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Studies on Pyridazines. XXV.*,[1] The Ring-opening Reactions of N-Methoxypyridazinium Salts with Nucleophiles

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The reaction of 1-methoxypyridazinium methosulfate (**1**) with cyanide ion resulted in the ring fission and subsequent elimination of N_2 to give the cyano substituted vinyl acetylenes (**2** and **3**) and 1,3-butadienes (**4**).

On the other hand, reactions of the salt (**1**) with hydroxide and dicyanomethyl anion resulted in the similar ring-opening, followed by elimination of the methoxyl group, to give vinyl diazomethanes (**6** and **9**), which were easily converted into the corresponding pyrazole derivatives (**7** and **10**) by an intramolecular 1,3-dipolar cycloaddition.

The reaction mechanism is also discussed.

We have already reported that the reactions of 1-methylpyridazinium salts with cyanide ion afforded[3] 4-cyano-1,4-dihydro compounds along with the dimers having cyclobutane rings and the salts also gave the different type of dimers by the reaction with hydroxide ion.[4]

On the other hand, the reactions of N-alkoxypyridinium salts with bases have been widely studied[5] and well documented.[6]

These interesting results prompted us to investigate the reactions of N-methoxypyridazinium salts (**1**) with nucleophiles such as cyanide, hydroxide, and carbanions, and we now report the ring opening reactions of the salts with these nucleophiles, resulting in the formation of vinylacetylenes, 1,3-butadienes, and vinyl diazomethane.

I. Reaction with Cyanide Ion

It has been already reported[7] that the N-methoxypyridazinium salts (**1**) were susceptible to nucleophilic substitution and the reaction with cyanide ion involved addition of the ion to α-position to the N-methoxy group, followed by loss of the methoxy group to give 3-cyanopyridazines. However, the yields of the products were relatively low.

On the other hand, it has also been known[8,9] that in the reaction of pyridazine N-oxides with Grignard reagents, ring fission of the pyridazine ring occurred, followed by elimination

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* Dedicated to the memory of Prof. Eiji Ochiai.

1) Part XXIV: H. Igeta, H. Arai, H. Hasegawa, and T. Tsuchiya, *Chem. Pharm. Bull.* (Tokyo), **23**, 2791 (1975).

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3) H. Igeta, T. Tsuchiya, and C-S. Kaneko, *Tetrahedron Letters*, **1971**, 2883; C-S. Kaneko, T. Tsuchiya, and H. Igeta, *Chem. Pharm. Bull.* (Tokyo), **21**, 1764 (1973).

4) C-S. Kaneko, T. Tsuchiya, and H. Igeta, presented at the 7th Congress of Heterocyclic Chemistry, Chiba, Japan November, 1974.

5) *a*) R.A. Abramovitch, S. Kato, and G.M. Singer, *J. Am. Chem. Soc.*, **93**, 3074 (1971); R.E. Manning and F.M. Schaefer, *Tetrahedron Letters*, **1975**, 213, and refs. cited therein.; *b*) R. Eisenthal and A.R. Katritzky, *Tetrahedron*, **21**, 2205 (1965).

6) E. Ochiai, "Aromatic Amine N-oxides," Elsevier, Amsterdam, 1967; A.R. Katritzky and J.M. Logowsky, "Chemistry of Heterocyclic N-oxides" Academic Press, New York, 1971.

7) *a*) H. Igeta, *Chem. Pharm. Bull.* (Tokyo), **11**, 1472 (1963); *b*) M. Ogata, *ibid.*, **11**, 1522 (1963).

8) H. Igeta, T. Tsuchiya, and T. Nakai, *Tetrahedron Letters*, **1969**, 2667.

9) G. Okusa, M. Kumagai, and T. Itai, *Chem. Commun.*, **1969**, 710.

of molecular nitrogen. Therefore, in expectation of similar reaction course, the reaction of the salts (**1**) with cyanide ion was re-examined to afford β-ethynylacrylonitriles as expected.[10]

The salts (**1a—e**), prepared from pyridazine 1-oxides and dimethylsulfate, were allowed to react with potassium cyanide in water–tetrahydrofuran at 0—5° for *ca.* 15 min, and then the mixtures were extracted with dichloromethane. Every salt gave a mixture of *trans* (**2**)- and *cis* (**3**)-β-ethynylacrylonitrile derivatives in 20—30% and 2—3% yields in cases of **1a—d**, and in 3% and 2% yields in case of **1e**, respectively. Besides, in case of **1a**, 1-phenyl-1,4-dicyano-1,3-butadiene (**4a**) was obtained in *ca.* 1% yield as a mixture (3: 2) of *cis*- and *trans*-isomers. Moreover, in cases of **1a** and **1b**, whose R^6 represented H, 3-phenyl-6-cyanopyridazine[7] (**5a**) and 3-methyl-6-cyanopyridazine (**5b**)[7] were obtained in 2—3% yields, respectively.

