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Studies on Pyridazines. XXI.[1] Reaction of 1-Methylpyridazinium Salts with Potassium Cyanide

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The reactions of the methosulfates of pyridazines with KCN were carried out. Pyridazine (Ia), 3-methyl- and 3-methoxy-pyridazine (Ib and Ic) afforded two kinds of dimers (II and III), respectively. 3-Phenylpyridazine (Ih—j) afforded 4-cyano-1,4-dihydro compounds (XIV) as main products, along with small amounts of various kinds of cyano substituted monomers.

Other kinds of pyridazines (Id, f, g, and k) did not afford II, III, and XIV, but various kinds of monomers (IV, V, VI, VII, VIII, IX, XV, and XVI) in general. The mechanisms of their formations were also discussed.

Concerning the reaction of quaternary salts of pyridazines with cyanide anion, 3-substituted pyridazine 1-oxides were allowed to react with KCN *via* their methosulfates, affording the corresponding 3-substituted-6-cyanopyridazines.[3] And from 3,3′-bipyridazine 1,1′-dioxides, 6,6′-dicyano-1,1′,6,6′-tetrahydro compounds[4] were obtained, suggesting that α-position to the N-oxide group is sensitive to introduce cyano group. But, as for pyridazines themselves, only one report[4] has been published, describing the reaction of the 3,3′-dimers with cyanide anion to give 1,1′,4,4′-tetrahydro compounds having cyano groups at 4,4′-positions (γ-positions). These findings prompted us to investigate the reaction of various monomeric pyridazines, on which we now report.

Pyridazine (I) was methylated[5] with excess of dimethyl sulfate, followed by removal of excess of the reagent by extraction with ether. The quaternary salt thus obtained was dissolved in water, and saturated aqueous solution of KCN was added dropwise under stirring and ice cooling. Stirring was continued for further 5—10 min, followed by extraction with CH_2Cl_2. The products were separated by column chromatography.

Unsubstituted-, Methyl- and Methoxypyridazines

From Pyridazine (Ia), 3-methylpyridazine (Ib), and 3-methoxypyridazine (Ic), two kinds of dimers (II and III)[6] were obtained in 10—20% and 2—5% yields, respectively. Besides them, from Ia, 6-cyano-1-methyl-4(1H)pyridazinone (IVa) [δ[7]: 3.83 (s, 1-CH_3), 7.61 (d, 5-H), 7.86 (d, 3-H), $J_{3,5}$=4.8 cps] was obtained, and from Ib, similarly the compound (IVb) [δ: 2.35 (s, 3-CH_3), 3.75 (s, 1-CH_3), 7.51 (s, 5-H)] was obtained in 1—2% yields, respectively. But, from Ic, besides the dimers, any characteristic product was not obtained.

In cases of 4- and 5-substituted compounds, *i.e.*, 4-methylpyridazine (Id) and 4,5-dimethylpyridazine (Ie), any dimer was not obtained. But, from Id, 6-cyano-1,5-dimethyl-4(1H)-pyridazinone (IVd) [δ: 2.40 (s, 5-CH_3), 3.73 (s, 1-CH_3), 7.66 (s, 3-H)] was obtained in 5% yield. From Ie, any characteristic product was not obtained.

1) Part XX: H. Igeta, T. Tsuchiya, C. Kaneko, and S. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **21**, 125 (1973).
2) Location: *1–5–8, Hatanodai, Shinagawa-ku, Tokyo.*
3) H. Igeta, *Chem. Pharm. Bull.* (Tokyo), **11**, 1472 (1963); M. Ogata, *ibid.*, **11**, 1522 (1963).
4) H. Igeta, T. Tsuchiya, C. Okuda, and H. Yokogawa, *Chem. Pharm. Bull.* (Tokyo), **19**, 1297 (1971).
5) H. Lund and P. Lund, *Acta Chem. Scand.*, **21**, 1067 (1967).
6) We have reported the formation of the dimers in a preliminary communication; H. Igeta, T. Tsuchiya, and C. Kaneko, *Tetrahedron Letters*, **1971**, 2883.
7) 60 Mc in $CDCl_3$ with TMS as internal reference in all cases.

