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Photochemistry. X.[1] Photolysis of Tetrazolo[1,5-*b*]pyridazines

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Photolysis of 3-azidopyridazine, *i.e.*, tetrazolo[1,5-*b*]pyridazine (I) was examined. Unsubstituted and methyl-substituted compounds (Ia—d) afforded 3-cyanocyclopropenes (III). On the other hand, 6-methoxy compound (Ie) gave the triene (IV) and the ethylene (V and VI). These compounds are considered to be formed *via* the diazo intermediates (VIII) and the carbenes (X).

Concerning the photolyses of azides[3] and polyaza compounds such as tetrazoles[4] and triazoles,[5] many reports have been published. Most of them referred to the interesting result that the key intermediates were nitrenes and carbenes formed by elimination of molecular nitrogen. Similarly, photolysis of the diazo compounds[6] also gave various compounds *via* the carbenes.

Meanwhile, as for pyridazines, photolysis[2,7,8] of their N-oxide resulted in the formation of key intermediate of diazo compound and carbene. However, there have been no reports on the photolysis of tetrazolopyridazines.

On the azide-tetrazole tautomerism of 3-azidopyridazine, Wentrup[9] and Sasaki, *et al.*[10] reported that in solution it existed completely in the tetrazole form. And some reports have been already published on gas phase pyrolysis[11] and thermal reaction[10] of 3-azidopyridazine. Thus, we have been interested in the photolysis of this compound and have obtained some interesting results, on which we now report.[12]

Tetrazolo[1,5-*b*]pyridazine (I) was irradiated in dichloromethane for 6—7 hr and from Ia—d, the corresponding 3-cyanocyclopropenes (IIa—d) were obtained in 20—25% yields, respectively. The compound Ib gave also 3-cyano-5-methylpyrazole (IIIb) in a trace amount (0.1%) along with IIb. Except for Id, other compounds (Ia—c) afforded trace amounts of the compounds presumably to be the corresponding III, which were recognized by gas-liquid chromatography (GLC) and thin-layer chromatography (TLC) but could not be isolated. In all cases, an irradiation for 6—7 hr resulted in the recovery of the starting material in 20%,

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[1] Part IX: T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron*, **29**, 2747 (1973).

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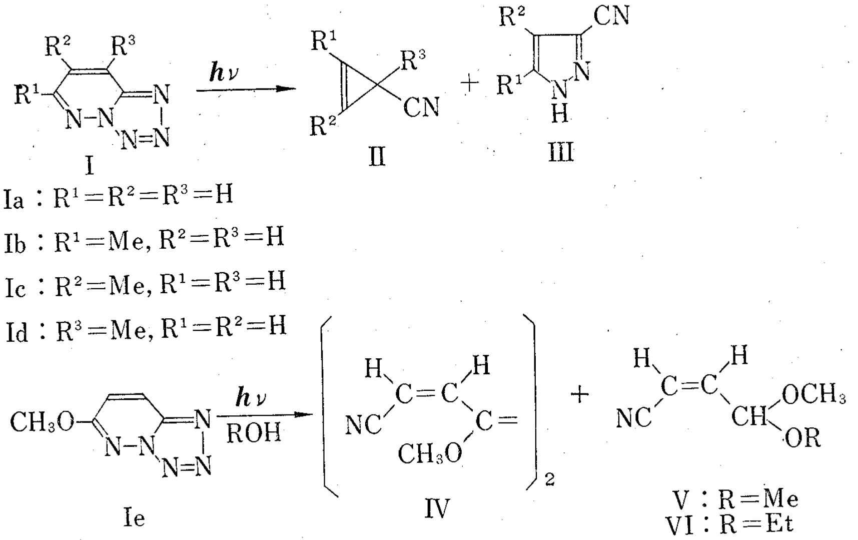
[11] C. Wentrup and W. D. Crow, *Tetrahedron*, **26**, 4915 (1970).

[12] A part of this work has been reported in a preliminary communication; T. Tsuchiya, H. Arai, and H. Igeta, *Chem. Commun.*, **1972**, 1059.

but the prolonged irradiation caused the decomposition of the product, lowering the yield.

