Chemistry of Cyanoacetylenes. Part XIV.[1] One-step Synthesis of Some Ethynyl Heterocycles and Their Reactions with Diazomethane

Tadashi SASAKI, Shoji EGUCHI, and Michio SUGIMOTO

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464

(Received May 9, 1972)

The Ritter reaction of cyano- and chlorocyanoacetylene with appropriate substrates provided a facile one step synthesis of 4,4-dimethyl-2-ethynyloxazoline (**5**), 4,4,6-trimethyl-2-ethynyl (**7**) and -2-chloroethynyl-5,6-dihydro-1,3-oxazine (**8**), 5,5-dimethyl-3-isopropylidene-2-ethynyl- (**10**) and -2-chloroethynyl-1-pyrroline (**11**). On treatment with diazomethane, **7** gave 4,4,6-trimethyl-2-(4-1*H*-pyrazolyl)- (**13**) and -2-(3-1*H*-pyrazolyl)-5,6-dihydro-1,3-oxazine (**14**) in 42 and 40% yields respectively, while **8** afforded only 4,4,6-trimethyl-2-[3-(4-chloro-1-methyl)-pyrazolyl]-5,6-dihydro-1,3-oxazine (**15**) in 52% yield. On the other hand, **10** gave 5,5-dimethyl-3-isopropylidene-2-(3-1*H*-pyrazolyl)-1-pyrroline (**16**) in 64% yield and **11**, 5,5-dimethyl-3-isopropylidene-2-[3-(4-chloro-1-methyl)-pyrazolyl]-1-pyrroline (**17**) in 16% yield.

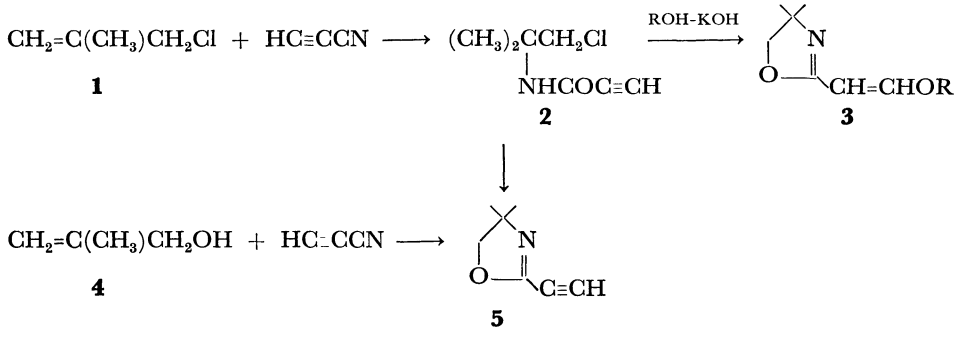
We reported that cyano- and chlorocyanoacetylene undergo the Ritter reaction with some olefins and alcohols to give the corresponding propiolamide derivatives.[2,3] As an extension of this study, we have applied the Ritter reaction[4] of the cyanoacetylenes to the synthesis of some ethynylheterocycles by using appropriate substrates.

We employed 2-methylallyl alcohol (**4**), hexylene glycol (**6**) and 2,5-dimethyl-2,5-hexanediol (**9**) with the hope of synthesizing 2-ethynyl- and 2-chloroethynyl derivatives of 4,4-dimethyloxazoline, 4,4,6-trimethyl-5,6-dihydro-1,3-oxazine, and 5,5-dimethyl-3-isopropylidene-1-pyrroline from our interest in their pharmacological activity[5] and utility as synthetic intermediates.[6]

Results and Discussion

The Ritter Reactions. The reaction of 2-methylallyl alcohol (**4**) with cyanoacetylene in sulfuric acid (95%) at 0°C for 1 hr afforded a complex mixture of products, from which an oily basic product **5** was obtained in 4.9% yield by distillation under reduced pressure. The structure of **5** was determined as 4,4-dimethyl-2-ethynyloxazoline from analytical and spectral data. The IR absorptions at 3300, 2160, and 1620 cm^{-1} demonstrated the presence of C≡CH and C=N functions, and NMR ($CDCl_3$) spectrum manifested signals at τ 6.05 (s, 2H, $C\underline{H}_2$), 7.05 (s, 1H, C≡C$\underline{H}$) and 8.70 (s, 6H, $C(C\underline{H}_3)_2$), supporting the above assignment. The Ritter reaction of 2-methylallylchloride (**1**) with cyanoacetylene is known to afford *N*-(chloro-*t*-butyl)propiolamide **2** in a good yield,[2] and the cyclization of **2** with ethanolic potassium hydroxide gives the corresponding 2-vinyloxazoline derivatives **3**.[2] We examined the direct cyclization of **2** with potassium hydroxide in tetrahydrofuran and proved that **2** gave also 2-ethynyloxazoline **5** in 24% yield (Scheme 1). Attempts to improve the yield of **5** in the Ritter reaction of **4** with cyanoacetylene were unsuccessful because of the formation of large amounts of intractable polymeric materials, and therefore, the cyclization method of **2** was concluded to be superior to the Ritter reaction of **4** in this case.