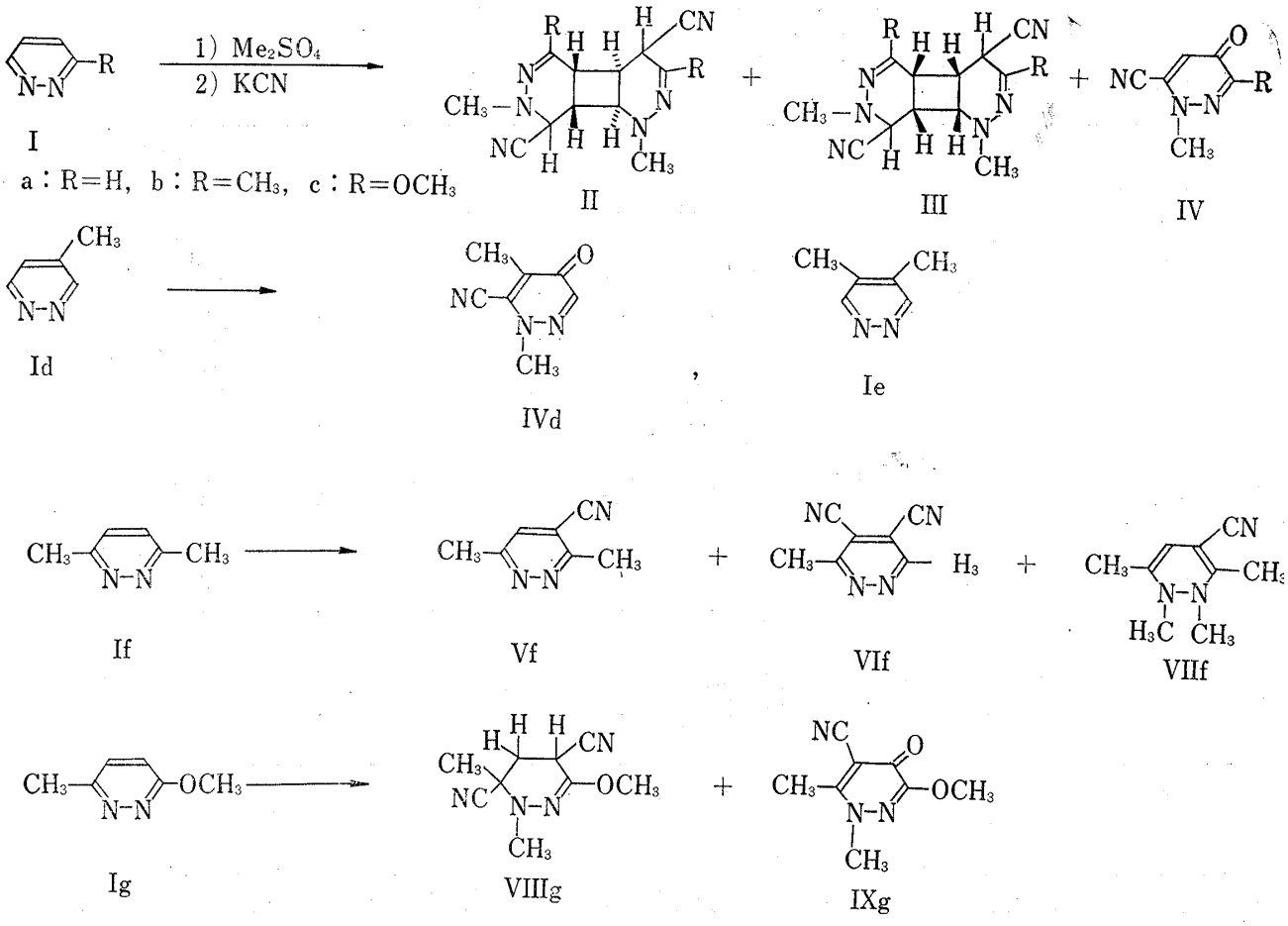


Chart 1

From 3,6-disubstituted pyridazines, the compounds seem to be dimers were recognized in gas-liquid chromatography (GLC) but could not be isolated and identified. Thus, 3,6-dimethylpyridazine (If) afforded 4-cyano-3,6-dimethylpyridazine (Vf) [δ: 2.84 (s, 3-CH_3), 2.96 (s, 6-CH_3), 7.70 (s, 4-H)], in *ca.* 1% yield, 4,5-dicyano-3,6-dimethylpyridazine (VIf) [δ: 3.12 (s, 6H, 3- and 6-CH_3)], in 1% yield, and 4-cyano-1,2,3,6-tetramethyl-1,2-dihydropyridazine (VIIf) [δ: 2.25 (s, 3H, 6-CH_3), 2.38 (s, 3H, 3-CH_3), 2.96 (s, 6H, 1- and 2-CH_3), 5.80 (s, 1H, 4-H)] in 0.2% yield. 3-Methoxy-6-methylpyridazine (Ig) afforded 4,6-dicyano-1,6-dimethyl-3-methoxy-1,4,5,6-tetrahydropyridazine (VIIIg) [δ: 1.58 (s, 6-CH_3), 2.40 (m, 2H, 5-H_2), 2.80 (s, 1-CH_3), 3.48 (m, 1H, 4-H), 3.75 (s, 3-OCH_3)], in *ca.* 1% yield, and 5-cyano-1-methyl-4(1H)pyridazinone derivative (IXg) [δ: 2.95 (s, 6-CH_3), 3.85 (s, 1-CH_3), 3.91 (s, 3-OCH_3)], in 1.5% yield, and any other characteristic product was not isolated.

Spectral data of the dimers are shown in Table I, indicating the coupling of two molecules of the cyanated compounds of 1-methyl-pyridazines to form the dimers, which are inferred from the values of elementary analyses and molecular weight determinations. Their infrared (IR) spectra exhibit the common absorptions at 2240—2260 cm^{-1} due to cyano group, and 850—950 cm^{-1} due to the cyclobutane ring.[8] Moreover, the spectra of nuclear magnetic resonance (NMR) also support the correctness of the structures of the dimers having the cyclobutane rings.

If the cyano substituted dihydro compounds are allowed to dimerize at 5- and 6- or 4- and 5-positions, similar to the photodimerization, the structures of the dimers should be X and XI. In these cases, the coupling of either "head to head" or "head to tail" should

8) D. Valentine, N.J. Turro Jr., and G.S. Hammond, *J. Am. Chem. Soc.*, **86**, 5202 (1964).

