then added to 100 ml of water, the mixture extracted with ether, the ethereal extract washed with sodium bicarbonate solution and dried (Na_2SO_4), and the solvent removed. The product was recrystallized from a mixture of benzene and hexane. Epoxide **1** yielded the monoacetate **7**, mp 161–162°, and the minor epoxide **2** gave monoacetate **8**, mp 168.5–170°.

Anal. Calcd for $C_{14}H_{16}ClNO_5$: C, 53.59; H, 5.14; N, 4.46. Found (**7**): C, 53.39; H, 5.14; N, 4.41. Found (**8**): C, 53.80; H, 5.21; N, 4.45.

trans-2-(*p*-Chlorophenyl)-*cis*-4-*trans*-5-dihydroxynitrocyclohexane (**5**).—A mixture of 1.5 g of epoxide **1** (or a mixture of the two epoxides), 7.5 ml of H_2O, and 2 drops of concentrated H_2SO_4 in 15 ml purified dioxane was allowed to stand for 2 days. The mixture was added to 60 ml of water and extracted with ether. The product was recrystallized from a mixture of benzene and hexane, mp 204–205°.

Anal. Calcd for $C_{12}H_{14}ClNO_4$: C, 53.03; H, 5.19; N, 5.16. Found: C, 52.96; H, 5.51; N, 5.09.

The diacetate **6** was prepared from **5** with acetic anhydride in dry pyridine by the usual manner and recrystallized from a mixture of benzene and hexane, mp 162–163°.

Anal. Calcd for $C_{16}H_{18}ClNO_6$: C, 54.02; H, 5.10; N, 3.94. Found: C, 53.91; H, 5.14; N, 3.78.

Registry No.—**1**, 27390-71-2; **2**, 27390-72-3; **4**, 17321-89-0; **5**, 27390-74-5; **6**, 27390-75-6; **7**, 27390-76-7; **8**, 27390-77-8.

Orientation in the 1,3-Dipolar Cycloaddition Reactions of Heteroaromatic Nitrogen Methylides with Dipolarophiles[1]

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The orientation in the 1,3-dipolar cycloaddition reactions of several ring-substituted nitrogen methylides with dipolarophiles was investigated. The cycloaddition reactions of 3-substituted pyridazinium methylides with dimethyl acetylenedicarboxylate (DAC) and cyanoacetylene afforded the corresponding cycloadducts. In reactions of 3,6-dialkoxypyridazinium methylides with DAC, one of two alkoxyl groups was expelled in the formation of the adducts. A mixture of isomeric adducts was obtained in the reactions of 3-substituted pyrazinium methylides and 3-substituted pyridinium methylides, in which the major product was produced by cyclization at the C-2 position. An isomeric mixture of the adducts was also obtained by the reaction of 3,4-dimethylpyridinium methylide; however, the major product was afforded by cyclization at the C-6 position. Although the thermal addition of 4-carbomethoxypyridinium methylide to DAC afforded the cycloadduct, the methylide was photochemically too stable to undergo the photocycloaddition.

Indolidines and polyazaindolidines of the 10-π-electron system are of interest for the studies on azulene heteroanalogs, and recent studies[2,3] have focused on the convenient one-step synthesis of these aromatic heterocycles by 1,3-dipolar cycloaddition reactions.

Although the mechanism of 1,3-dipolar cycloaddition reactions has been extensively discussed by Huisgen and Firestone,[4] little is known about the orientation in 1,3-dipolar cycloaddition reactions of ring-substituted heteroaromatic nitrogen methylides with dipolarophiles. Recent results[3,5] in the 1,3-dipolar photocycloaddition reactions of isoelectronic 3-methyl-1-carbethoxyiminopyridinium ylide disclose significant differences between ground state and the excited state properties. In continuation of these studies,[3,5] this paper deals with an extension of the 1,3-dipolar cycloaddition of a series of ring-substituted heteroaromatic nitrogen methylides with dipolarophiles.[6]

Results and Discussion

Pyridazine (**1**), substituted pyridazine derivatives (**2–6**), and β-substituted pyridine derivatives (**26** and **27**) reacted with tetracyanoethylene oxide (TCNEO) to give crystalline compounds **7**, **8–12**, **30**, and **32**, respectively. Their compositions corresponded to 1:1 adducts of the base and dicyanomethylene. The infrared spectra of these compounds exhibit common strong nitrile absorptions at 2225 and 2220 cm^{-1}, indicating a high degree of ionic character in the dicyanomethylides.[7] Pyrazinium *N*-phenacylide (**22**) and pyridinium *N*-phenacylides (**31**, **33–35**) were prepared by treatment of the corresponding phenacyl bromides with aqueous potassium carbonate.[3] The structures of these ylides are based on the structural elucidation of 1,3-dipolar cycloaddition products as discussed below. The physical data of the dicyanomethylides **7–12** and **32** are summarized in Table I.