Similar result was also obtained in methanol, and an irradiation in acetone for 3—4 hr resulted in the consumption of most of the starting material, leading to a decrease of the yield of II. Spectral data of the cyclopropene (II) thus obtained are shown in Table I. In infrared (IR) spectra, they have absorptions at 2220—2240 cm^{-1} due to cyano group, and their nuclear magnetic resonance (NMR) spectral data are well in accord with those of cyclopropenes.[13]



Ia : $R^1=R^2=R^3=H$

Ib : $R^1=Me, R^2=R^3=H$

Ic : $R^2=Me, R^1=R^3=H$

Id : $R^3=Me, R^1=R^2=H$

Chart 1

Table I. Spectral Data of 3-Cyanocyclopropene (II)

Compound	m/e (M^+)	$\nu_{C\equiv N}$ cm^{-1}	δ: (CCl_4), J=cps
IIa	65	2225	1.90 (1H, t, H_3), 7.13 (2H, d, H_1 and H_2), $J_{1,3}=1.2$
IIb, IIc	79	2240	1.77 (1H, d, H_3), 2.28 (3H, d, C_1-CH_3), 6.55 (1H, b, H_1), $J_{1,3}=1.2$, $J_{1\text{-}CH_3,2}=1.0$
IId	79	2260	1.45 (3H, s, C_3-CH_3), 7.30 (2H, s, H_1 and H_2)

6-Methoxytetrazolo[1,5-*b*]pyridazine (Ie) did not afford any cyclopropene and pyrazole derivatives, but the triene (IV) in *ca.* 5% yield in dichloromathane. In methanol, Ie gave ethylene derivative (V) as main product in 18—20% yield and IV in 2—3% yield, respectively. When ethanol was used instead of methanol, the compound (VI), in which formula R represents ethyl group, was obtained.

Photolysis of pyridazine N-oxides also gave cyclopropenyl ketones[1] and pyrazoles.[8] And gas phase thermolysis[11] of Ia afforded cyanoallene, tetrolonitrile, and propargyl cyanide as main products along with small amounts of 3-cyanocyclopropene, which was recognized by GLC and the spectral data but could not be isolated.

Thus, mechanism in the work might be as follows. The diazo compound (VIII) is formed from VII derived by irradiation of I, followed by intramolecular 1,4-addition to give pyrazole (III) thermally. The diazo compound (VIII) is converted into the carbene (X) by elimination of molecular nitrogen, as shown in Chart 2.

In the case of photolysis of pyridazine N-oxides, when the carbene (XI) has a hetero atom at the α-position, cyclopropene is not formed but furan is obtained. Similarly, owing to the

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[13] Ref. 1), 11), and references cited therein.

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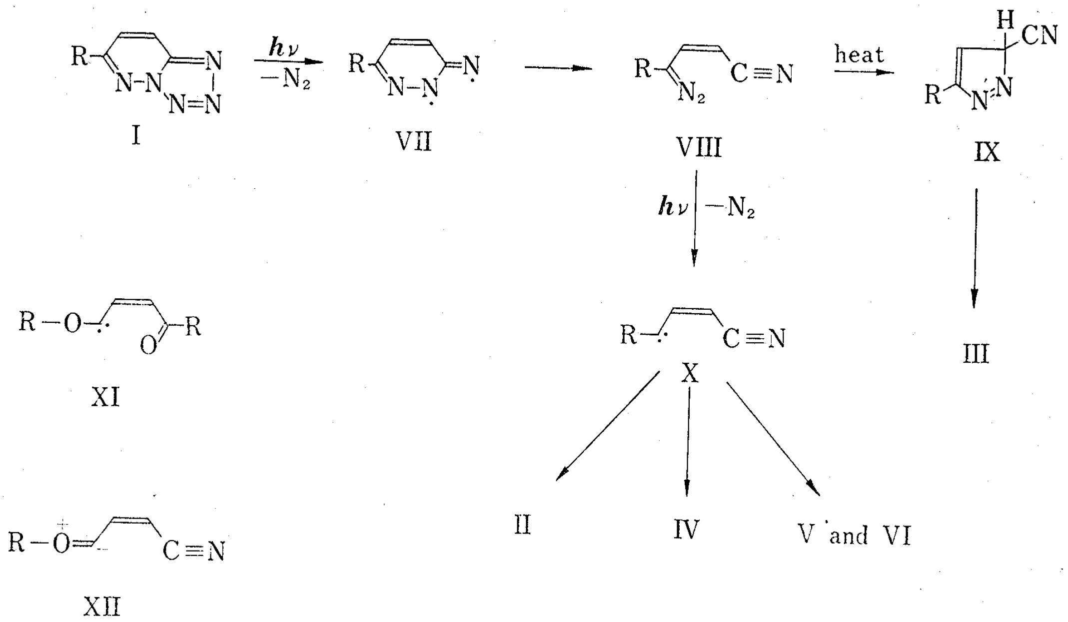