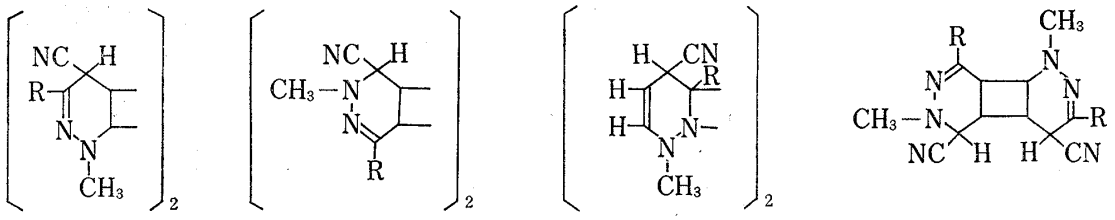
Table I. NMR Spectral Data[a] of Dimers, II and III, δ ($CDCl_3$)

Dimers		mp (°C)	N-CH_3 1 and 1′	H_6 and H_6'	H_4 and H_4'	H_5 and H_5'	Miscellaneous
							H_3 and H_3'
a	II	162—163	3.08, 2.99	3.98, b[b] mc 3.47 d, J=6.0	2.7—3.2 bmc	1.8—2.3 mc	6.75, 7.11 d.d, s J=1.2, 6.0
	III	151—152	3.05, 2.97	3.89, mc 3.81 mc	2.8—3.2 mc	2.0—2.2 mc	7.69, 7.90 d, d, J=4.0 J=4.0
							3- and 3′-CH_3
b	II	174—175	2.97, 2.87	3.90, bmc 3.60 d, J=5.0	3.0, mc 2.65 bmc	1.6—2.2 mc	2.12, 1.90 s s
	III	155—156	3.09, 2.92	3.91, d, J=2.0 3.52 bmc	2.9—3.2 mc	1.6—2.4 mc	2.55, 1.96 s s
							3- and 3′-OCH_3
c	II	194—195	2.88, 2.83	3.89, mc 3.71 mc	3.18, d.d, J=2.0, 5.0 2.45 bmc	1.6—1.8 mc	3.78, 3.67 s s
	III	175—176	2.78, 2.68	3.98, d, J=2.0 3.98 mc	3.05, mc 2.6—2.9 bmc	1.9—2.1 mc	3.79, 3.60 s s

a) 60 M/C with TMS as internal reference Coupling constants are expressed in Hz.
b) broad

result in the formation of symmetric compounds, whose chemical shifts of the N-CH_3, two CH_3- and CH_3O- groups must be coincidental of each other. Thus, these structures (X and XI) are denied. When the dimerization occurs at 2- and 3-positions to form the compound (XII), there must be protons attached to the carbon-carbon double bond. So the structure (XII) should also be abandoned from the NMR spectral data.

The structure (XIII), in which 4- and 6′-positions and 5- and 5′-positions are bonded to each other, can not be excluded from the NMR spectral data.



X XI XII XIII

Chart 2

But, from the mechanistic consideration, the dimer formed by bonding 4- and 5′-positions to each other, is more plausible. And the major product seems to be *anti*-dimer, and the minor product seems to be *syn*-dimer. However, this isomerism is not still definite from the present data.

The signals of NMR spectra are shown in Table I, and their assignments are reasonable. High field shifts of H_5- and H_5'-protons seem to be due to the effect of the cyano groups.

As for monomers, they exhibit absorptions at around 2240 cm^{-1} due to cyano groups. The compound (IV) exhibit absorption at 1660 cm^{-1} due to carbonyl group. NMR spectral, Mass spectrometric, and analytical data also support the correctness of the compounds (V, VI, VII, VIII, and IX).

3-Phenylsubstituted Pyridazines

3-Phenylpyridazines did not afford any dimer, but gave Reissert like dihydro compounds. Thus, 3-phenylpyridazine (Ih), 5-methyl-3-phenylpyridazine (Ii), and 6-methyl-3-phenylpyridazine (Ij) afforded 4-cyano-1,4-dihydropyridazines (XIV) in *ca.* 80% yield, respectively. Since these dihydro compounds gradually decomposed during separation by column chromatography and recrystallization, they could not be obtained as pure crystals except for XIVi. In IR spectra, they exhibit absorptions at 2220 cm^{-1} due to cyano groups, and their structures were inferred from mass spectrometric, analytical, and NMR spectral data (Table II).