1,3-Dipolar Cycloaddition of Pyridazinium Methylides with DAC and Cyanoacetylene.—The 1,3-dipolar cycloaddition reactions of pyridazinium dicyanomethylide (**7**) and 3-substituted pyridazinium dicyanomethylides **8** and **10** with DAC afforded the cycloadducts **13–15**, respectively, in 50–70% yields. The spectrum of **13** shows a doublet at τ 1.87 (1 H, H_4, $J_{4,3}$ = 6.0 Hz),[8] double doublets at τ 2.74 (1 H, H_3, $J_{2,3}$ = 6.0 Hz, $J_{3,4}$ = 3.0 Hz), a doublet at τ 1.90 (1 H, H_2, $J_{2,3}$ = 3.0 Hz),[8] and singlet signals of two methyl protons at τ 5.88 and 5.99. In contrast, the spectra of **14** and **15** exhibit two ring proton signals at τ 1.70–1.80 (1 H) and τ 2.93–3.35 (1 H) as each doublet with the coupling constant of 9–10 Hz. Since the coupling constants of compound **13** are considerably different from those of compounds **14** and **15**, the structural elucidation of **13** was

(1) Studies of Heteroaromaticity. XLIII.

(2) For a recent review, see V. Boekelheide and N. A. Fedoruk, *J. Amer. Chem. Soc.*, **90**, 3830 (1968), and references cited therein.

(3) T. Sasaki, K. Kanematsu, and Y. Yukimoto, *J. Chem. Soc. C*, 481 (1970).

(4) (a) R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968); (b) R. A. Firestone, *ibid.*, **33**, 2285 (1968).

(5) T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *ibid.*, **35**, 426 (1970).

(6) Contrary to extensive studies on the 1,3-dipolar cycloaddition reactions of the zwitterionic methylides with DAC, the same reactions of 1-alkoxycarbonyliminopyridinium ylides will be presented later [see Studies of Heteroaromaticity. LI (submitted for publication in *J. Org. Chem.*)].

(7) W. J. Linn, O. W. Webster, and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 3651 (1965).

(8) The assignment of the H_2 and H_4 signals is based on the magnitude of $J_{4,3}$ in **13** and of $J_{3,4}$ in **14** and **15**; it may be the reverse of that given.

TABLE I

PHYSICAL AND SPECTRAL DATA OF THE HETEROAROMATIC *N*-DICYANOMETHYLIDES[a,b]

Compd no.	Mp, °C	Yield, %	—Ir— $\nu_{C\equiv N}^{KBr}$, cm^{-1}	—Uv— λ_{max}^{EtOH} (log ϵ)
7	210	75	2225	427 (4.22)
			2220	
8	217–219	80	2225	428 (4.34)
			2220	330 (3.39)
				265 (3.44)
9	178–180	70	2250	454 (4.25)
			2225	310 (3.43)
				265 (3.57)
10	206–208	70	2225	429 (4.28)
			2220	330 (3.31)
				260 (2.96)
11	182–184	60	2230	460 (4.14)
			2220	326 (3.88)
12	182–183	72	2240	424 (4.33)
			2200	
32	255–257	15	2280	413 (4.18)
			2180	250 (3.73)
			2160	

[a] Compound **30**, mp 214° (lit.[7] 213.5–214°). [b] Satisfactory analytical data (±0.25% for C, H, and N) were reported for all compounds in the table: Ed.

accomplished by chemical degradation. Treatment of **13** with refluxing methanolic hydrogen chloride (20%) for 10 hr gave 5,6,7-tricarbomethoxypyrrolo[1,2-*b*]pyridazine in 50% yield, which was identical with an authentic sample prepared by independent synthesis[9] by 1,3-dipolar addition of the pyridazinium–methyl bromoacetate adduct and DAC. Treatment of dicyanomethylides **7**, **8**, and **10** with cyanoacetylene afforded the expected 5,7-dicyano compounds **16–18**.

Surprisingly, in the reactions of 3,6-dialkoxypyridazinium methylides **9** and **11** with DAC, an alkoxy and a cyano group must be expelled to give the 2-alkoxy derivatives **14** and **19**; the nmr spectra contained only one characteristic alkoxy resonance at τ 5.94 (3 H, s, OCH_3) and 2.70 (5 H, m, OC_6H_5), respectively (*cf.* Table II). A formally similar aromatization, with loss of methane, was observed in the reaction of 3,6-dimethylpyridazinium methylide with DAC.[9] Treatment of dicyanomethylide **12** with DAC afforded 3-methyl-5,6-dicarbomethoxy-7-cyanopyrrolo[1,2-*b*]pyridazine (**20**); the nmr spectrum of the latter established the N-1 position of the dicyanomethylene group in **12**. These results are summarized in Tables II and III and Scheme I.

1,3-Dipolar Cycloaddition of β-Substituted Pyrazinium and Pyridinium Methylides with DAC.—The reaction of 3-methylpyrazinium *N*-phenacylide (**22**) with DAC in acetonitrile at room temperature gave 4% yield of 1,2-dicarbomethoxy-3-benzoyl-8-methyl-7-azaindolidine (**23**). However, the same reaction in refluxing chloroform gave *ca.* 8.5% yield of a mixture of **23** and 1,2-dicarbomethoxy-3-benzoyl-6-methyl-7-azaindoline (**24**) in the ratio of 2:1 (by nmr analysis); the ratio of the integrated areas for each peak at τ 2.14 and 1.14 (each doublet, J = 5.5 Hz) attributable to the ring protons of **23**, and those at τ 0.91 and 0.41 (each singlet) due to the ring protons of **24** was 2:1. Since an isomeric mixture was obtained, an alternative structure **25**, which would arise from the 2-methylpyrazinium ylide, could be ruled out. (See Scheme II.)

