, and the oily mixture was separated by column chromatography (silica gel) using chloroform as eluent. The yields of these products were summarized in Table I.

Reaction of 1 with DAC.—From 0.72 g of **1** and 0.62 g of DAC there was obtained **3** (*ca.* 1%) as pale yellow crystals: mp 70–72°; ν_{max}^{KBr} 1727, 1683, 1630 cm^{-1}; λ_{max}^{EtOH} 223 nm (ϵ 2.34 × 10^4), 300 (5.85 × 10^3); identical with a material prepared by the reaction of pyridinium *N*-imine (0.4 g, 4.3 mmol) and DAC (0.6 g).[14]

Reaction of 2 with DAC.—From 0.54 g (3 mmol) of **2** and 0.43 g of DAC there was obtained 6-methyl- and 4-methyl-2,3-dimethoxycarbonylpyrazolo[1,5-*a*]pyridines (**4** and **5**) as a mixture in only 0.5% yield. The mixture could not be separated by column chromatography.

Reaction of 6 with DAC.—From 0.54 g of **6** and 0.43 g of DAC there was obtained 5-methyl-2,3-dimethoxycarbonylpyrazolo-[1,5-*a*]pyridine (**8**) (0.20 g, 27%) as pale yellow crystals: mp 119–120°; ν_{max}^{KBr} 1742, 1702, 1640 cm^{-1}; λ_{max}^{EtOH} 224 nm (ϵ 3.11 × 10^4), 293 (8.06 × 10^3).

Reaction of 7 with DAC.—From 0.45 g (2 mmol) of **7** and 0.28 g of DAC there was obtained 2,3,5-trimethoxycarbonylpyrazolo-[1,5-*a*]pyridine (**9**) (0.16 g, 28%) as yellow crystals: mp 141–143°; ν_{max}^{KBr} 1724, 1700, 1638 cm^{-1}; λ_{max}^{EtOH} 232 nm (ϵ 2.32 × 10^4), 329 (5.29 × 10^3).

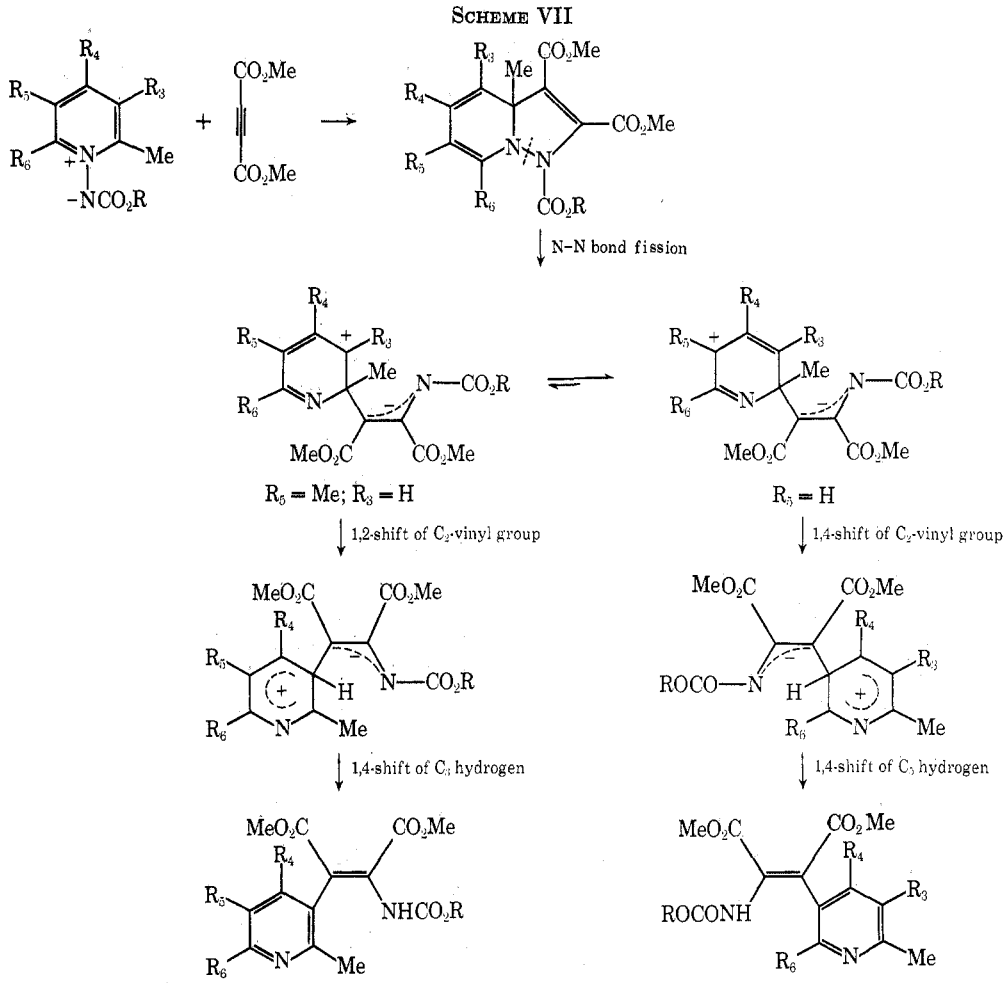
Reaction of 10 with DAC.—From 0.5 g (3 mmol) of **10** and 0.43 g (3 mmol) of DAC there was obtained 1,2,3-trimethoxycarbonyl-3a-methyl-1,3a-dihydropyrazolo[1,5-*a*]pyridine (**15**) (0.11 g, 12%) as a pale yellow oil (ν_{max}^{neat} 1745, 1713, 1631, 1589 cm^{-1}), and 2-methyl-5-(*cis*-1,2-dimethoxycarbonyl-2-methoxycarbonyl-aminoethenylpyridine (**20**) (0.20 g, 22%) as colorless crystals [mp 144–146°; ν_{max}^{KBr} 1740, 1708, 1610, 1600 cm^{-1}; λ_{max}^{EtOH} 275 nm (ϵ 1.9 × 10^4)].