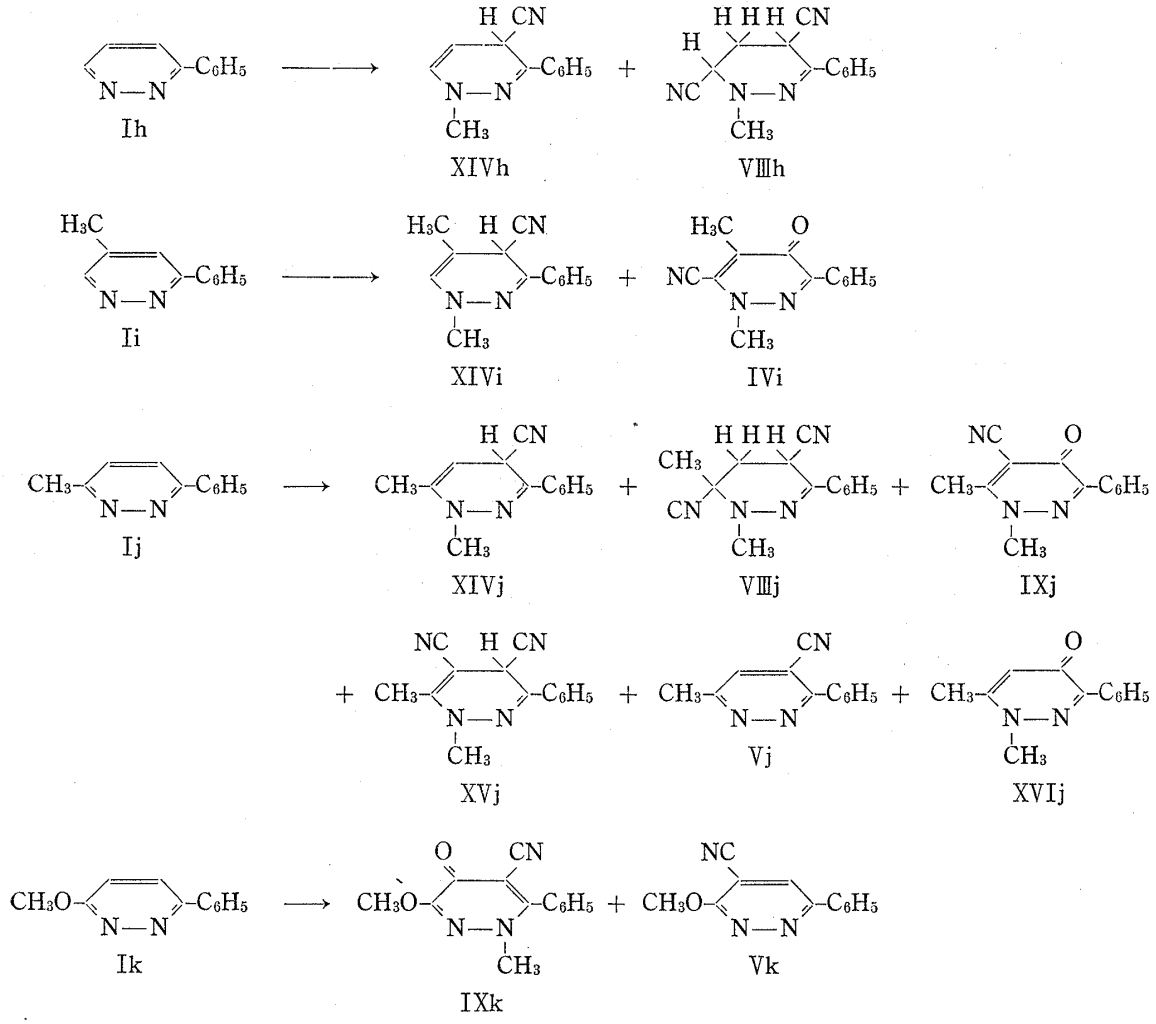


Chart 3

TABLE II. NMR Spectral Data of Dihydro Compounds (XIV)

Compound	4-H	5-H	6-H	N-CH_3	C-CH_3	C_6H_5
XIVh	4.65	4.72	6.40	3.38	—	7.3—7.9
XIVi	4.36	—	6.12	3.36	1.85	7.3—7.9
XIVj	4.40	4.52	—	3.26	1.76	7.1—7.7

$J_{4,5}=7.2$, $J_{5,6}=6.0$, $J_{4,6}=1.2$, $J_{6\text{-H},5\text{-CH}_3}=1.8$. (cps): δ ($CDCl_3$).

In all cases of 3-phenylpyridazines, other products were also recognized by Thin-layer chromatography (TLC), and GLC, but were hardly identified on account of small amounts except for the following substances. Namely, from Ih, similar to the case of Ig, dicyano-

tetrahydro compound (VIIIh) [δ: 2.65 (m, 2H, 5-H_2), 3.10 (s, 3H, 1-CH_3), 3.90 (m, 1H, 6-H), 4.00 (m, 1H, 4-H), 7.10—7.85 (m, 5H, C_6H_5)], 2%, was obtained. From Ii, similar to the case of Ia, Ib, and Id, 6-cyano-4(1H)pyridazinone derivative (IVi) [δ: 2.53 (s, 3H, 5-CH_3), 3.86 (s, 3H, 1-CH_3), 7.3—8.0 (m, 5H, C_6H_5)], 5%, was obtained. From Ij, dicyano-tetrahydro compound (VIIIj) [δ: 1.66 (s, 3H, 6-CH_3), 2.23 and 2.67 (q. each 1H, 5-H_2), 3.18 (s, 3H ,1-CH_3) 3.90 (q. 1H, 4-H), 7.25—7.9 (m, 5H, C_6H_5)], 2%, 5-cyano-1,6-dimethyl-3-phenyl-4(1H)pyridazinone (IXj) [δ: 2.59 (s, 3H, 6-CH_3), 3.93 (s, 3H, 1-CH_3), 7.3—8.3 (m, 5H, C_6H_5)], 5%, 4,5-dicyano-1,6-dimethyl-3-phenyl-1,4-dihydropyridazine (XVj) [δ: 2.35 (s, 3H, 6-CH_3), 3.61 (s, 3H, 1-CH_3), 4.87 (s, 1H, 4-H), 7.3—7.9 (m, 5H, C_6H_5)], 1%, 4-cyano-6-methyl-3-phenylpyridazine (Vj) [δ: 2.85 (s, 3H, 6-CH_3), 7.60 (s, 1H, 5-H)], 0.5%, and 1,6-dimethyl-3-phenyl-4(1H)pyridazinone (XVIj) [δ: 2.22 (s, 3H, 6-CH_3), 2.89 (s, 3H, 1-CH_3), 7.2—8.2 (m, 5H, C_6H_5)], 0.8%, were obtained.

6-Methoxy-3-phenylpyridazine (Ik) did not afford the dihydro compound (XIV), but gave 5-cyano-4(1H)pyridazinone (IXk) [δ: 4.00 (s, 3H, 1-CH_3), 4.02 (s, 3H, 3-CH_3), 7.3—7.7 (m, 5H, C_6H_5)], 5%, and 5-cyanopyridazine derivative (Vk) [δ: 4.35 (s, 3H, 6-OCH_3), 8.02 (s, 1H, 4-H), 7.5—8.1 (m, 5H, C_6H_5)], 1%. Structures of these products were reasonably accounted for their formulations from IR spectral, NMR spectral, and analytical data.

Mechanism and Discussion

It is well known[9] that the reaction of the quaternary salts of aromatic amines and their N-oxides with base generally afford the Reissert like dihydro compounds. As for pyridazines, in the case of 3,3′-bipyridazines, the dihydro compounds were isolated.[4]

Concerning the N-oxides, in the case of this reaction and the reaction with organometallic compounds, the dihydrocompounds were considered to be the intermediates[10] of the reactions.