(9) D. G. Farnum, R. J. Alamino, and J. M. Dunston, *J. Org. Chem.*, **32**, 1130 (1967).

SCHEME I

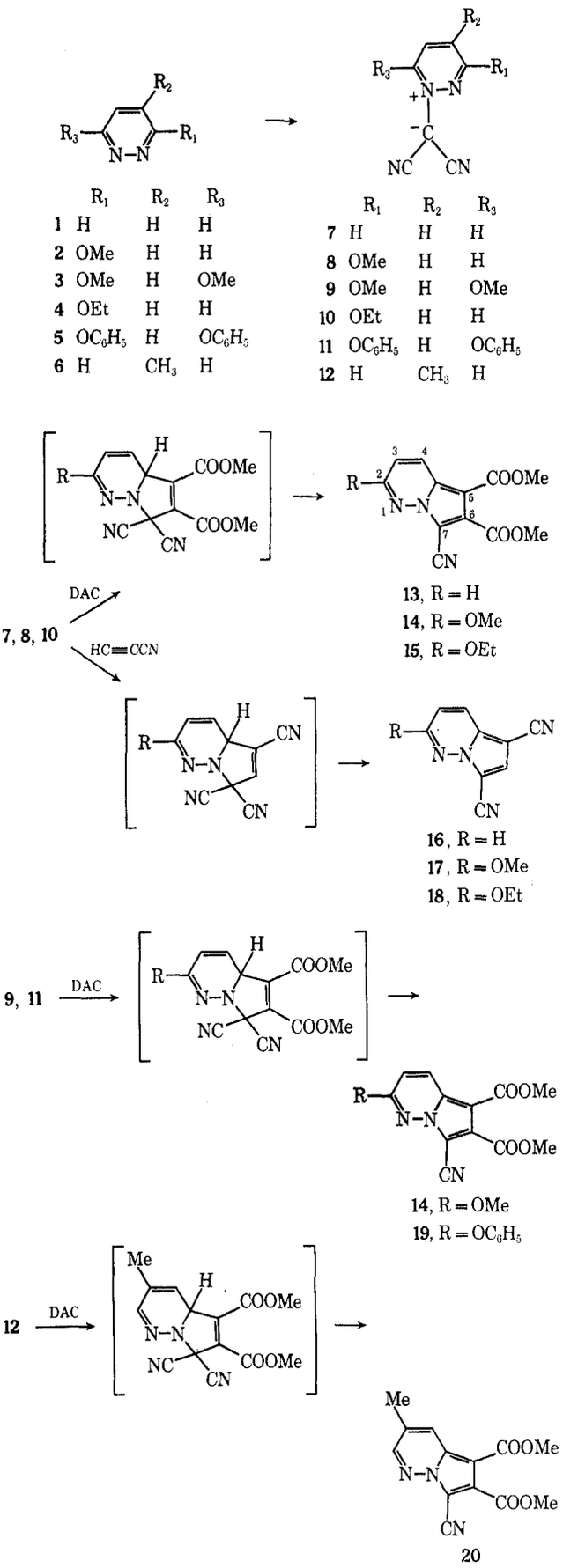


TABLE II

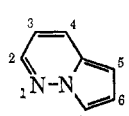
PHYSICAL AND SPECTRAL DATA OF THE CYCLOADDUCTS

Compd no.	Reaction conditions: Temp	Time, hr	Yield, %	Mp, °C	Uv: λ_{max}^{EtOH}, mμ (log ε)	M+, m/e	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
13	Room temp	12	50	141–143	348 (3.63) 302 (3.70) 290 (3.71) 260 (4.14) 246 (4.51) 217 (4.30)	259	$C_{12}H_9N_3O_4$	55.60	3.50	16.21	55.76	3.56	16.10
14	Room temp Reflux	12 15	70[a] 10[b]	155–156	330 (3.78) 260 (4.31) 243 (4.45) 236 (4.45) 220 (4.34)	289	$C_{13}H_{11}N_3O_5$	53.98	3.83	14.53	54.02	3.67	14.55
15	Room temp	15	50	170–171	340 (3.73) 262 (4.24) 245 (4.37) 240 (4.36) 220 (4.24)	303	$C_{14}H_{13}N_3O_5$	57.44	4.29	29.77	57.47	4.19	30.00
16	Reflux	4	30	202–204	343 (3.53) 298 (3.71) 286 (3.73) 245 (4.62)	168	$C_9H_4N_4$	64.28	2.40	33.32	64.34	2.38	33.46
17	Room temp	12	70	233–235	324 (3.76) 257 (4.48) 248 (4.52) 216 (4.60)	198	$C_{10}H_6N_4O$	60.60	3.05	28.27	60.57	2.85	28.09
18	Room temp	12	80	166–168	325 (3.65) 258 (4.37) 249 (4.30) 217 (4.41)	212	$C_{11}H_8N_4O$	62.25	3.80	26.40	62.28	3.96	26.54
19	Room temp	15	10	155–157	334 (3.78) 240 (4.50) 220 (4.46)	351	$C_{18}H_{13}N_3O_5$	61.54	3.73	11.96	61.42	3.77	12.13
20	Reflux	16	66	164–167	348 (3.53) 300 (3.79) 290 (3.77) 245 (4.48) 216 (4.23)	273	$C_{13}H_{11}N_3O_4$	57.14	4.06	15.38	57.20	4.10	15.40

