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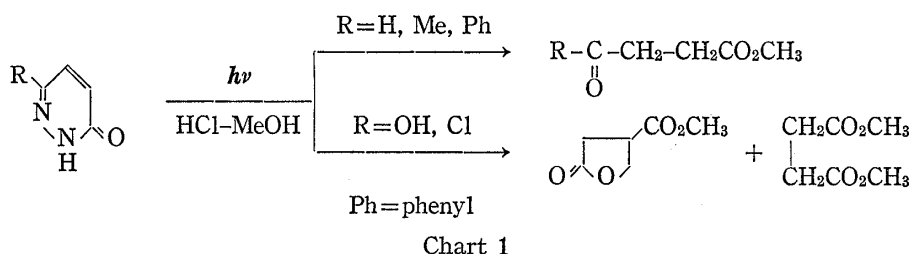
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Photochemistry. XI.¹⁾ Photochemical Ring Contraction of 3(2H)-Pyridazinones to 1-Amino- Δ^3 -pyrrolin-2-onesTAKASHI TSUCHIYA, MASATO HASEBE, HEIHACHIRO ARAI,
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Irradiation of 3(2H)-pyridazinone (**1a-f**) in methanol afforded 1-amino-5-methoxy- Δ^3 -pyrrolin-2-one (**2**) and 1-methylenimine-5-methoxy- Δ^3 -pyrrolin-2-one (**3**) by novel type ring contraction. Irradiation of them in EtOH or in the presence of Et₂NH gave 5-ethoxy- or 5-diethylaminopyrrolinone, respectively. Similarly, N-methyl-3(2H)-pyridazinone (**7**) gave N-methylamino-pyrrolinone (**8**). Some reactions of these compounds were carried out and the mechanism of the photochemical ring contraction was also discussed.

Several cases of thermal ring contraction of pyridazine derivatives have been known.³⁻⁵⁾ Concerning the photochemical reactions, in cases of 2-pyridones⁶⁾ and carbostyryles⁷⁾ having analogous structures to those of pyridazinones, interesting dimerization and isomerization occurred, whereas in case of the pyridazinones only a few reports have been published. Namely, we reported the formation of the N-free compounds,^{8,9)} i.e., methyl paraconates, dimethyl succinates, and methyl acrylpropanoates from pyridazones in methanol containing HCl.



Then, Rosen, *et al.*¹⁰⁾ reported the formation of the dimer from 2-phenyl-4-chloro-5-amino-3(2H)-pyridazinone by irradiation in water and Sasaki, *et al.*¹¹⁾ reported on the photolysis of azide substituted pyridazinones, and any other report has not been published.

- 1) Part X: T. Tsuchiya, H. Arai, and H. Igeta, *Chem. Pharm. Bull.* (Tokyo), **21**, 2517 (1973).
- 2) Location: 1-5-8, Hatanodai, Shinagawa-ku, Tokyo, 142, Japan.
- 3) K. Dury, *Angew. Chem.*, **77**, 282 (1965); Y. Maki, G.P. Beardsley, and M. Takaya, *Chem. Pharm. Bull.* (Tokyo), **19**, 1635 (1971) and Ref. cited.
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- 5) A. Pollak and M. Tisler, *Tetrahedron Letters*, **1964**, 253.
- 6) E.C. Taylor and R.O. Kan, *J. Am. Chem. Soc.*, **85**, 776 (1963); R.C. De Selms and W.R. Schleigh, *Tetrahedron Letters*, **1972**, 3563.
- 7) A.I. Meyer and P. Singh, *Chem. Commun.*, **1968**, 576; *idem*, *Tetrahedron Letters*, **1968**, 4073; G.R. Evanega and D.L. Fabig, *ibid.*, **1968**, 2241.
- 8) T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Letters*, **1970**, 3839; *idem*, *Chem. Pharm. Bull.* (Tokyo), **19**, 1108 (1971).
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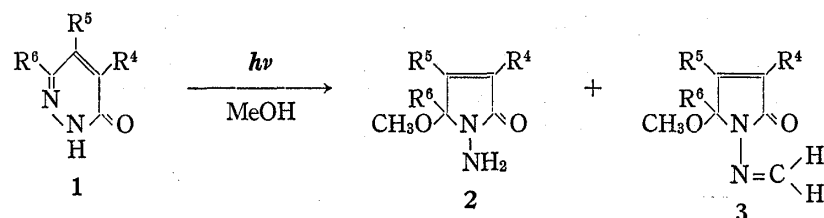
Meanwhile, we have examined the photolysis in neutral solvent and have obtained pyrrolinones by novel type ring contraction, on which we now report.