3-Phenylpyridazines (Ih—j) afforded 1,4-dihydro compounds [(XIV) (Ih—j) afford 1,4-dihydro compounds (XIV)] in considerable yields, owing to the stabilizing effect of the phenyl groups. But these products were still relatively unstable in solvent and in the course of purification on alumina. In other cases, the products were more unstable and decomposed to a great extent, since N-substituted groups were not easily eliminated and accordingly the aromatization was hindered.

Concerning the formation of the dimers (II and III), the same result was obtained in dark room, suggesting the dimerization is not due to the photo-sensitized reaction, but to thermal reaction.

Thus, the following mechanism can be proposed as the most reasonable.

4-Cyano-dihydro compound (**1**) couples with the quaternary salt (**2**) at the 4-position to form the compound (**3**), followed by the formation of the cyclobutane ring (**4**) and the addition of the cyanide anion. When **1** couples with **2** at the 6-position, the compound (XIII) will be formed, but this has been formerly denied.

As for the formation of stereoisomers, the intermediate compound (**3**) has a possibility of being two kinds of stereoisomers, (**5** and **6**). The compound (**5**) is capable to joint after rotation of the half moiety of the molecule by 180°, forming the *syn*-dimer (III). The relative configuration of CN and N-CH_3 groups is uncertain from the present data. Accordingly, the possibility can not be excluded that two kinds of dimers are stereoisomers in regard to CN groups of the *syn*-dimer (III), although it is denied from NMR spectral data to be stereoisomer of the anti-dimer (II). In order to clarify the definite correlation between two kinds of the dimers in question, the examination by X ray analysis is now being undertaken.

9) T. Okamoto and H. Tani, *Chem. Pharm. Bull.* (Tokyo), **7**, 925 (1959); T. Kato and H. Yamanaka, *J. Org. Chem.*, **30**, 910 (1965).

10) R.L. Letsinger and R. Lasco, *J. Org. Chem.*, **21**, 812 (1956); I. Crossland, *Acta Chem. Scand.*, **16**, 1877 (1962), **22**, 2700 (1968); H. Igeta, T. Tsuchiya, and T. Nakai, *Tetrahedron Letters*, **1969**, 2667.

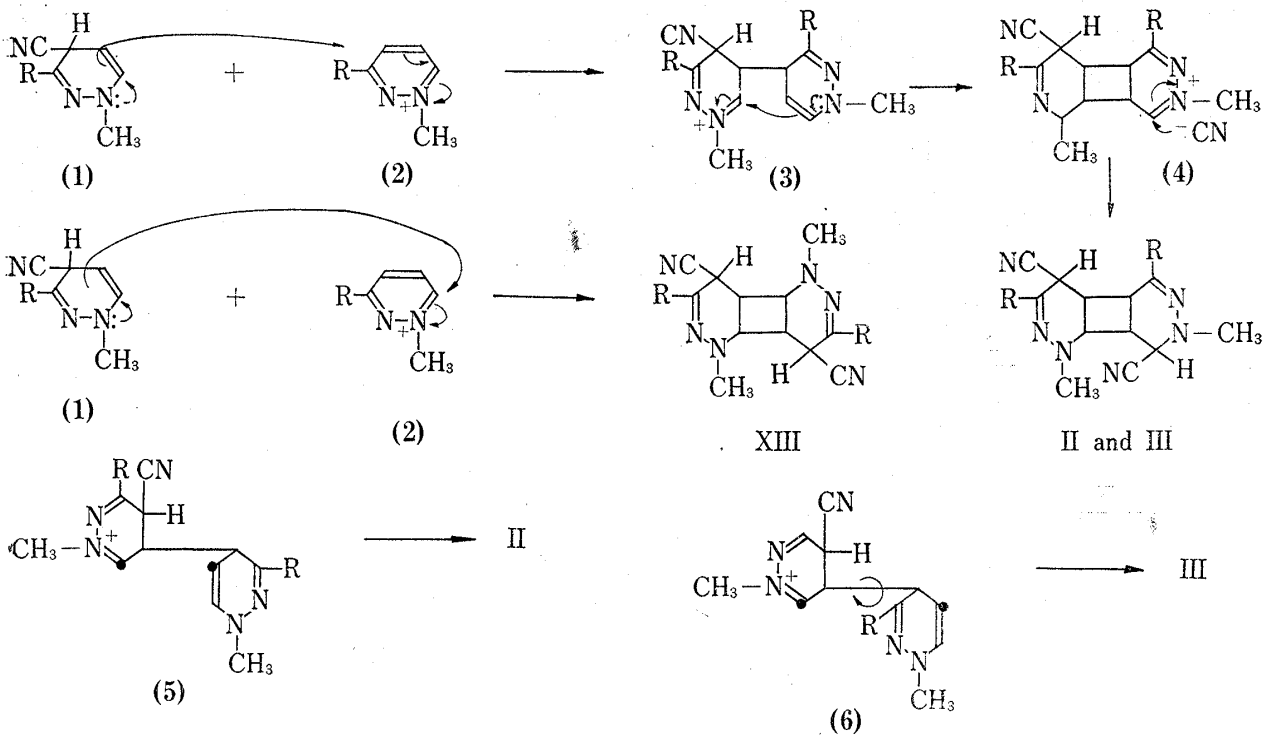


Chart 4

On the formation of dimers having the cyclobutane rings, many reports have been published, most of which concerned the photosensitized dimerization. In the case of the Reissert compound of quinoline, photochemical formation of the dimers has been reported.[11] And the reaction of pyridinium salts[12] with cyanide anion afforded the dimer, 1,1′-dihydro-4,4′-biphenyl, in which no cyano group was added. Furthermore, 1,2-dihydro compound, derived from 4-cyanopyridinium by reduction with $NaBH_4$, afforded[13] two kinds of dimers. Thus, it is interesting that aromatic amines afford the dimer having the cyclobutane ring by the thermal reaction.