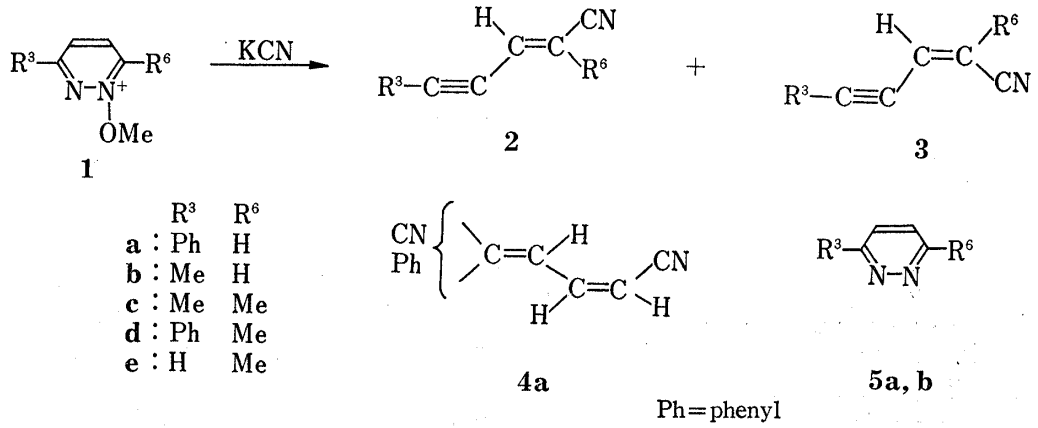


Chart 1

The prolonged reaction time resulted in a decrease of the formation of acetylenes (**2** and **3**) and an increase of the formation of 6-cyanopyridazine (**5**). In the event, the reaction at 0—5° for 30 min and then at room temperature for 30 min, followed by extraction, did not afford **3**, but gave **2** in *ca.* 10% and **5** in 20—25% yields, respectively.

Unsubstituted pyridazine 1-oxide did not afford any characteristic product, presumably due to the unstability of β-ethynylacrylonitrile thus formed and to the rapid polymerization even at room temperature, which was already known.[11]

The separation of *trans*- and *cis*-isomers (**2** and **3**) was so difficult that their physical and spectral data were measured in the state of mixture. The compounds (**2b** and **3b**) were known substances[12] and the structures of other compounds (**2** and **3**) were confirmed in comparison with spectral data[12] of analogous β-ethynylacrylonitrile derivatives, whose data were also taken in the state of mixtures. The formation ratio of the two kinds of isomers was calculated from the nuclear magnetic resonance (NMR) spectral data.

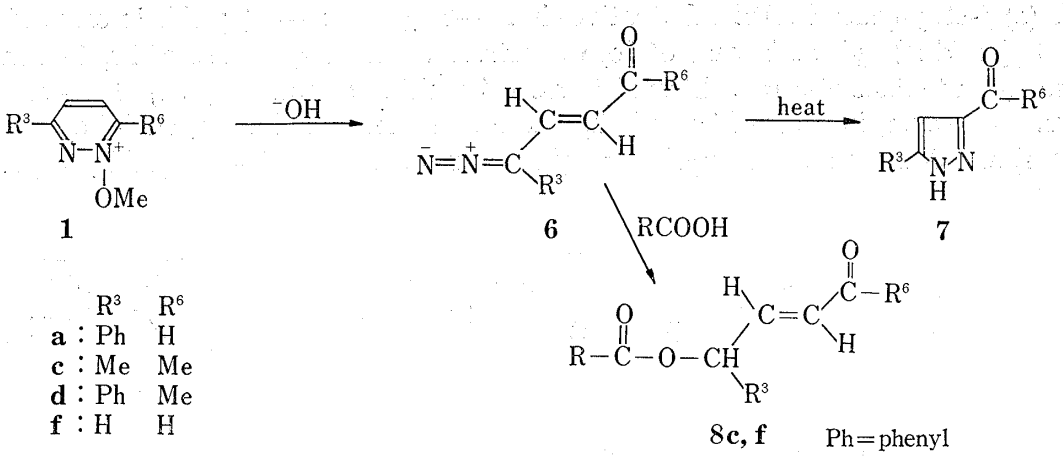
Structures of butadiene derivatives (**4a**) were confirmed in comparison with the spectral data[13] of the cyano substituted butadiene derivatives.