A solution of 3(2H)-pyridazinone (**1a-f**) was irradiated for 10–12 hr to afford 1-amino-5-methoxy- Δ^3 -pyrrolin-2-one (**2a-f**) and 1-methyleneimino-5-methoxy- Δ^3 -pyrrolin-2-one (**3a-f**) in every case.

When R^6 was H or Me (**1a-d**), yields were fairly good, *i.e.*, 40–50%, **2** and 5–20% **3**, respectively. And when R^6 was amino or hydroxymethyl group, it did not give any pyrrolinone, but afforded a small amount of the decomposition product along with a large amount of the starting material. In all cases of **1** (**a-f**), *ca.* 10% of the starting materials were recovered under this condition.

It needed more than 20 hr irradiation to consume the starting material completely, but in turn, the total yields of the products showed a decrease.

Short time irradiation gave **2** mainly, but continued irradiation resulted in an increase of the formation of **3**, and irradiation for 20 hr resulted in the formation of **2** and **3** in about equal amount. Thus, irradiation of the isolated **2** under similar condition led to the forma-



	R^4	R^5	R^6	
a :	H	H	H	
b :	Me	H	H	
c :	H	Me	H	
d :	H	H	Me	
e :	H	H	OMe	
f :	H	H	Ph	Ph=phenyl

Chart 2

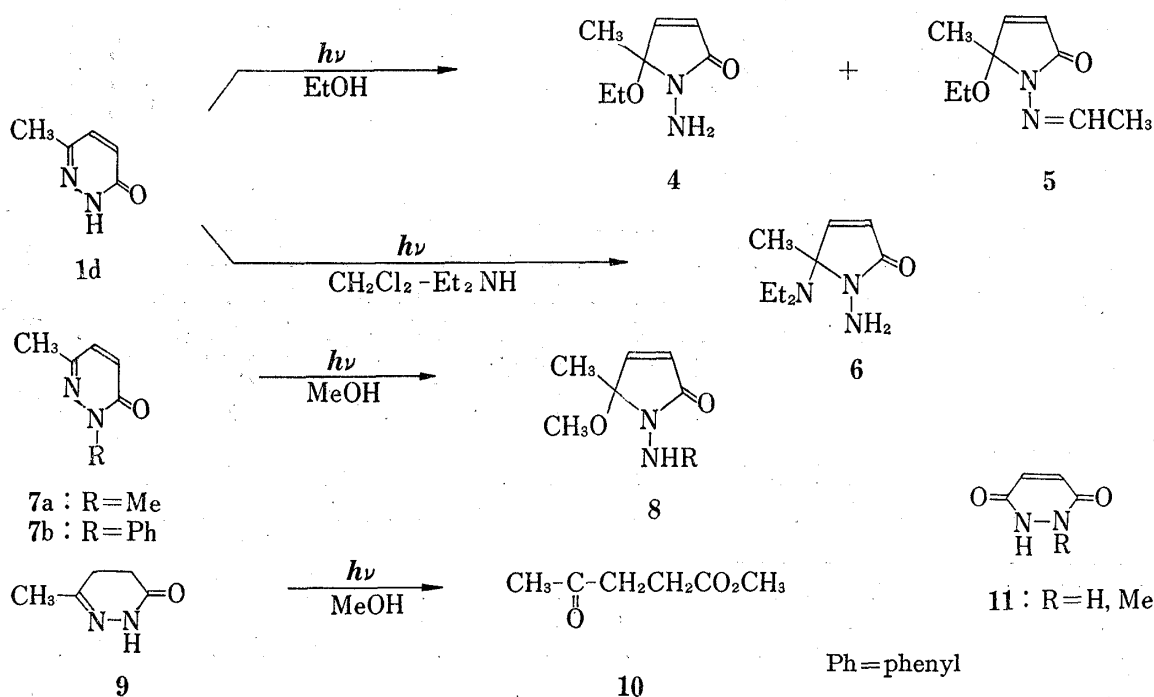


Chart 3

tion of **3**, suggesting that **2** was formed initially and was then reacted with formaldehyde, derived from methanol by oxidation, to give **3**.