Chart 2

larger contribution of the structure (XII), Ie may not afford cyclopropene but the triene (IV) by dimerization and ethylene (V and VI) by addition[14] of the solvent alcohol.

Experimental

Photolyses were carried out in an immersion apparatus equipped with 200W high pressure mercury lamp (Nikko Sekiei Co., Japan) and cooled internally with running water. IR spectra were determined with a JASCO IRA-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 in CCl_4 or $CDCl_3$ solution using TMS as internal standard. Melting points were measured on a Yamato MP-1 apparatus and are uncorrected. Column and thin layer chromatography were carried out with alumina and silica gel obtained from Merck Co., Ltd.

Preparation of Tetrazolo[1,5-*b*]pyridazines (I)——According to the method[15] described by Itai and Kamiya, one drop of conc. HCl was added to a solution of 3-chloropyridazine derivatives and sodium azide dissolved in $EtOH-H_2O$ (2: 1) and heated in a sealed tube at 80—90° for 7—8 hr. After cooling the deposited crystals were collected and recrystallized from benzene to give I in 40—60% yield.

i) Tetrazolo[1,5-*b*]pyridazine (Ia): This compound was prepared from 3-chloropyridazine, mp 108—109° (lit.[13] 110—111°).

ii) 6-Methyltetrazolo[1,5-*b*]pyridazine (Ib): This compound was prepared from 3-chloro-6-methylpyridazine,[16] mp 139—141°. Mass Spectrum *m/e*: 135 (M^+). *Anal.* Calcd. for $C_5H_5N_5$: C, 44.44; H, 3.73; N, 51.83. Found: C, 44.71; H, 3.83; N, 51.54.

iii) 5-Methyltetrazolo[1,5-*b*]pyridazine (Ic): This compound was prepared from 3-chloro-5-methylpyridazine,[17] mp 130—131°. Mass Spectrum *m/e*: 135 (M^+). *Anal.* Calcd. for $C_5H_5N_5$: C, 44.44; H, 3.73; N, 51.83. Found: C, 44.57; H 3.61; N, 51.73.

iv) 4-Methyltetrazolo[1,5-*b*]pyridazine (Id): This compound was prepared from 3-chloro-4-methylpyridazine,[17] mp 119—121°. Mass Spectrum *m/e*: 135 (M^+). *Anal.* Calcd. for $C_5H_5N_5$: C, 44.44; H, 3.73; N, 51.83. Found: C, 44.38; H, 3.52; N, 51.82.

v) 6-Methyltetrazolo[1,5-*b*]pyridazine (Ie): This compound was prepared from 3-chloro-6-methylpyridazine, mp 155—156° (lit.[10] 154.5°).

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Photolysis of Tetrazolo[1,5-*b*]pyridazine (Ia—d)——A solution of I (2 g) dissolved in dichloromethane (250 ml) was irradiated for 6—7 hr and the reaction mixture was evaporated *in vacuo*. The residue was chromatographed on alumina. From the eluate with benzene, 3-cyanocyclopropene (IIa—d) was obtained. Their spectral data are collected in Table I. Then, from the eluate with dichloromethane, the starting material (I) was recovered in 18—20% yield. In the case of Ib, from the first eluate with CH_2Cl_2, 3-cyanopyrazole (IIIb) was obtained.

3-Cyanocyclopropene (IIa): Yield 24%, bp_{10} 55° (bath temp.). *Anal.* Calcd. for C_4H_3N: C, 73.83; H, 4.65; N, 21.53. Found: C, 73.78; H, 4.88; N, 21.31.