Treatment of hexylene glycol **6** with an equimolar amount of cyanoacetylene in sulfuric acid afforded the desired 2-ethynyl-5,6-dihydro-1,3-oxazine derivative **7** (Scheme 2). The best yield of **7** was 26.5% which



1 2 3 4 5

Scheme 1.

1) Part XIII: T. Sasaki and A. Kojima, *Tetrahedron Lett.*, **1971**, 4593.

2) T. Sasaki, S. Eguchi, and K. Shoji, *J. Chem. Soc. C*, **1969**, 406.

3) T. Sasaki, S. Eguchi, and T. Oyobe, This Bulletin, **43**, 1252 (1970).

4) For recent reviews, see (a) L. I. Krimen and D. J. Cota, "Organic Reactions," Vol. 17, p.p. 213—325 (1969); (b) F. Johnson, "Advances in Heterocyclic Chemistry," Vol. 6, p.p. 95—146, ed. by A. R. Katritzky and A. J. Boulton, Academic Press, New York and London (1966).

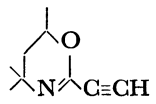
5) For example, see Z. Eckstein and T. Urbânski, "Advances in Heterocyclic Chemistry," Vol. 2, p. 311, ed. by A. B. Katritzky and A. J. Boulton, Academic Press, New York and London (1963).

6) For example, see (a) A. I. Meyers and E. W. Collington, *J. Amer. Chem. Soc.*, **92**, 1176 (1970); (b) A. I. Meyers, E. M. Smith, and A. F. Jurjevich, *ibid.*, **93**, 2314 (1971), and preceding papers.

was obtained under drastic conditions at 50°C. Only a trace amount of **7** was produced under milder conditions at room temperature. The structural elucidation of the product was based on the analytical and spectral data: **7** showed a molecular ion peak at *m/e* 151 (M^+) in the mass spectrum, and strong IR (KBr) absorptions at 3200 and 2130 (C≡CH) and 1625 (C=N) cm^{-1}. The NMR ($CDCl_3$) signals at τ 5.5—6.1 (broad m, 1H, 6-H), 7.38 (s, 1H, C≡CH), 8.0—8.5 (m of AB portion of an ABX pattern, 2H, CH_2), 8.65 (d, J=6.1 Hz, 3H, 6-CH_3) and 8.78 (s, 6H, 4,4-$(CH_3)_2$) were in line with the assigned structure.

$(CH_3)_2C(OH)CH_2CH(OH)CH_3$ + HC≡CCN ⟶

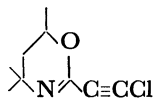
6



7

$(CH_3)_2C(OH)CH_2CH(OH)CH_3$ + ClC≡CCN ⟶

6



8

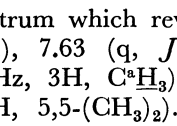
Scheme 2.

The Ritter reaction of **6** with chlorocyanoacetylene under the same conditions at 50°C gave 2-chloroethynyl-4,6,6-trimethyl-5,6-dihydro-1,3-oxazine (**8**) in 21.6% yield. The assigned structure was evidenced by analytical and spectral data.

The reaction of 2,5-dimethyl-2,5-hexanediol (**9**) with cyanoacetylene afforded 2-ethynyl-5,5-dimethyl-3-isopropylidene-1-pyrroline (**10**) as a colorless oil. A molecular formula $C_{11}H_{15}N$ was evidenced by analysis and mass spectral molecular weight, *m/e* 161 (M^+). The assigned structure was compatible with the NMR spectrum which revealed signals at τ 6.83 (s, 1H, C≡CH), 7.63 (q, J=2.3 Hz, 2H, CH_2), 7.78 (t, J=2.3 Hz, 3H, C^aH_3), 8.22 (s, 3H, C^bH_3) and 8.75 (s, 6H, 5,5-$(CH_3)_2$). The yield of **10** varied 46—60% depending on the addition method (see Experimental) (Scheme 3).

$(CH_3)_2C(OH)CH_2CH_2C(CH_3)_2OH$ + HC≡CCN ⟶

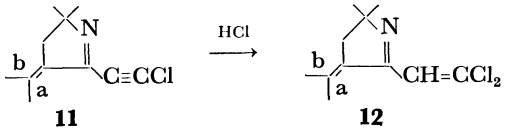
9



10

$(CH_3)C(OH)CH_2CH_2C(CH_3)_2OH$ + ClC≡CCN ⟶

9



11 **12**

Scheme 3.