Concerning the formation of the monomers, Kaufmann, *et al.*[14] reported the formation of 4-cyanoquinoline from quinoline methiodide and Janzen, *et al.*[15] reported that of N-methylacridone from acridine methiodide, explaining the formation of them by oxidation of the intermediate dihydro compound with oxygen.

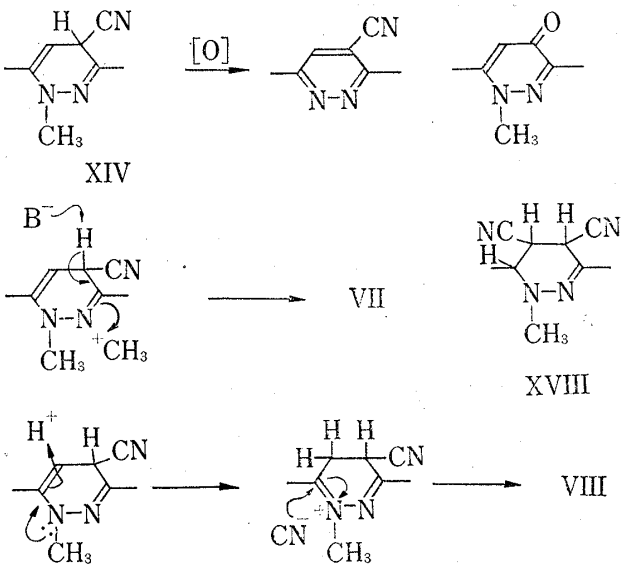


Chart 5

In the present work, the formation of 4-cyanopyridazine (V) and 4(1H)pyridazinone (XVI) is considered to be the same case. 1,2-Dimethyl-1,2-dihydro compound (VII) might

11) P.T. Izzo and A.S. Kende, *Tetrahedron Letters*, **1966**, 5731.
12) L.T. Winters, N.G. Smith, and M.I. Cohen, *Chem. Commun.*, **1970**, 642.
13) F. Liberatore, A. Casini, V. Carelli, A. Arone, and R. Mondelli, *Tetrahedron Letters*, **1971**, 3829.
14) A. Kaufmann, *Chem. Ber.*, **51**, 116 (1918).
15) J.W. Happ, E.G. Janzen, and B.C. Rudy, *J. Org. Chem.*, **35**, 3382 (1970).

be formed by abstraction of hydrogen atom in the 4-position of the dihydro compound (XIV) and by addition of methyl cation to the nitrogen atom in the 2-position (Chart 5).

Tetrahydro compound (VIII) might be formed by addition of a proton to the 5-position and then by addition of cyanide anion to the 6-position, followed by oxidation of VIII to afford 6-cyano-4(1H)pyridazinone (IV).

The compound (XVIII), in which cyanide anion was added to the 5-position, was not isolated. But, 5-cyano-4(1H)pyridazinone derivative (IX) and 4,5-dicyano-1,4-dihydro compound (XV) are likely formed by oxidation of XVIII.

Except for the dimers and dihydro compounds, the yields of the products were relatively low. But it is interesting that the reaction of the quaternary salts of pyridazines with cyanide anion afford such various kinds of the products. As shown in early part of this paper, there are some compounds, which can not be isolated on account of small amounts, though they are recognized in GLC and TLC. Therefore, in all cases of the reactions, all types of the compounds might be formed, but the compounds having higher formation ratio might be isolated, depending on the kinds and positions of the substituents.

Experimental

General Procedure for the Reaction of Pyridazines (I) with Me_2SO_4 and KCN——To pyridazine (I, 3—5 g) excess of dimethyl sulfate (10—20 ml) was added and heated at 60—80° [in the case of phenyl-substituted pyridazines (Ih—k), at 110—120°] for 2—3 hr. After removal of unreacted dimethyl sulfate by extraction with ether, 1-methylpyridazinium methosulfate thus obtained was dissolved in water (20—30 ml) and saturated aqueous solution of KCN (2—3 equivalent moles) was added at 0—5° and the solution was stirred for 5—10 min. The reaction mixture was extracted with CH_2Cl_2 and the CH_2Cl_2 layer was dried on $MgSO_4$ and evaporated. The residue was dissolved in benzene and purified by column chromatography on alumina.

Reaction of Pyridazine (Ia)——From the eluate with benzene, *anti*-dimer (IIa) and *syn*-dimer (IIIa) were obtained successively. IIa: colorless prisms, mp 162—163° (from benzene), yield *ca.* 20%. *Anal.* Calcd. for $C_{12}H_{14}N_6$: C, 59.48; H, 5.82; N, 34.67. Found: C, 59.75; H, 5.70; N, 34.97. Mass Spectrum *m/e*: 242 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2250. IIIa: colorless crystals, mp 151—152° (from benzene), yield 3%. *Anal.* Calcd. for $C_{12}H_{14}N_6$: C, 59.48; H, 5.82; N, 34.68. Found: C, 59.08; H, 5.95; N, 34.33. Mass Spectrum *m/e*: 242 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2255. Then, from the eluate with CH_2Cl_2, 6-cyano-1-methyl-4(1H)pyridazinone (**IVa**) was obtained, colorless crystals, mp 131° (from benzene–iso-Pr_2O), yield *ca.* 2%. *Anal.* Calcd. for $C_6H_5ON_3$: C, 53.33; H, 3.73; N, 31.10. Found: C, 53.01; H, 3.75; N, 30.51. IR ν_{max}^{KBr} cm^{-1}: 1665, 2240.