1-Methyl-3-cyanocyclopropene (IIb): Yields 20% from Ib, 23% from Ic, bp_{10} 60° (bath temp.). *Anal.* Calcd. for C_5H_5N: C, 75.92; H, 6.37; N, 17.71. Found: C, 76.25; H, 6.13; N, 17.70.

3-Methyl-3-cyanocyclopropene (IId): Yield 26%, bp_{10} 60° (bath temp.). *Anal.* Calcd. for C_5H_5N: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.66; H, 6.47; N, 17.43.

3-Cyano-5-methylpyrazole (IIIb): Yield 0.1%, mp 112—114° (from iso-Pr_2O), Mass Spectrum *m/e*: 107 (M^+), IR ν_{max}^{KBr}: 2270 cm^{-1} (CN), NMR δ ($CDCl_3$); 2.48 (3H, s, 5-CH_3), 6.49 (1H, s, H_4). *Anal.* Calcd. for $C_5H_5N_3$: C, 56.06; H, 4.71; N, 39.23. Found: C, 55.81; H, 4.75; N, 39.11.

Photolysis of 6-Methoxytetrazolo[1,5-*b*]pyridazine (Ie)——i) Dichloromethane Solution: Similar to the cases of Ia—d, the residue was chromatographed on alumina. From the eluate with benzene, 1,6-dicyano-3,4-dimethoxy-1,3,5-hexatriene (IV) was obtained in *ca.* 5% yield. Colorless crystals, mp 177—179° (from benzene), Mass Spectrum *m/e*: 190 (M^+), IR ν_{max}^{KBr}: 2220 cm^{-1} (CN), NMR δ ($CDCl_3$); 3.68 (6H, s, $-OCH_3$), 5.72 (2H, d, $J=16.0$, H_1 and H_6), 7.25 (2H, d, $J=16.0$, H_2 and H_5) *Anal.* Calcd. $C_{10}H_{10}O_2N_2$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.06; H, 5.10; N, 14.67. Then, from the eluate with CH_2Cl_2, the starting material was recovered in 17% yield.

ii) Methanol Solution: Under similar condition to i), irradiation was continued until the starting material was consumed (about 3 hr). The reaction mixture was evaporated and the residue was chromatographed on alumina. The eluate with benzene was again chromatographed on silica gel. From the eluates with benzene containing 5% AcOEt, 1-cyano-2-dimethoxymethyl-ethylene (V) and then IV were obtained in 21% and 2—3% yields, respectively. V: bp_{10} 80° (bath temp.), Mass Spectrum *m/e*: 127 (M^+), IR ν_{max}^{KBr}: 2230 cm^{-1} (CN), NMR δ ($CDCl_3$); 3.73 (6H, s, $-OCH_3$), 5.02 (1H, d, $J=6.0$, $-\underline{H}C(OCH_3)_2$), 5.47 (1H, d, $J=12.0$, H_1), 6.28 (1H, d.d, $J=6.0$ and 12.0, H_2). *Anal.* Calcd. for $C_6H_9O_2N$: C, 56.68; H, 7.14; N, 11.02. Found: C, 56.39; H, 7.03; N, 11.35.

iii) Ethanol Solution: Similar to ii), 1-cyano-2-(ethoxymethoxymethyl)-ethylene (VI) and IV were obtained in 19% and 2—3% yields, respectively. VI: bp_3 80° (bath temp.), Mass Spectrum *m/e*: 141 (M^+), IR ν_{max}^{KBr}: 2230 cm^{-1} (CN), NMR δ ($CDCl_3$): 1.23 (3H, t, $-CH_2C\underline{H}_3$), 3.36 (3H, s, $-OCH_3$), 3.60 (2H, q, $-C\underline{H}_2CH_3$), 5.07 (1H, d, $J=6.0$, $-CH-$), 5.45 (1H, d, $J=12.0$, H_1), 6.28 (1H, d.d, $J=6.0$ and 12.0, H_2). *Anal.* Calcd. for $C_7H_{11}O_2N$: C, 59.55; H, 7.85; N, 9.92. Found: C, 59.64; H, 7.60; N, 10.16.

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