[a] It was obtained from the reaction of compound 8 and DAC. [b] It was obtained from the reaction of compound 9 and DAC.

TABLE III

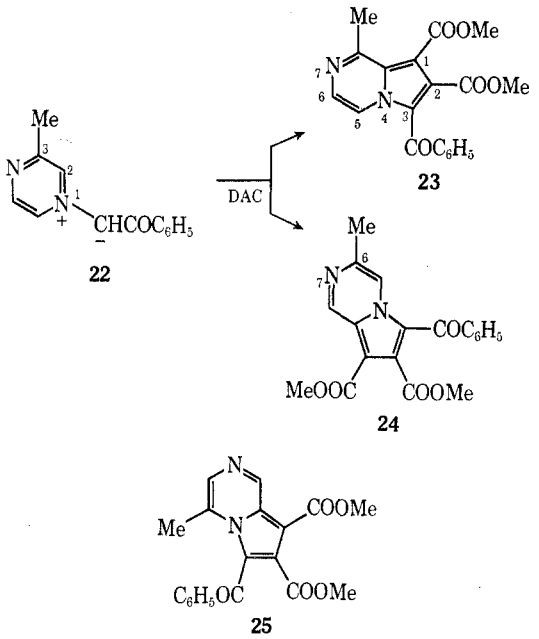
NMR SPECTRA OF PYRROLO[1,2-*b*]PYRIDAZINE DERIVATIVES IN $CDCl_3$ AT 60 MHz



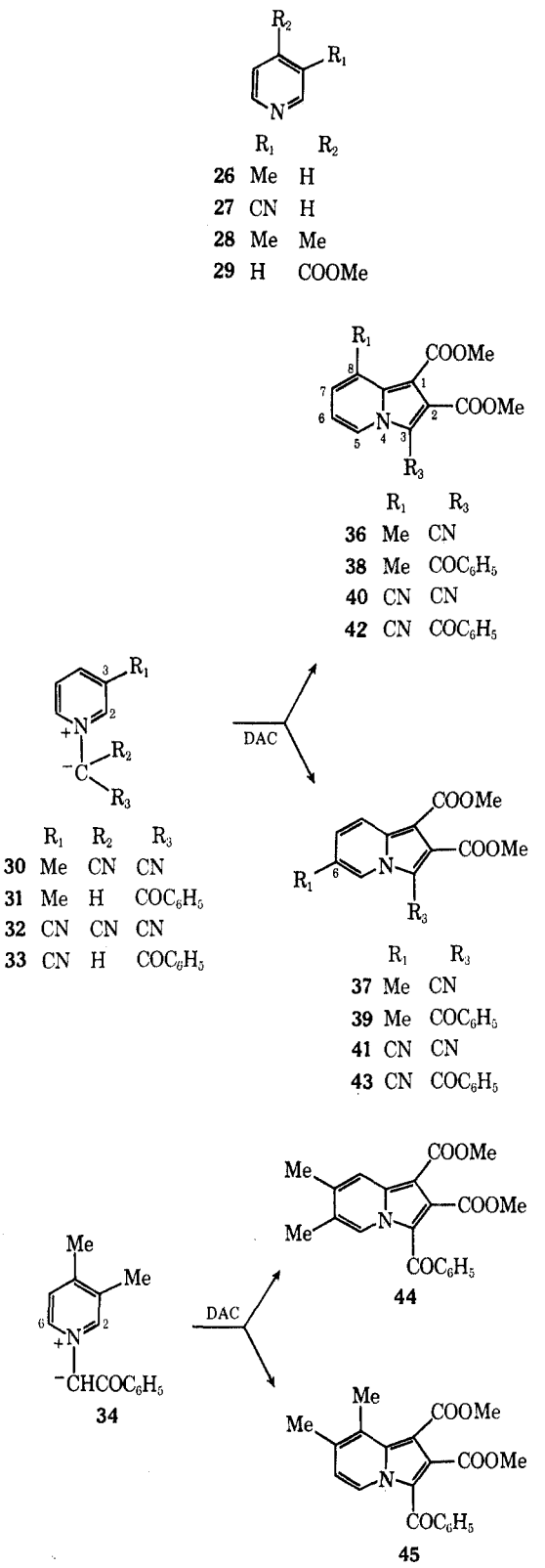
Compd no.[a]	Chemical shifts (τ) and coupling constants (J in Hz): C_2	C_3	C_4	C_5	C_6
13	1.87 (d), J = 6.0	2.74 (dd), J = 6.0, 3.0	1.90 (d), J = 3.0	5.99 (s) 5.88 (s)	$2COOCH_3$
14	5.94 (s, OCH_3)	3.35 (d), J = 9.0	1.80 (d), J = 9.0	6.10 (s) 6.02 (s)	$2COOCH_3$
15[b]	5.6 (q), 8.59 (t), J = 7.0 (OC_2H_5)	2.93 (d), J = 10.0	1.70 (d), J = 10.0	6.14 (s) 6.09 (s)	$2COOCH_3$
17	5.0 (s, OCH_3)	2.88 (d), J = 10.0	1.70 (d), J = 10.0		1.92 (s)
18	5.52 (q), 8.52 (t), J = 6.8 (OC_2H_5)	3.25 (d), J = 9.0	2.18 (d), J = 9.0		1.65 (s)
19	2.6~2.8 (OC_6H_5) (complex m)	3.02 (d), J = 10.5	1.56 (d), J = 10.5	6.10 (s) 6.03 (s)	$2COOCH_3$
20	1.69[c] (m, overlapping with ring protons)	7.46 (s, CH_3)	1.69[c] (m, overlapping with ring protons)	6.03 (s) 5.93 (s)	$2COOCH_3$