Reaction of 3-Methylpyridazine (Ib)——From the eluate with benzene, *anti*-dimer (IIb) and *syn*-dimer (IIIb) were obtained successively. Then, from the eluate with benzene–CH_2Cl_2, 6-cyano-1,3-dimethyl-4(1H)-pyridazinone (IVb) was obtained. IIb: Colorless plates, mp 174—175° (from benzene), yield 12%. *Anal.* Calcd. for $C_{14}H_{18}N_6$: C, 62.20; H, 6.71; N, 31.09. Found: C, 61.86; H, 6.69; N, 30.75. Mass Spectrum *m/e*: 270 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2240, IIIb: Colorless prisms, mp 155—156° (from benzene), yield 3%. *Anal.* Calcd. for $C_{14}H_{18}N_6$: C, 62.20; H, 6.71; N, 31.09. Found: C, 62.53; N, 6.50; H, 30.83. Mass Spectrum *m/e*: 270 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2240. IVb: Colorless crystals, mp 142—143° (from *n*-hexane–iso-Pr_2O), yield *ca.* 1%. *Anal.* Calcd. for $C_7H_7ON_3$: C, 56.37; H, 4.73; N, 28.18. Found: C, 56.17; H, 5.05; N, 27.82. IR ν_{max}^{KBr} cm^{-1}: 1660, 2240.

Reaction of 3-Methoxypyridazine (Ic)——From the eluate with benzene, *anti*-dimer (IIc) and *syn*-dimer (IIIc) were obtained successively. IIc: Colorless needles, mp 194—195° (from $CHCl_3$), yield 21%. *Anal.* Calcd. for $C_{14}H_{18}O_2N_6$: C, 55.61; H, 6.00; N, 27.80. Found: C, 55.52; H, 5.99; N, 27.87. Mass Spectrum *m/e*: 302 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2260. IIIc: Colorless needles, mp 175—176° (from $CHCl_3$), yield 5%. *Anal.* Calcd. for $C_{14}H_{18}O_2N_6$: C, 55.61; H, 6.00; N, 27.80. Found: C, 55.46; H, 5.90; N, 27.59. Mass Spectrum *m/e*: 302 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2250.

Reaction of 4-Methylpyridazine (Id)——From the eluate with benzene, 6-cyano-1,5-dimethyl-4(1H)-pyridazinone (IVd) was obtained, colorless needles, mp 80—81° (sublimated), yield 5%. *Anal.* Calcd. for $C_7H_7ON_3$: C, 56.86; H, 4.85; N, 28.17. Found: C, 56.37; H, 4.73; N, 28.18. Mass Spectrum *m/e*: 149 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1650, 2245.

Reaction of 3,6-Dimethylpyridazine (If)——From the eluate with benzene, 4-cyano-1,2,3,6-tetramethyl-1,2-dihydropyridazine (VIIf), 4,5-dicyano-3,6-dimethylpyridazine (VIf), and 4-cyano-3,6-dimethylpyridazine (Vf) were obtained successively. VIIf: Colorless solid, mp 47—48° (from *n*-hexane), yield 1.8%. *Anal.* Calcd. for $C_9H_{13}N_3$: C, 66.21; H, 8.03; N, 25.75. Found: C, 66.31; H, 7.86; N, 25.51. Mass Spectrum *m/e*: 163 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2230, VIf: Colorless crystals, mp 118—120° (from ether–*n*-hexane), yield *ca.* 1%. *Anal.* Calcd. for $C_8H_6N_4$: C, 60.75; H, 3.82; N, 35.43. Found: C, 60.23; H, 3.72; N, 34.80. Mass Spectrum *m/e*: 158 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2230. Vf: Colorless crystals, mp 102—103° (from *n*-hexane), yield 0.8%.

Anal. Calcd. for $C_7H_7N_3$: C, 63.14; H, 5.30; N, 31.56. Found: C, 62.78; H, 5.55; N, 31.98. Mass Spectrum *m/e*: 133 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2220.

Reaction of 3-Methoxy-6-methylpyridazine (Ig)——From the eluate with benzene, 4,6-dicyano-3-methoxy 1,6-dimethyl-1,4,5,6-tetrahydropyridazine (VIIIg) was obtained. Then, from the eluate with benzene–CH_2Cl_2, 5-cyano-3-methoxy-1,6-dimethyl-4(1H)pyridazinone (IXg) was obtained. VIIIg: Colorless needles, mp 94—95° (from CCl_4), yield 5%. *Anal.* Calcd. for $C_9H_{12}ON_4$: C, 56.23; H, 6.10; N, 29.15. Found: C, 56.27; H, 6.10; N, 29.26. Mass Spectrum *m/e*: 192 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2220. IXg: Colorless needles, mp 230—231° (from benzene), yield 1.5%. *Anal.* Calcd. for $C_8H_9O_2N_3$: C, 53.62; H, 5.06; N, 23.45. Found: C, 53.20; H, 5.19; N, 23.14. Mass Spectrum *m/e*: 179 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1660, 2225.