II. Reaction with Hydroxide Ion

N-Methoxypyridazinium methosulfates (**1a,c,d,f**) were allowed to react with potassium hydroxide in water at 0—5° for *ca.* 5 min, followed by extraction with ether or dichlorometh-

10) We have reported a part of the work in a preliminary communication; C-S. Kaneko, T. Tsuchiya, and H. Igeta, *Tetrahedron Letters*, **1973**, 2347.
11) M.P. Cava, M.J. Mitchell, D.C. DeJough, and R.Y. Van Fossen, *Tetrahedron Letters*, **1966**, 2947.
12) K.G. Golodva, S.I. Yakimovich, and F. Ya. Perveev, *Zh. Org. Khim.*, **8**, 2244 (1972).
13) J.H. Hall and E. Patterson, *J. Am. Chem. Soc.*, **89**, 5856 (1967); K. Nakagawa and H. Onoue, *Tetrahedron Letters*, **1965**, 1433.

ane. Evaporation of the extract under reduced pressure below room temperature[14] yielded vinyl diazomethane (**6**) in 70—90% yields. The β-aldehyde diazo compounds (**6a** and **6f**) were so stable that they were purified by column chromatography on alumina to give yellow liquids. However, the acetyl compounds (**6c** and **6d**) were relatively unstable and were decomposed or isomerized to give the pyrazoles during separation.



	R^3	R^6
a	Ph	H
c	Me	Me
d	Ph	Me
f	H	H

Chart 2

Infrared (IR) spectra of the products (**6**) exhibit common absorptions at around 2030—2080 cm^{-1} due to $C{=}N_2$ group. In the mass spectrum of **6**, the M−28 ($M-N_2$) ion constitutes the base peak. The assignment of a *trans* geometry to the olefin function of **6** is indicated by an H–H coupling constant of 16 Hz.

These spectral data are consistent with the proposed structure (**6**), which was also confirmed by the following chemical studies.

α,β-Unsaturated diazoalkanes are known[15] to undergo an intramolecular 1,3-dipolar cycloaddition, resulting in the formation of pyrazoles.

The diazo compounds (**6**) thus obtained were heated in benzene to give pyrazole-3-aldehydes (**7a,f**)[16] and 3-acetylpyrazoles (**7c,d**)[17] in 60—80% yields, respectively. The compounds (**6**) also readily reacted with carboxylic acids such as acetic acid in ether at a low temperature to give the corresponding esters (**8**) in moderate yields.

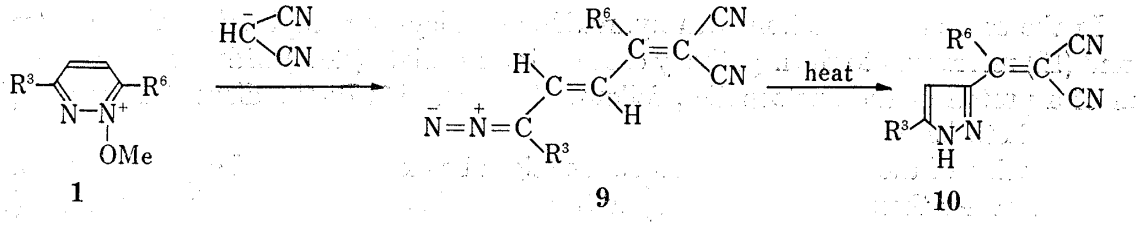
III. Reaction with Dicyanomethyl Anion

N-Methoxypyridazinium methosulfates (**1a,f**) were allowed to react with dicyanomethane in the presence of sodium bicarbonate[18] in water-tetrahydrofuran at 0—5° for *ca.* **15** min, followed by extraction with ether. Evaporation of the extract under reduced pressure below room temperature yielded 1,3-butadienyl diazomethanes (**9**) in *ca.* 80% yield, analogous to the case of the reaction with hydroxide ion.

IR spectra of the compound (**9**) show absorptions at 2200 and 2060 cm^{-1} due to CN and $C{=}N_2$ groups, respectively.