[a] Compound 16 is insoluble for nmr measurement. [b] In DMSO-d_6. [c] This signal is assigned by integrating to 2 H.

SCHEME II



SCHEME III



Treatment of 3-methyl- and 3-cyanopyridinium methylides (**30–33**) with DAC gave a mixture of 8-substituted (**36**, **38**, **40**, and **42**) and 6-substituted indolizine derivatives (**37**, **39**, **41**, and **43**) in the ratio of *ca.* 3:1 by the nmr analysis. The isomeric mixture from the reaction of **33** and DAC was separated by column chromatography to give **42** and **43**. However, the isomeric mixtures **36–37**, **38–39**, and **40–41** could not be separated by column chromatography or by repeated recrystallization. The ring protons in compound **42** exhibit signals at τ 0.35 (double doublet, 1 H, H_5, $J_{5,6}$ = 7.5 Hz, $J_{5,7}$ = 1.0 Hz), 2.10 (double doublet, 1 H, H_7, $J_{7,6}$ = 7.5 Hz, $J_{7,5}$ = 1.0 Hz), and 2.85 (triplet, 1 H, H_6, $J_{6,7}$ = 7.5 Hz), and those in compound **43**, at τ 0.05 (doublet, 1 H, H_5, $J_{5,7}$ = 1.0 Hz), 1.50 (doublet, 1 H, H_8, $J_{7,8}$ = 9.0 Hz), and 2.45 (1 H, H_7, m, overlapping with phenyl protons). The isomeric adducts were assigned on the basis of the nmr spectra of **42** and **43** in Table IV. The anisotropy of a benzoyl group is sufficient to account for the low-field displacement of C-5 indolizine ring proton in **38**, **39**, **42**, and **43**. The reaction of 3,4-dimethylpyridinium-*N*-phenacylide (**34**) with DAC yielded a mixture of isomeric adducts **44** and **45** in the ratio of 2:1, in which the major product was produced by cyclization at C-6 in contrast to the above reactions. The reasons underlying these differences in orientation are not yet resolved. (See Scheme III.)

1,3-Dipolar Cycloaddition of γ-Substituted Pyridinium Methylide with DAC.—Recently Snieckus, *et al.*,[10] suggested that the photochemical stability of 1,4-dicarbethoxy-1-iminopyridinium ylide might be associated with the negative charge on the exocyclic nitrogen. In an attempt to compare the reactivities of 4-carboalkoxypyridinium methylide (**35**) and the isoelectronic iminopyridinium ylide, in the ground state and the excited state, it was found that compound **35** was photochemically too stable to undergo the photocycloaddition in our present experimental data, while the reaction of **35** with DAC in acetonitrile at the refluxing temperature afforded the expected cycloadduct **46** in 38% yield, indicating that the betaine forms might be predominant in the resonance contribution at the ground state as shown in Scheme IV.

(10) A. Balasubramanian, J. M. McIntosh, and V. Snieckus, *J. Org. Chem.*, **35**, 433 (1970).