Reaction of 3-Phenylpyridazine (Ih)——The extract with CH_2Cl_2 was evaporated, affording amorphous powder, 4-cyano-1-methyl-3-phenyl-1,4-dihydropyridazine (XIVh), in *ca.* 80% yield. This was relatively unstable and could not be recrystallized. Therefore, its physical data were measured without further purification. From NMR spectral data, this powder has a purity of *ca.* 95%. Thus, the powder was separated by column chromatography on alumina, affording 4,6-dicyano-1-methyl-3-phenyl-1,4,5,6-tetrahydropyridazine (VIIIh), in *ca.* 2% yield. XIVh: Colorless amorphous powder, Mass Spectrum *m/e*: 197 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2235. *Anal.* Calcd. for $C_{12}H_{11}N_3$: C, 73.07; H, 5.62; N, 21.31. Found: C, 73.51; H, 5.35; N, 21.91. VIIIh: Colorless crystals, mp 71° (from iso-Pr_2O). *Anal.* Calcd. for $C_{13}H_{12}N_4$: C, 69.62; H, 5.39; N, 24.99. Found: C, 69.25; H, 5.68; N, 25.10. Mass Spectrum *m/e*: 224 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2220.

Reaction of 5-Methyl-3-phenylpyridazine (Ii)——Similar to the case of Ih, 5-methyl-3-phenylpyridazine (Ii) was obtained as amorphous powder in 85% yield. This powder was chromatographed on alumina and from the eluate with benzene, 6-cyano-1,5-dimethyl-3-phenyl-4(1H)pyridazinone (IVi) was obtained in 5% yield. XIVi: Colorless crystals, mp 59—62° (from *n*-hexane). *Anal.* Calcd. for $C_{13}H_{13}N_3$: C, 73.90; H, 6.20; N, 19.89. Found: C, 73.13; H, 6.15; N, 19.48. Mass Spectrum *m/e*: 211 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2220. IVi: Colorless needles, mp 180° (from iso-Pr_2O). *Anal.* Calcd. for $C_{13}H_{11}ON_3$: C, 69.22; H, 4.92; N, 18.66. Found: C, 69.66; H, 4.98; N, 18.91. Mass Spectrum *m/e*: 225 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1650, 2210.

Reaction of 6-Methyl-3-phenylpyridazine (Ij)——Similar to the case of Ih, 4-cyano-1,6-dimethyl-3-phenyl-1,4-dihydropyridazine (XIVj) was obtained as a mixture of powder in *ca.* 75% yield. Then, other components were separated by chromatography on alumina. Thus, from the eluate with benzene, 4-cyano-6-methyl-3-phenylpyridazine (Vj), 4,5-dicyano-1,6-dimethyl-3-phenyl-1,4-dihydropyridazine (XVj), 4,6-dicyano-1,6-dimethyl-3-phenyl-1,4,5,6-tetrahydropyridazine (VIIIj), 5-cyano-1,6-dimethyl-3-phenyl-4(1H)-pyridazinone (IXj), and 1,6-dimethyl-3-phenyl-4(1H)pyridazinone (XVIj) were obtained successively. XIVj: Amorphous powder. *Anal.* Calcd. for $C_{13}H_{13}N_3$: C, 73.90; H, 6.20; N, 19.80. Found: C, 73.32; H, 5.95; N, 19.22. Mass Spectrum *m/e*: 211 (M^+). IR ν_{max}^{film} cm^{-1}: 2220. Vj: Colorless prisms, mp 174—175° (from iso-Pr_2O), yield 0.5%. *Anal.* Calcd. for $C_{12}H_9N_3$: C, 73.80; H, 4.65; N, 21.53. Found: C, 73.61; H, 4.95; N, 21.11. Mass Spectrum *m/e*: 195 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2220. XVj: Colorless crystals, mp 120° (from iso-Pr_2O), yield 0.7%. *Anal.* Calcd. for $C_{14}H_{12}N_4$: C, 71.16; H, 5.12; N, 23.72. Found: C, 70.76; H, 4.92; N, 23.19. Mass Spectrum *m/e*: 237 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2220. VIIIj: Colorless prisms, mp 121—122° (from iso-Pr_2O), yield 2%. *Anal.* Calcd. for $C_{14}H_{14}N_4$: C, 70.56; H, 5.92; N, 23.51. Found: C, 70.22; H, 6.18; N, 23.32. Mass Spectrum *m/e*: 238 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2230. IXj: Colorless crystals, mp 180° (from benzene–iso-Pr_2O), yield 5%. *Anal.* Calcd. for $C_{13}H_{11}ON_3$: C, 69.22; H, 4.92; N, 18.66. Found: C, 69.56; H, 4.88; N, 18.62. Mass Spectrum *m/e*: 225 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1640, 2215. XVIj: Colorless crystals, mp 143—144° (from AcOEt–iso-Pr_2O), yield 0.3%. *Anal.* Calcd. for $C_{12}H_{12}ON_2$: C, 71.98; H, 6.04; N, 13.99. Found: C, 71.44; H, 5.62; N, 13.69. Mass Spectrum *m/e*: 200 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1610.

Reaction of 6-Methoxy-3-phenylpyridazine (Ik)——The extract was evaporated. From the residue, the dihydro compound (XIV) was not detected. Thus, according to the general procedure, the products were separated by column chromatography on alumina. From the eluate with benzene, 5-cyano-6-methoxy-3-phenylpyridazine (Vk) was obtained. Then, from the eluate with benzene–CH_2Cl_2, 5-cyano-3-methoxy-1-methyl-6-phenyl-4(1H)pyridazinone (IXk) was obtained. Vk: Colorless crystals, mp 136—137° (from iso-Pr_2O), yield 0.8%. *Anal.* Calcd. for $C_{12}H_9ON_3$: C, 68.23; H, 4.30; N, 19.90. Found: C, 68.29; H, 4.34; N, 19.98. Mass Spectrum *m/e*: 211 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2240. IXk: Colorless crystals, mp 228° (from benzene–iso-Pr_2O), yield 5%. *Anal.* Calcd. for $C_{13}H_{11}O_2N_3$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.49; H, 4.63; N, 17.88. Mass Spectrum *m/e*: 241 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1625, 2220.