Reaction of 11 with DAC.—From 0.54 g (3 mmol) of **11** and 0.43 g (3 mmol) of DAC there was obtained 1-ethoxycarbonyl-2,3-dimethoxycarbonyl-3a-methyldihydropyrazolo[1,5-*a*]pyridine

(13) The 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 Laboratory Co., Ltd., Model C-60-XL, nmr spectrometer and with a Varian A-60 recording spectrometer with tetramethylsilane as an internal standard. The chemical shifts are expressed in τ values. The ir spectra were taken with a JASCO Model IR-S spectrophotometer.

(14) 2,3-Dimethoxycarbonylpyrazolo[1,5-*a*]pyridine **3** was obtained in 22% yield by the reaction of *N*-iminopyridinium ylides and DAC but without detail: R. Huisgen, R. Grashey, and R. Krischke, *Tetrahedron Lett.*, 387 (1962).

SCHEME VII



(16) (0.11 g, 11%) as a pale yellow oil (ν_{max}^{neat} 1755, 1711, 1634, 1592 cm^{-1}), and 2-methyl-5-(*cis*-1,2-dimethoxycarbonyl-2-ethoxycarbonylamino)ethenylpyridine (21) (0.23 g, 24%) as colorless crystals [mp 134–136°; ν_{max}^{KBr} 1732, 1703, 1613, 1600 cm^{-1}; λ_{max}^{EtOH} 275 nm (ϵ 1.14 × 10^4)].

Reaction of 12 with DAC.—From 0.54 g of 12 and 0.43 g of DAC there was obtained 1,2,3-trimethoxycarbonyl-3a,7-dimethyl-1,3a-dihydropyrazolo[1,5-*a*]pyridine (17) (0.78 g, 80%) as a pale yellow oil (ν_{max}^{neat} 1744, 1718, 1659, 1639, 1608 cm^{-1}), and 2,6-dimethyl-3-(*cis*-1,2-dimethoxycarbonyl-2-methoxycarbonylamino)ethenylpyridine (22) (0.03 g, 3%) as colorless crystals [mp mp 185–188°; ν_{max}^{KBr} 1743, 1708, 1618, 1597 cm^{-1}; λ_{max}^{EtOH} 269 nm (ϵ 1.53 × 10^4)]. However, when 17 was allowed to stand at room temperature, 22 was obtained after 3 days in quantitative yield.