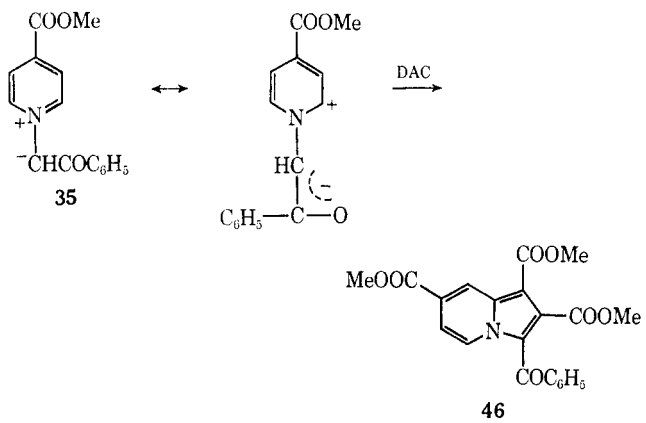
TABLE IV

RATIOS OF ISOMERIC CYCLOADDUCTS AND THEIR SPECTRAL DATA

Compd no.	Reaction conditions—Temp	Time, hr	Total yield, %	Ratio	M+, m/e	Nmr at 100 MHz (DMSO-d_6), τ, J in Hz[a] at C-5 H
36 + 37	Room temp	4	40	3.0:1.0[b]	272	2.0 (dd, J = 7.0, 1.0), 1.8 (d, J = 1.0)
38 + 39	Reflux	12	20	2.5:1.0	351	0.72 (dd, J = 7.0, 1.0), 0.65 (d, J = 1.0)
40 + 41	Room temp	4	80	3.1:1.0	283	1.14 (dd, J = 7.0, 1.0), 0.57 (d, J = 1.0)
42 + 43	Room temp	5	15	2.5:1.0	362	0.35 (dd, J = 7.5, 1.0), 0.05 (d, J = 1.0)
44 + 45	Room temp	5	12	2.0:1.0	365	0.61 (s), 0.93 (d, J = 7.5)

[a] $J_{5,6} = J_{6,7} = J_{7,8} = 7.0\sim7.5$ Hz; $J_{5,7} = J_{6,8} = 1.0$ Hz (Scheme III). [b] The ratio was also determined by the integrated areas for the methyl proton signals appeared at τ 7.50 in **36** and τ 7.55 in **37**.

SCHEME IV



Experimental Section[11]

Preparation of the Dicyanomethylides.—The dicyanomethylides were prepared by a modified method of Linn, *et al.*[7] To a stirred and cooled (ice bath) solution of 0.3 mol of the base [**1–6**, 3-methylpyridine (**26**), and 3-cyanopyridine (**27**)] in 100 ml of tetrahydrofuran was added slowly a solution of 0.1–0.15 mol of TCNEO in 50 ml of tetrahydrofuran over 1 hr. The mixture was stirred for an additional hour at room temperature or under gentle reflux condition and filtered. The ylides were purified by recrystallization from methanol. The yields, analyses, and spectral data of the dicyanomethylides (**7–12** and **32**) are given in Table I.

Preparation of the Phenacylides.—The phenacylides were prepared by a modified method of Kröhnke[3] as follows. A mixture of 0.11 mol of the base (**1**, **21**, **26**, **27**, **28**, and **29**) and 0.1 mol of phenacyl bromide in 20 ml of chloroform or acetonitrile was stirred at room temperature for 1 hr. The mixture was warmed for an additional hour at 50° for complete crystallization. The resulting slurry was filtered and recrystallized from methanol. Subsequent treatments of these phenacyl salts with 10% potassium carbonate in 20 ml of water afforded the phenacylides **22**, **31**, **33**, **34**, and **35**, which are slightly hygroscopic, and directly used to 1,3-dipolar cycloaddition reactions without further purification.

1,3-Dipolar Cycloaddition Reactions of the Pyridazinium Dicyanomethylides with Dipolarophiles.—A suspension of 0.1 mol of the dicyanomethylides (**7–12**) and 0.1 mol of DAC or cyanoacetylene in 20 ml of acetonitrile was stirred at room temperature or at the refluxing temperature for 4–16 hr. The solvent was removed under reduced pressure and the residue was purified on a silica gel column with benzene as an eluent to give the corresponding adducts (**13–20**). The yields and analytical and spectral data are given in Tables II and III.

Methanolysis of Compound 13.—A mixture of **13** (0.1 g) and 20% methanolic hydrogen chloride solution (30 ml) was refluxed at 100° in an oil bath for 15 hr. The solvent was removed *in vacuo*, the residue was dissolved in water (50 ml), and the solution was adjusted to pH 7 with 10% sodium hydroxide solution. Then the solution was concentrated under reduced pressure to give a 50% yield of 5,6,7-tricarbomethoxypyrrolo[1,2-*b*]-pyridazine as a colorless solid, mp 160–161° (lit.[9] 163°).

1,3-Dipolar Cycloaddition Reaction of 3-Methylpyrazinium *N*-Phenacylide (22) with DAC. 1.—A solution of **22** (0.9 g, 0.004 mol) and DAC (0.6 g, 0.004 mol) in acetonitrile (100 ml) was stirred at room temperature for 17 hr. The solvent was then removed under reduced pressure and the residue was purified by silica gel chromatography with chloroform as an eluent to give a yellow crystal **23** (0.06 g, 4%): mp 141–142°; τ ($CDCl_3$) 7.16 (s, CH_3), 6.75 (s, $COOCH_3$), 6.09 (s, $COOCH_3$), 2.46 (m, C_6H_5), 2.14 (d, J = 5.5 Hz, 1 H, ring proton), 1.14 (d, J = 5.5 Hz, 1 H, ring proton).

Anal. Calcd for $C_{19}H_{16}O_5N_2$: C, 64.77; H, 4.58; N, 7.95. Found: C, 64.50; H, 4.60; N, 7.90.