Irradiation of **1d** in ethanol instead of methanol, gave 5-ethoxy derivative (**4**) and the hydrazone (**5**), derived from **4** and acetaldehyde, in 35–40% and 5–10% yields, respectively. In other solvent such as methylene chloride and benzene, the reactions hardly proceeded, recovering the starting material. But the presence of amine such as diethylamine in these solvents, resulted in the formation of 5-diethylaminopyrrolinone (**6**) in low yield.

Irradiation of N-substituted pyridazinone such as 2,6-dimethyl-3(2H)-pyridazinone (**7a**) under similar condition gave 1-methylaminopyrrolinone (**8a**) in 10% yield. But N-phenyl compound (**7b**) gave a trace amount of the compound corresponding to **8a**, which could not be isolated on account of small amount, and most of the starting material was recovered.

In case of 6-methyl-4,5-dihydro-3(2H)-pyridazinone (**9**), the ring fission and elimination of molecular nitrogen occurred to give methyl levulinate (**10**) in 13% yield. And pyridazine-3,6-dione (II) was unaffected at all. Thus, in all above-mentioned cases, any dimerization or isomerization was not observed.

In infrared (IR) spectra, pyrrolinones thus obtained have generally absorptions at 1715–1720 cm^{-1} due to carbonyl groups. Nuclear magnetic resonance (NMR) spectral data are collected in Table I. Data of pyrrolinone functions are well in accord with those¹²⁾ of the N-free 5-methoxy- Δ^3 -pyrrolin-2-ones, and the data of methyleneimino functions of **3** are reasonable compared with those¹³⁾ of the hydrazones of formaldehyde.

TABLE I. NMR Spectral Data of Pyrrolinones (2 and 3)

Compound	3-H	4-H	5-H	CH ₃	OCH ₃	NH ₂ or N=CH ₂
2a	6.05(m)	6.65(bd)	5.45(m)	—	3.15	3.70
2b	—	6.35(m)	5.30(m)	1.80(m)	3.20	3.60
2c	5.70(m)	—	5.28(m)	1.84(b)	3.12	3.60
2d	6.09(d)	6.69(d)	—	1.41(s)	2.98	3.95
2e	6.40(d)	6.79(d)	—	—	3.25	4.30
2f	6.12(d)	6.68(d)	—	—	3.15	3.60
3a	6.07(d)	6.75(d)	5.50(b)	—	3.26	6.70, 7.90
3b	—	6.32(m)	5.32(m)	1.89(m)	3.22	6.69, 7.90
3c	5.79(m)	—	5.28(m)	1.99(b)	3.19	6.63, 7.76
3d	6.07(d)	6.75(d)	—	1.53(s)	2.98	6.81, 8.25
3e	6.43(d)	6.84(d)	—	—	3.28	6.86, 7.70
3f	6.13(d)	6.67(d)	—	—	3.16	6.40, 6.26

$J_{3,4}=6.0$ cps, NH₂: broad, $J_{N=CH_2}=12.0$ cps

In order to confirm the structures of the pyrrolinones thus obtained, some reactions were carried out. The compound (**2**), a kind of hydrazine, was allowed to react with the carbonyl compounds to form the hydrazones. Thus, treatment of **2a–d** with formaldehyde gave **3a–d**, and with acetone afforded 1-isopropylideneimino-pyrrolinones (**12a–d**). Treatment of **2d** with cyclohexanone gave 1-cyclohexylimino-pyrrolinone (**13**). The yields of these hydrazones were high. And the reaction of **2d** with acetic anhydride easily gave the acetylated compound (**14**).

In the presence of the olefins, generally used for the carbene traps, the hydrazines of this type are known to be oxidized with lead tetraacetate to form the corresponding aziridines.¹⁴⁾

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In the event, from **2d** and cyclohexene, the corresponding aziridine (**15**) was obtained in a small amount. In cases of other olefins and acetylenes such as styrene, 1,2-diphenylethylene, indene, diphenylacetylene, and dimethylacetylenedicarboxylate, the corresponding aziridines and azirines were not isolated. In these cases, most of the starting materials (**2d**) were consumed, suggesting that the formed aziridines and azirines were unstable and easily decomposed. These reactions of the compounds (**2**) also support the correctness of the structures.