Reaction of 13 with DAC.—From 0.58 g of 13 and 0.43 g of DAC there was obtained 1-ethoxycarbonyl-2,3-dimethoxycarbonyl-3a,7-dimethyl-1,3a-dihydropyrazolo[1,5-*a*]pyridine (18) (0.69 g, 68%) as a pale yellow oil (ν_{max}^{neat} 1760, 1710, 1669, 1640, 1607 cm^{-1}) and 2,6-dimethyl-3-(*cis*-1,2-dimethoxycarbonyl-2-ethoxycarbonylamino)ethylpyridine (23) (0.17 g, 17%) as pale yellow crystals [mp 152–154°; ν_{max}^{KBr} 1735, 1710, 1614, 1595 cm^{-1}; λ_{max}^{EtOH} 270 nm (ϵ 1.74 × 10^4)].

Reaction of 14 with DAC.—From 0.39 g (2 mmol) of 14 and 0.28 g of DAC there was obtained 1,2,3-trimethoxycarbonyl-3a,5,7-trimethyl-1,3a-dihydropyrazolo[1,5-*a*]pyridine (19) (0.38 g, 56%) as a pale yellow oil (ν_{max}^{neat} 1750, 1720, 1675, 1640, 1620 cm^{-1}) and 2,4,6-trimethyl-3-(*cis*-1,2-dimethoxycarbonyl-2-methoxycarbonylamino)ethenylpyridine (24) (0.29 g, 44%) as colorless crystals [mp 145–146°; ν_{max}^{KBr} 1750, 1720, 1620, 1600 cm^{-1}; λ_{max}^{EtOH} 268 nm (ϵ 7.64 × 10^3)].

Reaction of 32 with DAC.—From 0.58 g (3 mmol) of 32 and 0.43 g of DAC there was obtained 2,3-dimethyl-5-(*cis*-1,2-dimethoxycarbonyl-2-ethoxycarbonylamino)ethenylpyridine (35) (0.44 g, 43%) as colorless crystals [mp 144–146°; ν_{max}^{KBr} 1733, 1703, 1608 cm^{-1}; λ_{max}^{EtOH} 277 nm (ϵ 9.60 × 10^3)].

Reaction of 33 with DAC.—From 0.58 g of 33 and 0.43 g of DAC there was obtained 2,4-dimethyl-5-(*cis*-1,2-dimethoxycarbonyl-2-ethoxycarbonylamino)ethenylpyridine (36) (0.28 g, 27%) as colorless crystals: mp 144–146°; ν_{max}^{KBr} 1735, 1715, 1700, 1610 cm^{-1}; λ_{max}^{EtOH} 272 nm (ϵ 1.39 × 10^4).

Reaction of 34 with DAC.—From 0.58 g of 34 and 0.43 g of DAC there was obtained 2,5-dimethyl-3-(*cis*-1,2-dimethoxycarbonyl-2-ethoxycarbonylamino)ethenylpyridine (37) (0.05 g, 5%) as colorless crystals: mp 158–161°; ν_{max}^{KBr} 1732, 1704, 1614 cm^{-1}; λ_{max}^{ExOH} 270 nm (ϵ 1.40 × 10^4). The reaction was carried out under the refluxing temperature conditions.

Thermal Cis–Trans Isomerization Reactions of the Vinylpyridine Derivatives.—Heating of 22 and 23 (each 50 mg) without solvent at 120° in a sealed tube for 10 hr afforded 41 and 42, respectively, in quantitative yields.

2,6-Dimethyl-3-(*trans*-1,2-dimethoxycarbonyl-2-methoxycarbonylamino)ethenylpyridine (41): mp 93–95°; pale yellow prisms; λ_{max}^{MeOH} 269 nm (ϵ 1.60 × 10^4); ν_{max}^{KBr} 3260, 1735, 1677, 1615, 1603 cm^{-1}; τ (CCl_4) −0.50 (br s, 1 H), 2.83 (d, 1 H, J = 7.5 Hz); 3.16 (d, 1 H, J = 7.5 Hz), 6.20 (s, 3 H, $NCOOCH_3$), 6.33 (s, 3 H, $COOH_3$), 6.54 (s, 3 H, $COOCH_3$), 7.51 (s, 3 H, CH_3), 7.70 (s, 3 H, CH_3).