The compounds (**9**) were also readily isomerized by heating in benzene to give the corresponding 3-(2,2-dicyanoethynyl)-pyrazoles (**10**), whose structures were confirmed in comparison with the samples prepared by the method in the literature.[19]

14) A higher temperature resulted in the formation of pyrazole derivatives and in a decrease of the yield of the diazo compounds.
15) G.L. Closs, L.E. Closs, and W.A. Böll, *J. Am. Chem. Soc.*, **85**, 3796 (1963); R.H. Findlay and J.T. Sharp, *J.C.S. Chem. Comm.*, **1970**, 909; J.L. Brewbaker and H. Hart, *J. Am. Chem. Soc.*, **91**, 711 (1969).
16) R. Hüttel, *Chem. Ber.*, **74**, 1680 (1941).
17) W. Ried and J. Omran, *Chem. Ber.*, **96**, 144 (1963).
18) Any ring-opened product was not obtained in the reaction of the salt (1) with sodium bicarbonate under the condition.
19) J. Streith and J-M. Cassal, *C.R. Acad. Sc.* Paris, **264**, 1307 (1967).



a : R^3=Ph, R^6=H
f : R^3=R^6=H

Ph=phenyl

Chart 3

IV. Mechanism and Discussion

The results may be summarized by the mechanism outlined in Chart 4. The mechanism for the formation of the observed products involves the addition of the nucleophiles to the 6-position of the pyridazine ring and subsequent ring fission of the 1,6-dihydro compound (**11**) to form the ring-opened intermediate (**12**).

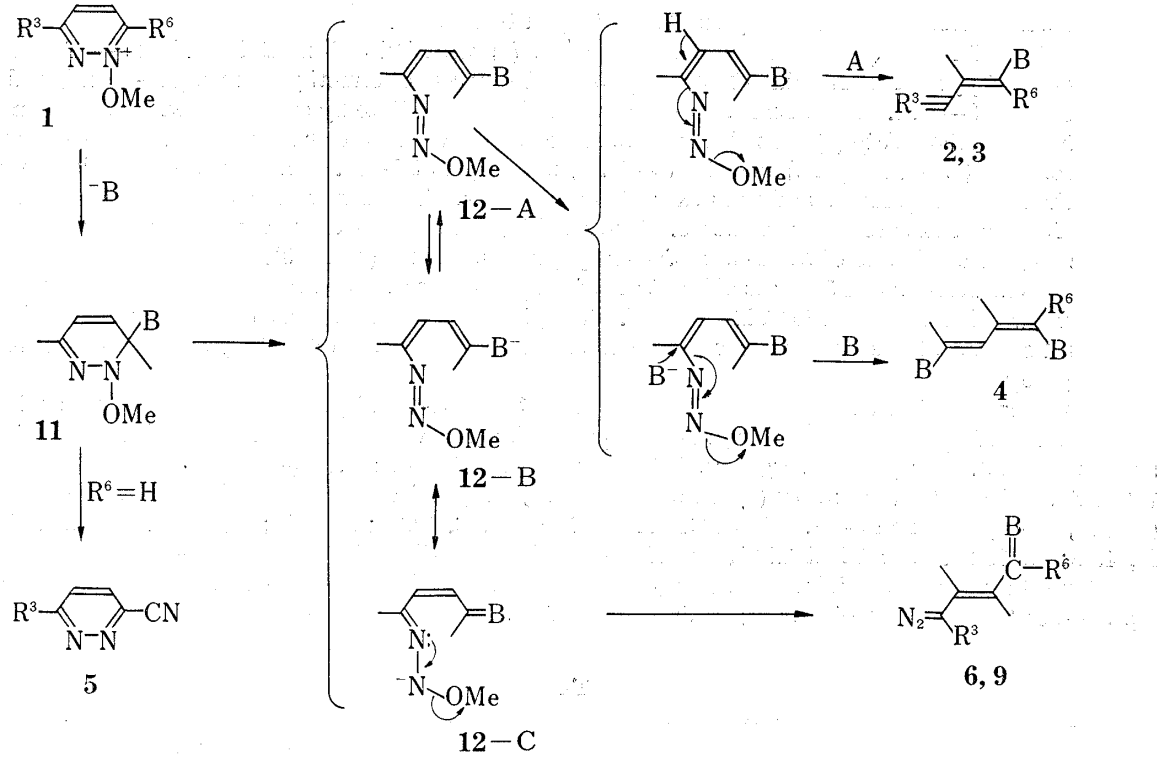


Chart 4

In the case of the reaction with cyanide ion, the intermediate (**12-A**) derived from **11** by Cope-rearrangement, gives rise to the vinyl acetylenes (**2** and **3**) *via* path A and the butadiene derivative (**4**) *via* path B, by analogy with the case[9] of the reaction of pyridazine N-oxides with Grrignard reagents.