The mechanism of this ring contraction might be analogous to that of photoisomerization of 2,4-cyclohexadienones, which is well known in many examples.¹⁵⁾ Namely, the ketene

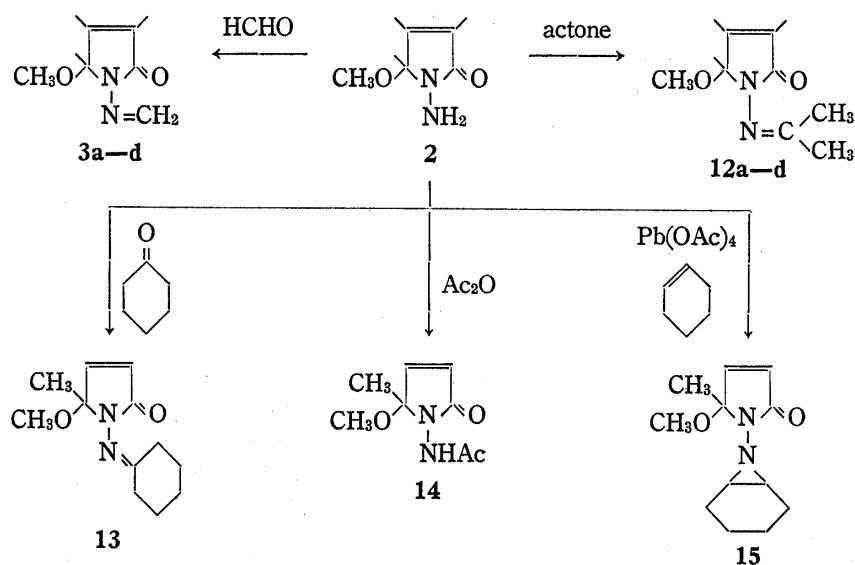


Chart 4

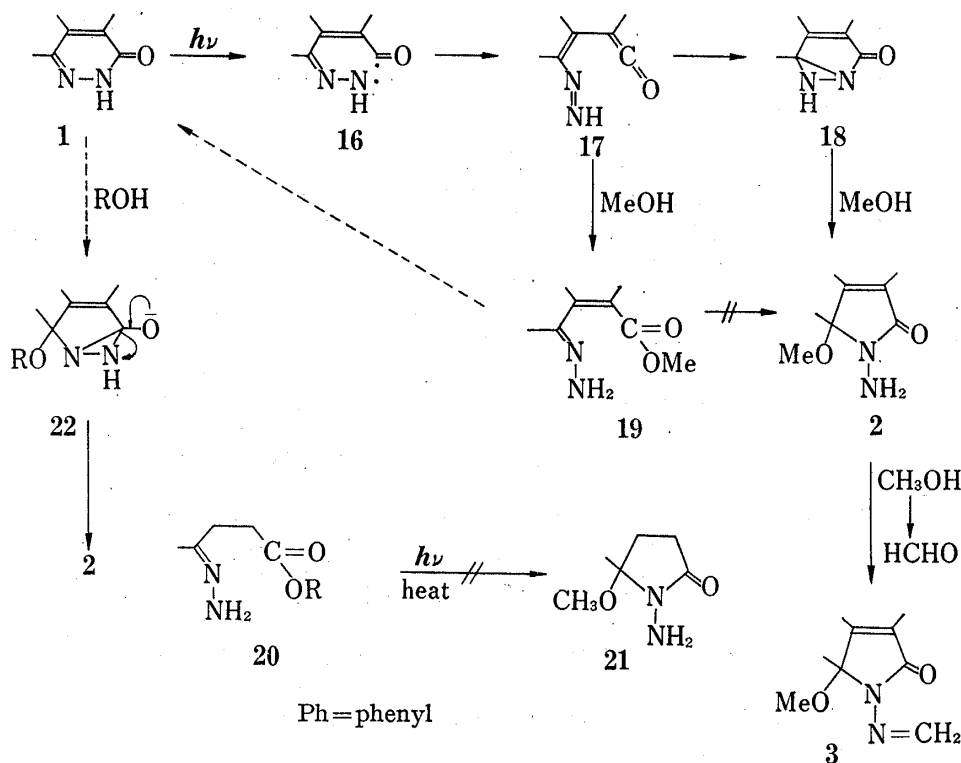


Chart 5

15) H. Hart, P.M. Collins, and A.J. Waring, *J. Am. Chem. Soc.*, **88**, 1005 (1966); H. Hart and R.J. Bastiani, *J. Org. Chem.*, **37**, 4018 (1972); D. Lemmer and H. Perst, *Tetrahedron Letters*, **1972**, 2735.