Anal. Calcd for $C_{15}H_{18}N_2O_6$: 55.89; H, 5.63; N, 8.69. Found: C, 56.04; H, 5.71; N, 8.47.

2,6-Dimethyl-3-(*trans*-1,2-dimethoxycarbonyl-2-ethoxycarbonylamino)ethenylpyridine (42): mp 110–112°; ν_{max}^{KBr} 3260, 1735, 1677, 1616, 1598 cm^{-1}; λ_{max}^{MeOH} 271 nm (ϵ 2.05 × 10^4); τ (CCl_4) −0.55 (br s, NH), 2.79 (d, 1 H, J = 7.5 Hz), 3.14 (d, 1 H, J = 7.5 Hz), 5.76 (q, 2 H, $NCOOCH_2$), 6.31 (s, 3 H, CH_3), 6.54 (s, 3 H, CH_3), 7.51 (s, 3 H, CH_3), 7.68 (s, 3 H, CH_3), 8.66 (t, 3 H, $NCOOCH_2CH_3$, J = 7.0 Hz).

Anal. Calcd for $C_{16}H_{20}N_2O_6$: C, 57.13; H, 5.99; N, 8.33. Found: C, 57.09; H, 6.01; N, 8.40.

1,3-Dipolar Cycloaddition Reactions of the Ylides and DAC in the Presence of TCNE. General Method.—To a dry benzene or acetonitrile solution of DAC and the ylides an equimolar amount of TCNE was added under stirring at room temperature, and then the reaction solution turned a black color. After the precipitated tarry substance was decanted, the solvent was removed *in vacuo*, and the residue was purified by column chromatography

(silica gel) using chloroform as eluent. The pyrazolo[1,5-*a*]-pyridine derivatives were eluted from the first fraction and the recrystallized from chloroform–*n*-hexane or carbon tetrachloride–*n*-hexane. These data are summarized in Table II.

Reaction of 1 and DAC in the Presence of TCNE.—From 0.17 g (1 mmol) of **1**, 0.14 g of DAC, and 0.13 g of TCNE there was obtained 2,3-dimethoxycarbonylpyrazolo[1,5-*a*]pyridine (**3**) (0.01 g, 5%), identical in all respects with that formed from the reaction of pyridinium *N*-imine and DAC.[13]

Reaction of 6 and DAC in the Presence of TCNE.—From 0.18 g of **6** and each equimolar of DAC and TCNE there was obtained 2,3-dimethoxycarbonyl-5-methylpyrazolo[1,5-*a*]pyridine (**8**) (0.1 g, 44%) as pale yellow crystals, mp 119–120°.

Reaction of 7 and DAC in the Presence of TCNE.—From 0.22 g of **7** and each equimolar amount of DAC and TCNE there was obtained 2,3,5-trimethoxycarbonylpyrazolo[1,5-*a*]pyridine (**9**) (0.13 g, 45%) as pale yellow crystals, mp 141–143°.

Reaction of 10 and DAC in the Presence of TCNE.—From 0.17 g of **10** and each equimolar amount of TCNE there was obtained 2,3-dimethoxycarbonyl-7-methylpyrazolo[1,5-*a*]pyridine (**28**) (0.09 g, 40%) as pale yellow crystals: mp 99–100°; ν_{max}^{KBr} 1738, 1693, 1640 cm^{-1}; λ_{max}^{EtOH} 222 nm (ϵ 2.78 × 10^4), 300 (9.47 × 10^3), and **25** (0.05 g, 12%) as a colorless crystals, mp 170° dec.

Reaction of 11 and DAC in the Presence of TCNE.—From 0.18 g of **11** and each equimolar amount of DAC and TCNE there was obtained **28** (0.13 g, 51%) as pale yellow crystals, mp 99–100°, and **26** (0.13 g, 15%) as colorless crystals, mp 170° dec.