As stated above, whereas the reaction for short time results in an increase of the formation of acetylenes, the prolonged reaction time results in a decrease of their formation and in turn, an increase of the formation of 3-cyanopyridazines. The reason might be as followed. The dihydro-intermediate (**11**) is relatively stable and is gradually converted into **5** in the reaction mixture. However, in case of the reaction for short time, extraction by dichloromethane results in the movement of unchanged dihydrocompound (**11**) into the solvent, followed by formation of acetylenes in the course of the treatment. This is confirmed by the fact that evolution of N_2 is observed during evaporation of the solvent.

In the case of the reaction with hydroxide and dicyanomethyl anion, the dihydro compound (**11**) rearranges to the negatively charged intermediate (**12-B**) with concomitant elimination of a proton of the nucleophiles, followed by formation of the diazo compounds (**6** and **9**) via the keto form (**12-C**).

Formation of the trans diazo compounds might be explained by the postulation of enolate (**12-B**) rather than keto form (**12-C**) as the predominant form of the intermediate (**12**) in alkaline solution, analogous to that observed in pyridine derivative.[5b]

To our knowledge, this is the first example of the isolation of a diazo compound in the reaction of pyridazine derivatives, although the intermediacy of similar diazo compounds has been observed in the photolyses of pyridazine N-oxides[20] and the related compounds,[21] in which the intermediates were confirmed only by the spectral experiments and not isolated.

Experimental

IR spectra were determined with a JASCO IR-1 spectrometer and mass spectra were recorded on a Hitachi RMS-4 instrument. NMR spectra were recorded on Hitachi R-20 and R-22 spectrometers using tetramethylsilane (TMS) as internal standard. NMR spectral assignment were confirmed by spin-decoupling experiments. Melting points were measured on a Yamato MP-1 apparatus and are uncorrected. Microanalyses were performed in the analytical laboratory of this school.

Reaction of 1-Methoxypyridazinium Methosulfate (1) with KCN General Procedure——To the corresponding parent pyridazine N-oxide (0.04 mole) was added excess of dimethyl sulfate (15—20 ml) and heated at 90—100° for 3—4 hr. After removal of unreacted dimethyl sulfate by extraction with ether, 1-methoxypyridazinium methosulfate (**1**) thus obtained was dissolved in water–tetrahydrofuran (1: 2, 50—60 ml) and a solution of KCN (1.5—2.0 equiv.) in water (3—5 ml) was added at 0—5°. The mixture was stirred for 5—10 min at the same temperature and then extracted with ether. The extract was dried over $MgSO_4$ and evaporated *in vacuo* below room temperature. The resulting residue was chromatographed over alumina with benzene to give a mixture of *trans*- and *cis*-*β*-ethynylacrylonitriles (**2** and **3**).

The separation of **2** and **3** was so difficult that their physical and spectral data were measured in the state of mixture, which are collected in Table I and II. The yields of **2** and **3** were calculated from the NMR spectral data. IR spectra of the products showed common absorptions (**2**: 2200—2100, **3**: 2100—2200 cm^{-1}) due to –CN group.

In the case of 3-phenylpyridazininium salt (**1a**), 1-phenyl-1,4-dicyano-1,3-butadienes (**4a**: mixture of two isomers on 1-position) and 3-phenyl-6-cyanopyridazine (**5a**) were obtained from the elution with benzene, besides **2** and **3**. **4a**: yield *ca.* 1%, mp 115—120° (from CCl_4), IR: 2115 (–CN) cm^{-1}, Mass Spectrum *m/e*: 180 (M^+), NMR δ (CD_3OD): 6.12 (2/5H, d J=11.0 Hz, 4-H) and 6.16 (3/5H, d J=11.0 Hz, 4-H), 7.3—7.8 (7H, m, Ph-H, 2-H, and 3-H). *Anal.* Calcd. for $C_{12}H_8N_2$: C, 79.98; H, 4.48; N, 15.55. Found: C, 79.80; H, 4.39; N, 15.35. **5a**: Yield 1.5%, mp 184—185° (from EtOH) (lit.[8b] mp 184.5—185.5°).