The same reaction of **9** with chlorocyanoacetylene gave 2-chloroethynyl-5,5-dimethyl-3-isopropylidene-1-pyrroline (**11**), purification of which was difficult because of facile decomposition; **11** was characterized by the spectral data: *m/e* 196 (M^+) and 198 (M+2) in 3 : 1 ratio; ν_{max}^{film} 2260, 1655, and 1540 cm^{-1}; τ (CD-Cl_3) 7.65 (q, J=2.3 Hz, 2H, CH_2), 7.83 (t, J=2.3 Hz, 3H, C^aH_3), 8.25 (s, 3H, C^bH_3), and 8.79 (s, 6H, 5,5-$(CH_3)_2$). The assigned structure of **11** was also supported by the reaction with diazomethane as described below. On distillation of crude **11** under reduced pressure, a crystalline product **12** was obtained in a low yield, which gave *m/e* 232 (M^+) and 234 (M+2) with a ratio of 3 : 2; ν_{max}^{KBr} 1650, 1620, 1565, and 750 cm^{-1}; τ ($CDCl_3$) 3.38 (s, 1H, C=CH), 7.60 (q, J=2.3 Hz, 2H, CH_2), 8.05 (t, J=2.3 Hz, 3H, C^aH_3), and 8.71 (s, 6H, 5,5-$(CH_3)_2$). The structure of **12** was assigned as 2-β,β-dichlorovinyl-5,5-dimethyl 3-isopropylidene-1-pyrroline. The formation of **12** is rationalyzed by the Markownikov addition[7,8] of hydrogen chloride to **11** (Scheme 3). It is uncertain whether the origin of hydrogen chloride is **11** itself or some other chloroethynyl side-products in the Ritter reaction.

Reaction of **7**,**8**,**10**, *and* **11** *with Diazomethane.* The formation of pyrazole derivatives by 1,3-dipolar cycloaddition reactions of diazomethane to acetylenic bonds is well-known.[9] However, only a few studies have been made on unsymmetrically substituted acetylenes with a bulky heterocyclic rings.[10,11]

On treatment with a large excess of diazomethane in ether at room temperature, **7** afforded two crystalline products **13** and **14** in 42 and 40% yields, respectively. Both products were 1 : 1 adducts on the basis of their mass spectra, *m/e* 193. Compound **13** was assigned as 4,4,6-trimethyl-2-(4-1*H*-pyrazolyl)-5,6-dihydro-1,3-oxazine by appearance of a singlet signal at τ 2.15 for two protons, and **14** as 4,4,6-trimethyl-2-(3-1*H*-pyrazolyl)-5,6-dihydro-1,3-oxazine by the NMR signals at τ 2.48 and 3.38 (both d, J=1.9 Hz, each 1H) (Scheme 4). On the other hand, the reaction of **8** with diazomethane afforded only one product **15** in 52% yield, which was characterized as 4,4,6-trimethyl-2-[3-(4-chloro-1-methyl)pyrazolyl]-5,6-dihydro-1,3-oxazine by analysis and spectral data: *m/e* 241 (M^+) and 243 (M+2) with a 3 : 1 ratio; τ ($CDCl_3$) 2.68 (s, 1H, 5-H of the pyrazole), 5.70 (m, 1H, 6-H), 6.01 (s, 3H, NCH_3), 8.10 (m, 2H, CH_2), 8.62 (d, J=6.0 Hz, 3H, 6-CH_3) and 8.70 (s, 6H, 4,4-$(CH_3)_2$). The fact that

7) S. W. Benson and G. R. Haugen, *J. Phys. Chem.*, **70**, 3336 (1966).

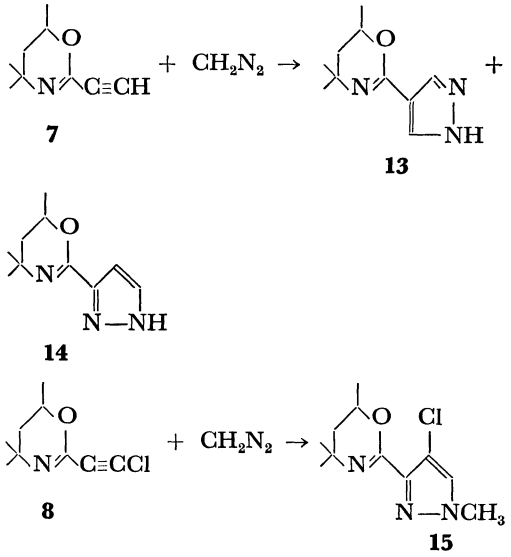
8) R. C. Fahey, "Topics in Stereochemistry," Vol. 3, p. 237, ed. by E. L. Eliel and N. L. Allinger, John Willey and Sons, Inc. (1968).