Reaction of 33 and DAC in the Presence of TCNE.—From 0.19 g of **33** and each equimolar amount of DAC and TCNE there was obtained 2,3-dimethoxycarbonyl-5,7-dimethylpyrazolo-[1,5-*a*]pyridine (**39**) (0.12 g, 46%) as pale yellow crystals: mp 124–126°; ν_{max}^{KBr} 1740, 1700, 1641 cm^{-1}; λ_{max}^{EtOH} 223 nm (ϵ 3.34 × 10^4), 297 (1.16 × 10^4).

Preparation of the Adducts 25 and 26. Method A.—The reactions of dihydropyrazolopyridine derivatives and TCNE were carried out in dry benzene under stirring at room temperature. Then the cycloadducts were precipitated and filtered. The crude adducts were recrystallized from chloroform–*n*-hexane to give colorless crystals.

Reaction of 15 with TCNE.—From 0.11 g (0.36 mmol) of **15** and 0.05 g of TCNE there was obtained cycloadducts **25** (0.11 g, 71%) as colorless crystals: mp 170° dec; ν_{max}^{KBr} 2280, 1743, 1697, 1630 cm^{-1}; λ_{max}^{EtOH} 312 nm (ϵ 6.67 × 10^3).

Reaction of 16 with TCNE.—From 0.09 g (0.28 mmol) of **16** and 0.04 g of TCNE there was obtained **26** (0.09 g, 68%) as colorless crystals: mp 170° dec; ν_{max}^{KBr} 2280, 1755, 1730, 1710, 1627 cm^{-1}; λ_{max}^{EtOH} 312 nm (ϵ 7.61 × 10^3).

Preparation of the Adducts 29–31. Method B.—In benzene solution of the ylides **12**, **13**, and **14** with DAC, an equimolar amount of TCNE was added under stirring at room temperature. Then the precipitated cycloadducts were filtered and recrystallized from benzene.

Reaction of 12 and DAC in the Presence of TCNE.—From 0.18 g (1 mmol) of **12**, DAC (0.14 g), and TCNE (0.13 g) there was obtained **29** (0.34 g, 75%) as colorless crystals: mp 150° dec; ν_{max}^{KBr} 2280, 1770, 1746, 1713, 1630 cm^{-1}.

Reaction of 13 and DAC in the Presence of TCNE.—From 0.19 g (1 mmol) of **13** and equimolar amounts of DAC and TCNE there was obtained **30** (0.29 g, 62%) as colorless crystals: mp 150° dec; ν_{max}^{KBr} 2280, 1770, 1750, 1703, 1629 cm^{-1}.

Reaction of 14 and DAC in the Presence of TCNE.—From 0.19 g (1 mmol) of **14** and equimolar amounts DAC and TCNE there was obtained **31** (0.31 g, 67%) as colorless crystals: mp 150° dec; ν_{max}^{KBr} 2280, 1768, 1737, 1705, 1643, 1632 cm^{-1}.

Reaction of 12 with Ethyl Propiolate.—From 0.54 g of **12** and 0.40 g of ethyl propiolate there was obtained 2,6-dimethyl-3-(1-ethoxycarbonyl-2-methoxycarbonylamino)ethenylpyridine (**45**) (0.48 g, 58%), as colorless crystals: mp 174–177°; ν_{max}^{KBr} 1729, 1700, 1632, 1595 cm^{-1}; λ_{max}^{EtOH} 263 nm (ϵ 1.64 × 10^4); τ ($CDCl_3$) 1.92 (d, 1 H, J = 13.0 Hz, vinyl proton), 2.70 (d, 1 H, J = 7.5 Hz, ring proton), 3.03 (d, 1 H, J = 7.5 Hz, ring proton), 3.15 (br d, 1 H, J = 13 Hz, NH), 5.81 (q, 2 H, J = 7.0 Hz, OCH_2), 6.25 (s, 3 H, OCH_3), 7.51 (s, 3 H, CH_3), 7.65 (s, 3 H, CH_3), 8.76 (s, 3 H, J = 7.0 Hz, CH_2CH_3).

Anal. Calcd for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.30; H, 5.55; N, 9.86.