2.—A solution of **22** (4.35 g, 0.02 mol) and DAC (5.83 g, 0.04 mol) in chloroform (20 ml) was refluxed for 17 hr. The solvent was then removed under reduced pressure, and the residue was purified by silica gel chromatography with chloroform as an eluent to give a yellow crystal (0.062 g, 8.5%), mp 120–135°, which was identified as a 2:1 mixture of **23** and **24** by nmr. A mixture of **23** and **24** was separated by repeated recrystallization from methanol: **23** had mp 185–188° [τ ($CDCl_3$) 7.41 (s, CH_3), 6.69 (s, $COOCH_3$), 6.09 (s, $COOCH_3$), 2.46 (m, C_6H_5), 0.91 (s, 1 H, ring proton), 0.41 (s, 1 H, ring proton)], and **24** had mp 141–142°.

Anal. Calcd for $C_{19}H_{16}O_5N_2$: C, 64.77; H, 4.58; N, 7.95. Found for **23**: C, 64.61; H, 4.55; N, 7.92. Found for **24**: C, 64.70; H, 4.49; N, 7.89.

1,3-Dipolar Cycloaddition Reactions of Substituted Pyridinium Ylides (30–34) with DAC. 1.—A solution of 0.1 mol of the dicyanomethylides (**30** and **32**) and 0.1 mol of DAC in 50 ml of acetonitrile was stirred at room temperature or under the refluxing conditions for 4–12 hr, and the solvent was then removed under reduced pressure. The residue was found to be a mixture of isomeric adducts. However, the isomers could not be separated from the mixture by column chromatography. The ratios of the isomeric adducts and their spectral data are given in Table IV.

2.—A solution of 0.1 mol of the phenacylides (**31**, **33**, and **34**) and 0.2 mol of DAC in 50 ml of acetonitrile was treated as described above to give an isomeric mixture of the adducts (Table IV). A mixture of adducts **42** and **43** was separated by column chromatography with benzene as an eluent: **42** had mp 190–196° [ν_{max}^{KBr} 2280 (C≡N), 1745 ($COOCH_3$), 1710 ($COOCH_3$), 1640 cm^{-1} (COC_6H_5)], and **43** had mp 210–218° [ν_{max}^{KBr} 2280 (C≡N), 1745 ($COOCH_3$), 1710 ($COOCH_3$), 1640 cm^{-1} (COC_6H_5)].

Anal. Calcd for $C_{29}H_{14}O_5N_2$: C, 66.29; H, 3.89; N, 7.73. Found for **42**: C, 66.31; H, 3.90; N, 7.80. Found for **43**: C, 66.29; H, 3.85; N, 7.70.

A mixture of adducts (**38 + 39**, **44 + 45**) could not be separated from the mixture either by column chromatography or by repeated recrystallization.

1,3-Dipolar Cycloaddition Reaction of 4-Methoxycarbonylpyridinium-*N*-phenacylide (35) with DAC.—A solution of **35** (1.2 g) and DAC (1.5 g) in acetonitrile (30 ml) was refluxed for 21 hr. The solvent was removed under reduced pressure to give yellow powder. Recrystallization from methanol gave **46** (0.7 g, 40%): mp 189–191°; τ ($CDCl_3$) 6.63 (s, $COOCH_3$), 6.03 (s, $COOCH_3$), 5.97 (s, $COOCH_3$), 2.37 (m, 6 H, C_6H_5, and 1 H of H_6, ring proton), 0.83 (d, J = 1.0 Hz, 1 H, H_8, ring proton), 0.16 (d, J = 7.0 Hz, 1 H, H_5 ring proton).

(11) The melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were determined with a Perkin-Elmer 240 elemental analyzer. The uv spectra were taken with a JASCO Model ORD/UV-5 analyzer. The nmr spectra were taken with a Jeolco Model C-60-XL and a Minimer-100 nmr spectrometers 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. The mass spectra were obtained on a Hitachi RMU-D double-focusing mass spectrometer operating at an ionization potential of 70 eV.

Anal. Calcd for $C_{21}H_{17}O_7N$: C, 63.79; H, 4.33; N, 3.54. Found: C, 63.81; H, 4.40; N, 3.50.

Registry No.—**7**, 27391-06-6; **8**, 27391-07-7; **9**, 27391-08-8; **10**, 27391-09-9; **11**, 27391-10-2; **12**, 27391-11-3; **13**, 27425-46-3; **14**, 27425-47-4; **15**, 27425-48-5; **16**, 27391-12-4; **17**, 27391-13-5; **18**, 27391-14-6; **19**, 27425-49-6; **20**, 27415-61-8; **23**, 27415-62-9; **24**, 27415-63-0; **32**, 27415-64-1; **36**, 27371-68-2; **37**, 27415-66-3; **38**, 27415-67-4; **39**, 27425-50-9; **40**, 27415-68-5; **41**, 27415-69-6; **42**, 27415-70-9; **43**, 27415-71-0; **44**, 27415-72-1; **45**, 27415-73-2; **46**, 27415-65-2.