From 3-methylpyridazinium salt (**1b**), 3-methyl-6-cyanopyridazine (**5b**) was obtained. **5b**: Yield 3%, mp 89—90° (from benzene–iso-Pr_2O) (lit.[7b] mp 90—91°).

Table I

Mixture of 2 and 3	bp °C/5 mmHg (bath temp.)	Formula(*m/e* M^+)	Analyses (%) Calcd. C	H	N	Found C	H	N
a	135—140	$C_{11}H_7N$ (153)	86.25	4.61	9.15	85.99	4.42	8.85
b	45— 50	C_6H_5N (91)	79.09	5.53	15.38	78.95	5.41	15.21
c	50	C_7H_7N (105)	79.96	6.71	13.32	79.75	6.58	13.29
d	155—160	$C_{12}H_9N$ (167)	86.20	5.43	8.38	86.01	5.33	8.31
e	45— 50	C_6H_5N (91)	79.09	5.53	15.38	79.00	5.43	15.30

20) K.B. Tomer, N. Harrit, I. Rosenthal, O. Buchardt, P.L. Kumler, and D. Creed, *J. Am. Chem. Soc.*, **95**, 7402 (1973); T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron*, **29**, 2747 (1973).

21) T. Tsuchiya, H. Arai, and H. Igeta, *J.C.S. Chem. Comm.*, **1972**, 1059; *idem*, *Chem. Pharm. Bull.* (Tokyo), **21**, 2517 (1973); H. Arai, H. Igeta, and T. Tsuchiya, *J.C.S. Chem. Comm.*, **1973**, 521.

TABLE II. Yields and NMR Spectral Data of the Compounds (2 and 3)

δ in $CDCl_3$, J=Hz, $-\overset{4}{C}\equiv\overset{3}{C}-\overset{2}{C}=\overset{1}{C}<$

	trans-isomer (2)		*cis*-isomer (3)	
	Yield	δ	Yield	δ
a	27	11-H(5.62, d), 2-H(6.60, d), Ph-H(7.33, m), $J_{1,2}$=18.0	2	1-H(5.52, d), 2-H(6.40, d), Ph-H(7.21, m), $J_{1,2}$=11.0
b	30	1-H(5.52, d), 2-H(6.31, dq), CH_3(2.02, d), $J_{1,2}$=11.0, $J_{2,4}$=2.5	1	1-H(5.50, d), 2-H(6.26, dd), CH_3(2.04, d), $J_{1,2}$=11.0, $J_{2,4}$=2.5
c	21	2-H(6.10, m), CH_3(2.06, m)	3	2-H(5.98, m), CH_3(2.05, m)
d	20	2-H(6.26, m), CH_3(2.09, d, J1.5), Ph-H(7.30, m)	3	2-H(6.06, m), CH_3(2.00,d, J=2.0), Ph-H(7.25, m)
e	3	2-H(6.05, m), 4-H(3.73, br. d, J=2.5), CH_3(2.00, d, J=1.6)	2	2-H(5.96, m), 4-H(3.47, br. d, J=2.5), CH_3(1.93, d, J=2.5)

Reaction of 1-Methoxypyridazinium Methosulfate (1) with KOH——General Pracedure: The salt (**1a, c, d, f**) prepared from the parent pyridazine N-oxide (0.02 mole) according to the general procedure for the reaction with KCN, was dissolved in water (80 ml) and a solution of KOH (1.5 equiv.) in water (2—4 ml) was added at 0—5°. The mixture was stirred for 5 min at the same temperature and then extracted with cold ether. The extract was dried over $MgSO_4$ and evaporated *in vacuo* below room temperature to give vinyl diazomethane derivative (**6**) as unstable yellow liquid in 70—80% yield.

The products (**6a** and **6f**) could be purified by chromatography over alumina with benzene in 20—30% yield, but **6c** and **6d** could not be purified due to the rapid isomerization to the pyrazoles (**7**) during separation. Therefore, the structures of **6c** and **6d** were confirmed by the chemical studies described below.