(17), derived from diradical (16), forms diaziridine (18), which is then converted into N-aminopyrrolinone by addition of the solvent alcohol or amine existed, followed by ring fission.

Another path *via* the ester (19), also might be taken in consideration. But hydrazones of 1,4-ketoacid or the reaction of 1,4-ketoacid with hydrazine generally give 3(2H)-pyridazinones in good yield.¹⁶⁾ However, thermal and photochemical treatment of the hydrazones (19 and 20), synthesized by the methods described in the literatures,¹⁷⁾ failed to get the corresponding pyrrolinones (2 and 21), but gave 1 and 4,5-dihydro-3(2H)-pyridazinone. This fact must lead to denial of the latter path.

The possible path *via* the intermediate (22) also must be left out consideration from the following facts. Namely, the dihydropyridazinone (9) did not give the corresponding pyrrolinone, but afforded the compound (10). And the treatment of 1 and 9 with methanol and methoxide anion also did not afford 2 at all.

As for the formation of methyleneimino compounds (3), it is considered that these were formed by reaction of 2 with the aldehyde derived from the solvent alcohol.

In conclusion, it is interesting that the products of photolyses in acidic alcohol differ from those in neutral alcohol, and further investigations are now in progress.

Experimental

Photolyses were carried out in an immersion apparatus equipped with a 400 W high pressure mercury lamp (Nikko Sekiei Co., Japan) and cooled internally with running water. IR spectra were determined with a JASCO IR-1 spectrometer and mass (MS) spectra were recorded on a Hitachi RMS-4 instrument. NMR spectra were recorded on Hitachi R-20 and R-22 spectrometers in CCl₄ or CDCl₃ solution using tetramethylsilane (TMS) as internal standard. Melting points were measured on a Yamato MP-1 apparatus and are uncorrected. Microanalyses were performed in the analytical laboratory of this school by Miss T. Kihara and Mrs. K. Shiobara. Column and thin-layer chromatography (TLC) were carried out with alumina obtained from Merck Co., Ltd.

General Procedure of the Photolysis—A solution of 1 (2–3 g) dissolved in freshly distilled MeOH (200–300 ml) was irradiated for 10–12 hr under N₂. The mixture was evaporated *in vacuo*. The residue was dissolved in benzene and chromatographed on alumina, eluting with CH₂Cl₂. From initial parts of the eluates, the hydrazone (3) and 1-amino compound (2) were obtained successively. Each fraction was checked by gas-liquid (GL) and TL chromatography and then purified by distillation under reduced pressure. From the last part of the eluates with CH₂Cl₂, the starting material (1) was recovered (6–10%), which was recrystallized and confirmed by mixture melting point and NMR spectra.

Photolyses of 3(2H)-Pyridazinone (1a),¹⁸⁾ 4-Methyl-3(2H)-pyridazinone (1b),¹⁹⁾ 5-Methyl-3(2H)-pyridazinone (1c),¹⁹⁾ 6-Methyl-3(2H)-pyridazinone (1d),²⁰⁾ 6-Methoxy-3(2H)-pyridazinone (1e),²¹⁾ and 6-Phenyl-3(2H)-pyridazinone (1f)²²⁾ in MeOH—According to the general procedure, photolyses were carried out, affording the corresponding 1-amino-4³-pyrrolin-2-ones (2) and 1-methyleneimino-4³-pyrrolin-2-ones (3) in 40–50% and 5–15% yields, respectively. Yields, especially the formation ratio, depended on the amount of MeOH, on bubbling velocity of N₂ and on the irradiation time. Spectral, physical, and analytical data of these compounds are collected in Table I and II. Their IR spectra show absorptions at 1715–1720 cm⁻¹ due to carbonyl groups. The compound (1) has absorptions at 3200 cm⁻¹ and 3260 cm⁻¹ due to NH₂.