Reaction of 13 with Ethyl Propiolate.—From 0.58 g of **13** and 0.40 g of ethyl propiolate there was obtained 2,6-dimethyl-3-(1-ethoxycarbonyl-2-ethoxycarbonylamino)ethenylpyridine (**46**) (0.39 g, 45%), as colorless crystals: mp 137–139°; ν_{max}^{KBr} 1726, 1690, 1645, 1602 cm^{-1}; λ_{max}^{EtOH} 263 nm (ϵ 1.75 × 10^4); τ ($CDCl_3$) 1.92 (d, 1 H, J = 13.0 Hz, vinyl proton), 2.74 (d, 1 H, J = 7.5 Hz, ring proton), 3.04 (d, 1 H, J = 7.5 Hz, ring proton), 3.27 (br d, 1 H, J = 13.0 Hz, NH), 5.82 (q, 4 H, J = 7.0 Hz, $2OCH_2$), 7.51 (s, 3 H, CH_3), 7.65 (s, 3 H, CH_3), 8.75 (t, 6 H, J = 7.0 Hz, $2CH_2CH_3$).

Anal. Calcd for $C_{15}H_{20}N_2O_4$: C, 61.63; H, 6.96; N, 9.58. Found: C, 61.68; H, 6.87; N, 9.51.

Ozonolysis of 45 and 46. 1.—A solution of 0.2 g of **45** in 30 ml of methylene chloride was treated with ozone at a rate of 40 l./hr, at 0° for 3 hr. After flushing with dry oxygen, the reaction mixture was evaporated to dryness under reduced pressure. The oily residue was poured into 20 ml of acetic acid, suspended with 1 g of zinc powder. After the solution was kept at room temperature overnight, the reaction mixture was filtered to remove syrupy zinc powder. This filtrate was evaporated to dryness *in vacuo*. The residue was purified by column chromatography (silica gel) using benzene as eluent to give **47** (colorless oil, n^{19}D 1.5174), **48** (colorless oil, n^{20}D 1.5255), and **49** (colorless crystals, mp 88–89°, 40–60 mg).

47: ν^{neat} 1729, 1684, 1590, 1567 cm^{-1}; τ ($CDCl_3$) 2.11 (d, 1 H, J = 8.0 Hz, ring proton), 2.91 (d, 1 H, J = 8.0 Hz, ring proton), 5.62 (q, 2 H, J = 7.0 Hz, OCH_2), 7.25 (s, 3 H, CH_3), 7.42 (s, 3 H, CH_3), 8.60 (t, 3 H, J = 7.0 Hz, OCH_2), 7.25 (s, 3 H, CH_3), 7.42 (s, 3 H, CH_3), 8.60 (t, 3 H, J = 7.0 Hz, CH_2CH_3)

Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.50; H, 6.22; N, 6.76.

48: ν^{neat} 3140, 1735, 1596, 1584 cm^{-1}; τ ($CDCl_3$) 2.45 (d, 1 H, J = 7.5 Hz, ring proton), 3.02 (d, 1 H, J = 7.5 Hz, ring proton), 4.70 (s, 1 H, =CH), 5.50 (br s, 1 H, OH), 5.82 (q, 2 H, J = 7.0 Hz, OCH_2), 7.40 (s, 3 H, CH_3), 7.50 (s, 3 H, CH_3), 8.80 (t, 3 H, J = 7.0 Hz, CH_2CH_3).

Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.10; H, 7.11; N, 6.43.

The total yield of two pyridine derivatives **47** and **48** was 40–60%.

49: mp 88–89°; ν_{max}^{KBr} 1759, 1684 cm^{-1}.

Anal. Calcd for $C_3H_5NO_3$: C, 34.95; H, 4.89; N, 13.59. Found: C, 35.18; H, 4.78; N, 13.47.

2.—From 0.3 g of **46**, there was obtained a mixture of **45** and **46**, and **50** (colorless crystals: mp 81–83°; ν_{max}^{KBr} 1759, 1693 cm^{-1}.

Anal. Calcd for $C_4H_7NO_3$: C, 41.02; H, 6.03; N, 11.96. Found: C, 41.20; H, 6.22; N, 11.90.