β-Formylvinyl-phenyldiazomethane (**6a**): IR (liq.): 2030 (C=N_2), 1658 (C=O) cm^{-1}, λ_{max}^{EtOH}: 353 nm, Mass Spectrum *m/e*: 172 (M^+), 144 (M–N_2), NMR δ ($CDCl_3$): N_2=C–C=C–CHO: 5.95 (dd, 3-H), 7.3 br (5H, Ph-H), 7.58 (d, 2-H), 9.59 (d, 4-H), $J_{2,3}$=16.0, $J_{3,4}$=7.5 Hz.

β-Formylvinyl-diazomethane (**6f**): IR (liq.): 2080 (C=N_2), 1648 (C=O) cm^{-1}, λ_{max}^{EtOH}: 325 nm, Mass Spectrum *m/e*: 96 (M^+), 68 (M–N_2), NMR δ (CCl_4): 5.18 (d, 1-H), 5.83 (dd, 3-H), 7.03 (dd, 2-H), 9.32 (d, 4-H), $J_{1,2}$=9.0, $J_{2,3}$=16.0, $J_{3,4}$=7.5 Hz.

Thermal Isomerization of Vinyl Diazomethanes (6) to 3-Acylpyrazoles (7)——A solution of **6** (*ca.* 0.1 g) dissolved in benzene was refluxed for 20 min. After removal of the solvent *in vacuo*, the residue was recrystallized to give the corresponding pyrazole (**7**) in *ca.* 60—80% yield.

5-Phenylpyrazole-3-aldehyde (**7a**): Yield 80%, colorless needles, mp 180—182° (from EtOH), Mass Spectrum *m/e*: 172 (M^+), NMR δ (CF_3COOH): 7.49 (s, 4-H), 7.51—7.90 (5H, m, Ph–H), 10.10 (s, CHO). *Anal.* Calcd. for $C_{10}H_8ON_2$: C, 69.75; H, 4.68; N, 16.27. Found: C, 69.51; H, 4.61; N, 16.18.

3-Acetyl-5-methylpyrazole (**7c**): Yield 70%, colorless needles, mp 98—99° (from pet. ether), IR (KBr): 3270, 1663 cm^{-1}. Mass Spectrum *m/e*: 124 (M^+), NMR δ ($CDCl_3$): 6.57 (s, 4-H), 2.35 (s, 5-CH_3), 2.56 (s, $COCH_3$). *Anal.* Calcd. for $C_6H_8ON_2$: C, 58.05; H, 6.50; N, 22.57. Found: C, 58.06; H, 6.27; N, 22.53.

3-Acetyl-5-phenylpyrazole (**7d**): Yield 60%, colorless needles, mp 153.5—154° (from benzene) (lit.[17] mp 154°), IR (KBr): 3205, 1660 cm^{-1}, Mass Spectrum *m/e*: 186 (M^+), NMR δ ($CDCl_3$): 2.63 (s, $COCH_3$), 7.03 (s, 4-H), 7.26—7.81 (5H, m, Ph–H). *Anal.* Calcd. for $C_{11}H_{10}ON_2$: C, 70.95; H, 5.21; N, 15.05. Found: C, 70.58; H, 5.40; N, 15.21.

Pyrazole-3-aldehyde (**7f**): Yield 80%, colorless needles, mp 149—150° (from water), NMR δ (CF_3COOH): 7.38 (d, 4-H), 8.30 (d, 5-H), 10.14 (s, CHO), J=2.5 Hz. This compound was identified with an authentic sample prepared according to the method described in the literatures.[16,22]

Reaction of Vinyl Diazomethanes (6) with Acetic Acid——To a solution of **6c, f** (0.1—0.2 g) in ether (20 ml), a solution of AcOH (1 ml) in ether (3—5 ml) was added under stirring at room temperature. After an additinal stirring for 1 hr, the mixture was evaporated *in vacuo*. The residue thus obtained was chromatographed over alumina and elution with benzene gave the ester (**8c, f**) as colorless liquid, which was purified by distillation under reduced pressure.

Ester (**8c**): Yield *ca.* 40%, bp 90—91°/2 mmHg (bath temp.), IR (liq.): 1745 (C=O), 1683 (C=O) cm^{-1}, Mass Spectrum *m/e*: 156 (M^+), NMR δ ($CDCl_3$): 1.40 (d, 1-CH_3), 2.06 (s, CH_3COO–), 2.21 (s, $COCH_3$), 5.49 (dq, 1-H), 6.09 br (d, 3-H), 6.63 (dd, 2-H), $J_{1,2}$=5.0, $J_{2,3}$=16.0, $J_{1,\ CH_3}$=7.0 Hz. *Anal.* Calcd. for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.31; H, 7.68.