Photolysis of 1d in EtOH—According to the general procedure, photolysis in EtOH was carried out, giving 1-amino-5-ethoxy-5-methyl-4³-pyrrolin-2-one (4) and 1-ethyleneimino-5-ethoxy-5-methyl-4³-pyrrolin-2-one (5). 4: bp₂ 90° (bath temp.), yield 28%, IR; 3200, 3260, and 1720 cm⁻¹, Mass Spectrum *m/e*; 156 (M⁺), NMR (δ); 1.52 (s, 5-CH₃), 4.40 (b, NH₂), 6.03 (d, 3-H, *J*_{3,4} = 6.0 cps), 6.80 (d, 4-H), 1.10 and 3.15 (3H, t, and 2H, q; OEt). *Anal.* Calcd. for C₇H₁₂O₂N₂: C, 53.84; H, 7.74; N, 17.94. Found: C, 53.91; H, 7.88; N, 17.64.

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- 21) W.G. Overend and L.F. Wiggins, *J. Chem. Soc.*, **1947**, 239.
- 22) S. Gabriel and J. Colmann, *Ber.*, **32**, 395 (1899).

TABLE II. Physical and Analytical Data of Pyrrolinones (2, 3 and 12)

	bp/1 mmHg (bath temp.)	<i>m/e</i> M ⁺	Molecular formula	Calcd.			Found		
				C	H	N	C	H	N
2a	80	128	C ₅ H ₈ O ₂ N ₂	46.87	6.29	21.87	47.15	6.30	21.77
2b	90	142	C ₆ H ₁₀ O ₂ N ₂	50.69	7.09	19.71	50.91	7.22	19.42
2c	90	142	C ₆ H ₁₀ O ₂ N ₂	50.69	7.09	19.71	50.41	7.48	19.30
2d	95	142	C ₆ H ₁₀ O ₂ N ₂	50.69	7.09	19.71	50.75	7.02	19.66
2e	85	158	C ₆ H ₁₀ O ₃ N ₂	45.56	6.37	17.71	45.64	6.14	17.48
2f	125	204	C ₁₁ H ₁₂ O ₂ N ₂	64.69	5.92	13.72	65.03	6.13	13.62
3a	85	140	C ₆ H ₈ O ₂ N ₂	51.42	5.75	19.99	51.44	5.93	19.67
3b	90	154	C ₇ H ₁₀ O ₂ N ₂	54.53	6.54	18.17	54.19	6.26	18.35
3c	90	154	C ₇ H ₁₀ O ₂ N ₂	54.53	6.54	18.17	54.22	6.59	17.91
3d	90	154	C ₇ H ₁₀ O ₂ N ₂	54.53	6.54	18.17	54.60	6.54	18.00
3e	85	170	C ₇ H ₁₀ O ₃ N ₂	49.40	5.92	16.46	49.81	6.11	16.31
3f	130	216	C ₁₂ H ₁₂ O ₂ N ₂	66.65	5.59	12.96	66.89	5.53	12.88
12a	90	168	C ₈ H ₁₂ O ₂ N ₂	57.13	7.19	16.66	56.83	7.03	16.64
12b	95	182	C ₉ H ₁₄ O ₂ N ₂	59.32	7.74	15.37	59.43	8.02	15.33
12c	95	182	C ₉ H ₁₄ O ₂ N ₂	59.32	7.74	15.37	59.15	7.86	15.09
12d	105	182	C ₉ H ₁₄ O ₂ N ₂	59.32	7.74	15.37	59.13	7.75	15.27

5: bp₂ 95° (bath temp.), yield 5%, IR; 1720 cm⁻¹, Mass Spectrum *m/e*; 182 (M⁺), NMR (δ); 1.51 (s, 5-H), 6.00 (d, 3-H, *J*_{3,4}=6.0 cps), 6.78 (d, 4-H), 1.08 and 3.12 (3H, t, and 2H, q; OEt), 2.01 (d, N=C-CH₃, *J*=5.7 cps), 8.65 (q, N=C-H). *Anal.* Calcd. for C₉H₁₄O₂N₂: C, 59.32; H, 7.74; N, 15.37. Found: C, 59.50; H, 7.91; N, 15.19.