Lithium Aluminum Hydride Reduction of 47 and 48.—To a solution of 0.1 g of a mixture of **47** and **48** in 10 ml of absolute tetrahydrofuran was added 0.1 g of $LiAlH_4$ with stirring at 5° and the reaction mixture was stirred at 70° for 5 hr. The mixture was added with 2 ml of water and filtrated. The solution was evaporated *in vacuo* and the residue was recrystallized from benzene to give **51** as colorless crystals: mp 130–132° (70–80%); ν_{max}^{KBr} 3290, 1601, 1581 cm^{-1}.

Anal. Calcd for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.70; H, 7.90; N, 8.43.

2,6-Dimethyl-3-ethylpyridine (**53**).—A mixture of 0.1 g of **51** and 1 ml of thionyl chloride was heated at 60–80° for 12 hr. The reaction mixture was evaporated *in vacuo*, and the residue (**52**) was reduced by hydrogen over 10% Pd/C (200 mg) in methanol at room temperature for 2 days. The reaction mixture was filtered and evaporated *in vacuo*. The residue was then neutralized with 10% NaOH and extracted with ether. The extract was dried (Na_2SO_4) and evaporated *in vacuo* to give a colorless oil (**53**) (25–30%): ν_{max}^{neat} 1597, 1580 cm^{-1}; τ (CCl_4) 2.89 (d, 1 H, J = 7.0 Hz, ring proton), 3.29 (d, 1 H, J = 7.0 Hz, ring proton), 7.47 (q, 2 H, J = 7.0 Hz, CH_2), 7.60 (s, 6 H, $2CH_3$), 8.82 (t, 3 H, J = 7.0 Hz, CH_2CH_3). Compound **53** was found to be identical with 2,6-dimethyl-3-ethylpyridine[12] by comparison of their ir and nmr spectra as described above and by mixed glpc.

Registry No.—DAC, 762-42-5; **3**, 5825-71-8; **4**, 30689-96-4; **5**, 30758-64-6; **7**, 30689-97-5; **8**, 30689-98-6; **9**, 30689-99-7; **15**, 30690-00-7; **16**, 30758-65-7; **17**, 30690-01-8; **18**, 30758-66-8; **19**, 30690-02-9; **20**, 30690-03-0; **21**, 30690-04-1; **22**, 30690-05-2; **23**,

30690-06-3; **24**, 30690-07-4; **25**, 30690-08-5; **26**, 30690-09-6; **28**, 30758-67-9; **29**, 30758-68-0; **30**, 30690-10-9; **31**, 30758-69-1; **35**, 30690-11-0; **36**, 30690-12-1; **37**, 30758-70-4; **39**, 30758-71-5; **41**, 30690-13-2; **42**, 30690-14-3; **45**, 30690-15-4; **46**, 30690-16-5; **47**, 30690-17-6; **48**, 30690-18-7; **49**, 30690-19-8; **50**, 18804-91-6; **51**, 30690-20-1; **53**, 23580-52-1.

Overcrowded Molecules. I. Substituted 8-*tert*-Butyl-1-(2-pyridyl)naphthalenes, Including a Thermodynamically Stable Ketonic Tautomer

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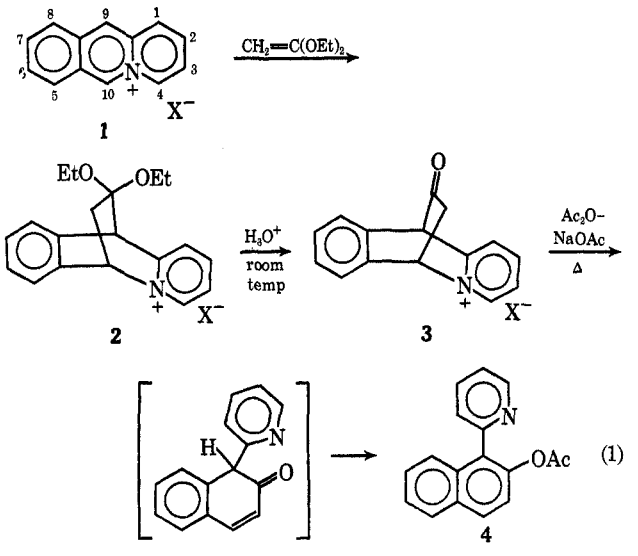
Condensation of appropriately substituted 4a-azoniaanthracene salts with ketene diethyl acetal followed by mild hydrolysis and then thermolysis in acetic anhydride has given several 8-*tert*-butyl-1-(2-pyridyl)naphthalenes. Their spectral properties and reactivity are adduced to indicate the high degree of steric strain present. Low-temperature nmr spectra of the *N*-methyl quaternary salt of 6-substituted 2,5-diacetoxy-8-*tert*-butyl-1-(2-pyridyl)naphthalenes indicate the existence of two isomers and are interpreted in terms of skewing of the naphthalene framework. 8-*tert*-Butyl-1-(2-pyridyl)naphthalenediol **13** is shown to exist exclusively as the thermodynamically stable keto tautomer **14**. 5-Acetoxy-8-*tert*-butyl-1-(2-pyridyl)-2-naphthol (**11**) has been oxidized (by Cu^{2+}) to give a novel intramolecular cyclization product formed by attack by N at the peri position to displace the *tert*-butyl group.