The Synthesis of 1-Fluorocycloalkenes

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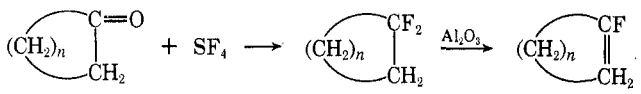
The reaction of anhydrous, neutral alumina, activity grade I, with a 1,1-difluorocycloalkane produces the corresponding 1-fluorocycloalkene in 20–70% yield. In this way, 1-fluorocyclopentene, 1-fluorocyclohexene, 1-fluorocycloheptene, 1-fluorocyclooctene, 1-fluorocyclododecene, and 4-methoxy-1-fluorocyclohexene were prepared and characterized, principally by proton and fluorine nmr and infrared spectra. The starting difluoro compounds were obtained by the action of sulfur tetrafluoride on the cyclic ketone. Thus, a facile, two-step entry into this elusive class of vinyl fluorides is provided.

Although linear vinyl fluorides are a well-known class of organic compounds, their cyclic counterparts are little described in the chemical literature. To our knowledge, the only example reported is 1-fluorocyclohexene (**6**).[1] We wish to report that the action of anhydrous, neutral alumina on a *gem*-difluorocycloalkane is a convenient, general route to cyclic vinyl fluorides. The difluoro compounds are obtained readily from the corresponding cyclic ketone and sulfur tetrafluoride[2] and this synthetic approach is outlined in Scheme I.

SCHEME I

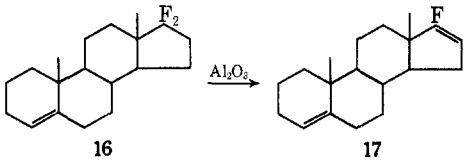
SYNTHESIS OF 1-FLUOROCYCLOALKENES



1, $n = 3$	**2**, $n = 3$	**3**, $n = 3$
4, $n = 4$	**5**, $n = 4$	**6**, $n = 4$
7, $n = 5$	**8**, $n = 5$	**9**, $n = 5$
10, $n = 6$	**11**, $n = 6$	**12**, $n = 6$
13, $n = 10$	**14**, $n = 10$	**15**, $n = 10$

Results and Discussion

Initially, the model reaction **16** → **17**[3] was chosen for study in order to establish optimum conditions of solvent, temperature, and type of alumina. This reaction proceeded under very mild conditions[4] and no side reactions were observed. In addition, integration of H-4 *vs.* H-16, which are well resolved in the 60-MHz nmr spectrum of **17**, provided accurate quantitative data. By this method, it was established that hydrocarbon solvents gave high yields of **17**, whereas polar solvents, *e.g.*, acetonitrile, ethyl acetate, and dimethyl sulfoxide, gave essentially no product under identical reaction conditions. The source of the alumina was critical. Several samples were tested but only Woelm or Guilini[5] neutral alumina,[6] activity grade I, gave good results. Woelm basic alumina gave lower yields and Woelm acidic alumina and other samples of alumina from various commercial sources returned only unchanged **16**. The reactivity of an alumina sample probably is a function of available Lewis acid and base sites on the alumina surface, since we have shown that blocking the former sites with pyridine *or* the latter sites with tetracyanoethylene[7] completely inhibited the above reaction. Additional evidence in support of active sites is the fact that alumina is required in stoichiometric amount. No more than about 1 mmol of difluoro compound per 5 g of alumina can be dehydrofluorinated under the conditions used, and, if this ratio is exceeded, a mixture of starting material and product is obtained.



16 **17**

When alumina was suspended in a hexane solution of 1,1-difluorocyclohexane (**5**) at reflux temperature, starting material was consumed completely, and a single volatile product was formed as evidenced by gas–liquid chromatography. However, it was not possible to separate product from solvent by careful distillation, and essentially all the product was lost in fractions over the boiling range of 80–92°. To circumvent this difficulty, neat **5** was admixed with alumina without solvent and heated in an oil bath in a nitrogen atmosphere after which the reaction vessel was evacuated through a cold trap. The volatile material in the trap was shown to be a mixture of 96% of **6** and 4% of cyclohexene by nmr, mass spectrum, and glc analysis. The yield was 63% compared to 66%[8] in the solvent-mediated reaction

(1) (a) G. N. Valkanas and H. Hopff, U. S. Patent 3,093,692 (1963); *Chem. Abstr.*, **59**, 11291e (1963). (b) G. Wittig and B. Mayer, *Ber.*, **96**, 329 (1963).

(2) (a) W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **82**, 543 (1960); (b) D. G. Martin and F. Kagan, *J. Org. Chem.*, **27**, 3164 (1962).

(3) The preparation of steroid vinyl fluorides will be the subject of a separate communication from this laboratory.

(4) In hexane at room temperature, yields of **17** were 50 and 60% after 1 and 18 hr, respectively. At reflux temperature, the yield was 95–98% in 1 hr.

(5) Supplied by Bodman Chemical Co., Narberth, Pa.

(6) Hereafter designated as alumina.

(7) F. Figueras Roca, A. Nohl, L. de Mourges, and Y. Trambourze, *C. R. Acad. Sci.*, **266**, 1123 (1968).

(8) Gas–liquid chromatographic analysis.