Photolysis of 1d in CH₂Cl₂ Containing Et₃NH—A solution of 1d (3 g) and Et₃NH (8 ml) dissolved in CH₂Cl₂ (250 ml) was irradiated according to the general procedure. The reaction mixture was chromatographed on alumina, eluting with CH₂Cl₂ to afford 1-amino-5-diethylamino-5-methyl-Δ³-pyrrolin-2-one (6), bp₂ 105°, yield 7%, IR; 1718 cm⁻¹, Mass Spectrum *m/e*; 183 (M⁺), NMR (δ); 1.60 (s, 5-CH₃), 3.68 (b, NH₂), 6.28 (d, 3-H, *J*_{3,4}=6.0 cps), 6.91 (d, 4-H), 1.15 and 3.37 (6H, t, and 4H, q; NEt₂). *Anal.* Calcd. for C₉H₁₇ON₃: C, 58.98; H, 9.35; N, 22.93. Found: C, 59.09; H, 9.49; N, 22.71.

Photolyses of 2,6-Dimethyl-3(2H)-pyridazinone (7a)²³ and 2-Phenyl-6-methyl-3(2H)-pyridazinone (7b)¹⁷—According to the general procedure, photolysis of 7a was carried out in MeOH, affording 1-methylamino-5-methyl-5-methoxy-Δ³-pyrrolin-2-one (8a). From 7b a small amount of the compound, presumably to be 8b by GL chromatography, was recognized but could not be isolated and identified. In both cases, from the eluates with CH₂Cl₂ the starting materials were recovered in 35% (7a) and 90% (7b), respectively. 8a: bp₂ 95° (bath temp.), yield 12%, IR; 3280 and 1715 cm⁻¹, Mass Spectrum *m/e*; 156 (M⁺), NMR (δ); 1.50 (s, 5-CH₃), 3.10 (s, OCH₃), 3.71 (bs, N-CH₃), 6.25 (d, 3-H, *J*_{3,4}=6.0 cps), 6.90 (d, 4-H). *Anal.* Calcd. for C₇H₁₂O₂N₂: C, 53.83; H, 7.74; N, 17.94. Found: C, 54.25; H, 7.81; N, 17.67.

Photolysis of 6-Methyl-4,5-dihydro-3(2H)-pyridazinone (9)²¹—According to the general procedure, a solution of 9 dissolved in MeOH was irradiated for 15 hr. The mixture was evaporated and the residue was chromatographed on alumina. From the eluate with CH₂Cl₂, methyl levulinate (10) was obtained in ca. 30% yield, whose NMR, IR, and MS spectral data were well in accord with those of authentic samples, obtained from Tokyo Chemical Ind. Co., Ltd., Tokyo, Japan.

Reaction of 2 with Formaldehyde—To a solution of 2a—d (0.5 g) dissolved in MeOH (5 ml), HCHO (35—37% solution, 20—30 ml) was added and the mixture was stirred overnight at room temperature. After evaporation of MeOH *in vacuo* the residue was extracted with CH₂Cl₂, dried over MgSO₄, and the solvent was evaporated. The residue was chromatographed on alumina. The eluate with CH₂Cl₂ was submitted to distillation under reduced pressure, affording the corresponding hydrazone (3a—d) in 75—85% yield. Structures of these compounds were confirmed by IR and NMR spectral data.

Reaction of 2 with Acetone—To 2a—d (0.2—0.3 g), acetone (ca. 10 ml) was added and the mixture was stirred for 6—7 hr at room temperature or heated under reflux for 1—2 hr. Excess acetone was removed by distillation *in vacuo*, affording quantitatively the corresponding 1-isopropylideneimino-5-methoxy-Δ³-pyrrolin-2-one (12a—d), which was purified by distillation under reduced pressure. Physical and analytical data of these compounds are collected in Table II. In IR spectra, they show absorptions at 1720 cm⁻¹ due to carbonyl group. NMR spectral data are as follows. 12a: 6.08 (d, 3-H, *J*_{3,4}=6.0 cps), 6.67 (bd, 4-H), 5.49 (b, 5-H), 3.25 (s, OCH₃), 1.89 and 2.09 [each s, N=C(CH₃)₂]. 12b: 1.89 (bs, 3-CH₃), 6.38 (m, 4-H), 5.29

23) T. Nakagome, *Yakugaku Zasshi*, **82**, 1206 (1962).