1-(2-Pyridyl)-2-naphthyl acetate (**4**) has recently been obtained by a three-step synthesis outlined in eq 1 involving the stereospecific 4 + 2 cycloaddition of ketene diethyl acetal to 4a-azoniaanthracene **1**, controlled hydrolysis of the resulting adduct (**2**) to ketone **3**, and sequential elimination, enolization, and acetylation reactions which occur as **3** is heated in acetic anhydride in the presence of sodium acetate.[1] Owing to the easy



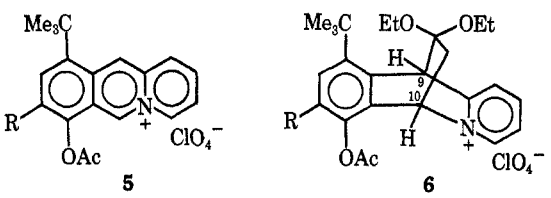
(1)

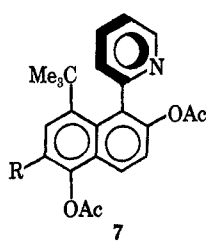
availability of a variety of types of substituted 4a-azoniaanthracene salts, especially those having substituents on the C_5–C_8 positions, this synthesis offers convenient access to 8-substituted 1-(2-pyridyl)naphthalenes, certain ones of which are of interest for peri-interaction studies. In succeeding papers we will describe some highly overcrowded pyridyl-substituted phenanthrenes and pentaphenes whose syntheses are based on this general approach. In this paper we report the synthesis of 8-*tert*-butyl-1-(2-pyridyl)naphthalenes and our observations of the consequences of steric strain on their physical and chemical properties.

(1) D. L. Fields and T. H. Regan, *J. Org. Chem.*, **35**, 1870 (1970).

Results and Discussion

The feasibility of the synthesis outlined in eq 1 to yield highly overcrowded naphthalenes was readily confirmed by the preparation of 8-*tert*-butyl-1-(2-pyridyl)naphthalenes **7a–c**. Some feeling for the high





a, R = H; **b**, R = Br; **c**, R = OAc

degree of overcrowding inherent in these compounds follows from the knowledge that even with the much less crowded 1,8-dimethylnaphthalene, peri interaction between the methyls is sufficient to cause distortion of the naphthalene skeleton as well as considerable bond-angle deformation.[2] Nonetheless, the syntheses of **7a–c** proved to be quite straightforward and free of complications.

As an example, adduct **6a** was obtained in quantitative yield following treatment of **5a** with an excess of ketene diethyl acetal for 10 min at room temperature. The stereochemistry of the addition was confirmed by

(2) A single-crystal X-ray analysis of 3-bromo-1,8-dimethylnaphthalene showed the normal C_1–C_8 distance in naphthalene of 2.44 Å extended to 2.56 Å, the methyls constrained to a 2.92-Å separation, a distance much less than the sum of their van der Waal's radii (4.0 Å) accompanied by some departure from planarity within the aromatic rings: M. D. Jameson and B. R. Penfold, *J. Chem. Soc.*, 528 (1965). The strain energy of 1,8-dimethylnaphthalene has been estimated at 7.9 kcal: J. Parker, J. Vaughan, and E. Wong, *J. Org. Chem.*, **23**, 1373 (1958).