Ester (**8f**): Yield *ca.* 80%, bp 84°/1.6 mmHg (bath temp.), IR (liq.) 1748 (C=O), 1695 (C=O) cm^{-1}, Mass Spectrum *m/e*: 128 (M^+), NMR δ ($CDCl_3$): 2.15 (s, $COCH_3$), 4.38 (dd, 1-H), 6.24 (ddt, 3-H), 6.88 (dt, 2-H),

22) L.T. Winters, N.G. Smith, and M.I. Cohen, *Chem. Commun.*, **1970**, 642.

9.57 (d, 4-H), $J_{1,2}=4.0$, $J_{1,3}=1.5$, $J_{2,3}=16.0$, $J_{3,4}=8.0$ Hz. *Anal.* Calcd. for $C_6H_8O_3$: C, 56.24; H, 6.29. Found: C, 56.12; H, 6.11.

Reaction of Methoxypyridazinium Methosulfate (1) with Dicyanomethyl Anion——The salt (**1a, f**) prepared from the parent pyrdazine N-oxide (0.02 mole) according to the general procedure for the reaction with KCN, was dissolved in water (60 ml) and a solution of dicyanomethane (1.0 equiv.) in tetrahydrofuran (5 ml) was added at 0—5°. To the mixture was added saturated aqueous solution of $NaHCO_3$ until the value of pH of the reaction solution became 8, and the mixture was stirred at the same temperature for further 15 min and then was extracted with ether.

The extract was dried over $MgSO_4$ and evaporated *in vacuo* below room temperature, to give 1-diazomethyl-4,4-dicyano-1,3-butadiene derivative (**9a, f**). which also unstable and was readily isomerized to the corresponding pyrazole (**10**), so it could not be purified.

9a: Yield 70—80%, red crystals, IR (KBr): 2205 (CN), 2060 (C=N_2) cm^{-1}, Mass Spectrum *m/e*: 220 (M^+), 192 (M–N_2), NMR δ ($CDCl_3$): 6.46 (dd, 3-H), 7.20 (d, 2-H), 7.53 (d, 4-H), 7.35 br (5H, Ph–H), $J_{2,3}=14.0$, $J_{3,4}=12.0$ Hz.

9f: Yield *ca.* 80%, yellow liquid, IR (KBr): 2200 (CN), 2062 (C=N_2) cm^{-1}, NMR δ ($CDCl_3$): 5.28 (d, 1-H), 6.32 (dd, 3-H), 6.96 (dd, 2-H), 7.40 (d, 4-H), $J_{1,2}=9.5$, $J_{2,3}=14.0$, $J_{3,4}=12.0$ Hz.

Thermal Isomerization of Diazomethanes (9) to Pyrazoles (10)——A solution of **9a, f** (0.1 g) dissolved in benzene was heated until yellow or red color of the solution changed to colorless (**9a**: 30°, 30 min, **9f**: 80°, 1 hr). After removal of th esolvent *in vacuo*, the resulting residue was recrystallized from benzene to give pyrazole derivative (**10**) in almost quantitative yield.

10a: Colorless needles, mp 188—189°, IR (KBr): 3320 (NH), 2239 (CN) cm^{-1}, Mass Spectrum *m/e*: 220 (M^+), NMR δ (CD_3OD): 7.25—7.40 (2H, m, Ph–H), 7.40—7.60 (4H, m, Ph–H and 4-H), 8.17 (s, –CH=C$(CN)_2$). *Anal.* Calcd. for $C_{13}H_8N_4$: C, 70.89; H, 3.66; N, 25.44. Found: C, 70.75; H, 3.63; N, 25.39.

10f: Colorless needles, mp 178—179°, IR (KBr): 3280 (NH), 2238 (CN) cm^{-1}, Mass Spectrum *m/e*: 144 (M^+), NMR δ (CD_3OD): 7.25 (d, 4-H), 7.74 (d, 5-H), 8.02 (s, –CH=C$(CN)_2$), $J_{4,5}=2.5$ Hz. *Anal.* Calcd. for $C_7H_4N_4$: C, 58.33; H, 2.80; N, 38.87. Found: C, 58.30; H, 2.81; N, 38.77. This compound was identified with the sample prepared from pyrazole-3-aldehyde (**7f**) according to the method of Streith, *et al.*[19]