(m, 5-H), 3.20 (s, OCH₃), 1.92 and 2.07 [each s, N=C(CH₃)₂]. **12c**: 5.80 (m, 3-H), 1.99 (m, 4-CH₃), 5.29 (m, 5-H), 3.20 (s, OCH₃), 1.85 and 2.07 [each s, N=C(CH₃)₂]. **12d**: 6.20 (d, 3-H, $J_{3,4}$ =6.0 cps), 6.75 (d, 4-H), 1.52 (s, 5-CH₃), 3.03 (s, OCH₃), 1.87 and 2.10 [each s, N=C(CH₃)₂].

Reaction of 2d with Cyclohexanone—To a solution of **2d** (0.3 g) dissolved in EtOH, cyclohexanone (3 ml) was added and the mixture was stirred for one day at room temperature. The mixture was evaporated *in vacuo* and the residue was chromatographed on alumina. From the eluate with CH₂Cl₂, the hydrazone (**13**) was obtained in *ca.* 90% yield, bp₁ 115°, IR; 1715 cm⁻¹, Mass Spectrum *m/e*; 222 (M⁺), NMR (δ); 6.19 (d, 3-H, $J_{3,4}$ =6.0 cps), 6.88 (d, 4-H), 1.61 (s, 5-CH₃), 3.10 (s, OCH₃), 1.4—2.0 (6H, m), 2.1—2.7 (4H, m). *Anal.* Calcd. for C₁₂H₁₈O₂N₂: C, 64.84; H, 8.16; N, 12.60. Found: C, 65.14; H, 7.86; N, 12.50.

Acetylation of 2d with Ac₂O—A solution of **2d** (0.5 g) dissolved in Ac₂O (20 ml) was warmed at 70—80° for 3 hr. Excess Ac₂O was removed by distillation *in vacuo*. The residue was dissolved in CH₂Cl₂ and chromatographed on alumina. From the eluate with CH₂Cl₂, 1-acetylamino compound (**14**) was obtained in 80% yield, colorless needles, mp 80—82° (from benzene-iso-Pr₂O), IR; 3460, 1715, and 1680 cm⁻¹, Mass Spectrum *m/e*; 184 (M⁺), NMR (δ); 6.20 (d, 3-H, $J_{3,4}$ =6.0 cps), 6.85 (d, 4-H), 1.48 (s, 5-CH₃), 3.10 (s, OCH₃), 8.28 (b, NH), 2.06 (s, COCH₃). *Anal.* Calcd. for C₈H₁₂O₃N₂: C, 52.16; H, 6.57; N, 15.21. Found: C, 52.13; H, 6.66; N, 15.02.

Oxidation of 2d with Pb(OAc)₄ in the Presence of Cyclohexene—To a solution of **2d** (1 g) and cyclohexene (2 g) dissolved in anhydrous CH₂Cl₂ (20 ml), Pb(OAc)₄ (1.8 g) was added in portions under stirring at 0—5°. Stirring was continued for further 15 min and the precipitates were removed by filtration. The filtrate was evaporated to dryness *in vacuo* and the residue was dissolved in a small amount of CH₂Cl₂. The solution was chromatographed on deactivated alumina. From the initial eluate with CH₂Cl₂, aziridine (**15**) was obtained in *ca.* 5% yield. The compound (**15**) was so unstable oil that the treatment had to be carried out promptly. Thus, the isolated compound easily decomposed to tarry substance, so it was difficult to purify by distillation. Consequently, the satisfactory analytical data could not be obtained. **15**: IR; 1720 cm⁻¹, Mass Spectrum *m/e*; 222 (M⁺), NMR (δ); 6.22 (d, 3-H, $J_{3,4}$ =6.0 cps), 6.90 (d, 4-H), 1.56 (s, 5-CH₃), 3.12 (s, OCH₃), 2.15 (2H, dd), 1.4—1.8 (8H, m). *Anal.* Calcd. for C₁₂H₁₈O₂N₂: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.40; H, 8.17; N, 11.98.