9) For reviews, see R. Huisgen, R. Grashey, and J. Sauer, "Cycloaddition Reactions of Alkenes," in "The Chemistry of Alkenes," p.p. 806—878, ed. by S. Patai, Interscience, New York (1964); (b) H. G. Viehe, "Chemistry of Acetylenes," p. 462, Marcel Dekker, New York (1969).

10) For the reaction of ethynyldiazomethane with acetylene, see H. Reimlinger, *Ann. Chem.*, **713**, 112 (1968).

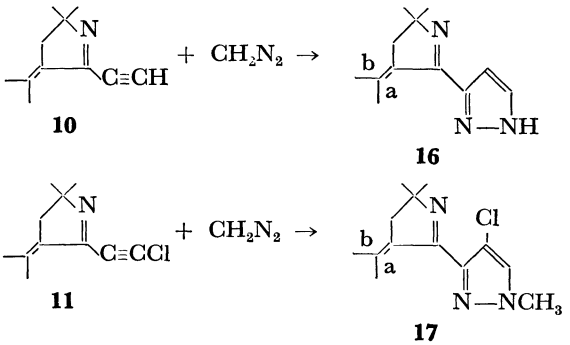
11) For 1,3-dipolar cycloaddition reactions of 5-nitro-2-furyldiazomethane, see T. Sasaki, S. Eguchi, and A. Kojima, *J. Heterocyclic Chem.*, **5**, 243 (1968).

7 affords an isomeric mixture of **13** and **14** in *ca.* 1 : 1 ratio and that **8** gave only **15** suggests that the orientation of the cycloaddition was controlled by the electronic factor rather than the steric one.[12]



Scheme 4.

The reaction of **10** and **11** with diazomethane afforded only one adduct each **16** and **17** in 64 and 16 (from **11**)% yields, respectively (Scheme 5). The structural assignments were based on analytical and spectral data: **16** showed characteristic vinyl proton signals at τ 2.52 (d, J=1.9 Hz, 1H, 5-H of the pyrazole), and 3.55 (d, J=1.9 Hz, 1H, 4-H of the pyrazole). **17** showed one vinyl proton signal at τ 2.63 (s) and *N*-methyl protons signal at τ 6.12 (s), supporting the assigned structures.



Scheme 5.

The formation of each single product in the above reactions indicates that 1-pyrroline ring in **10** and **11** is more electron-withdrawing than 1,3-oxazine ring in **7** and **8**. Simultaneous *N*-methylation of the pyrazole rings from the chloroethynyl derivatives is apparently ascribable to lower basicity of the pyrazole ring by the presence of an electronegative chloro-substituent.[13]

12) For the reaction of diazomethane with cyanoacetylenes, see T. Sasaki and K. Kanematsu, *J. Chem. Soc. C*, **1971**, 2147.

13) For a review, see R. Gompper, "Advances in Heterocyclic Chemistry," Vol. 2, p.p. 245—286, ed. by A. R. Katritzky, A. J. Boulton, and J. M. Lagowski, Academic Press, New York and London (1963).

Experimental

All mp and bp are uncorrected. NMR spectra were recorded on a JEOL-C-60HL spectrometer at 60 MHz with TMS as the internal standard, and mass spectra on a JEOL-OISG mass spectrometer at 75 eV. IR spectra were obtained with a JASCO IR-S spectrometer. Microanalyses were carried out with a Perkin-Elmer 240 Elemental Analyzer.

*Reaction of Cyanoacetylene with 2-Methylallyl Alcohol (**4**).* To a stirred sulfuric acid (95%, 15 ml) was added slowly a mixture of **4** (3.60 g, 0.050 mol) and cyanoacetylene[14] (2.55 g, 0.050 mol) under ice-cooling over a period of 10 min. After stirring was continued for further 1 hr, the mixture was poured onto ice-water (ca. 300 ml) and washed with chloroform (30 ml×5). The water layer was basified with 20% aqueous sodium hydroxide under ice-cooling and extracted with chloroform (30 ml×5). The dried (Na_2SO_4) extracts were evaporated to give 2.4 g of crude basic products. Flask distillation at 0.11 mmHg gave a distillate trapped at liquid nitrogen temperature, which was further purified by passing through a neutral alumina column using benzene as an eluent to give 0.301 g (4.9%) of analytically pure 2-*ethynyl-4,4-dimethyloxazoline* **5**: n_D^{18} 1.4905; *m/e* 123 (M^+); λ_{max}^{MeOH} 219 nm (ε 4000).

Found: C, 68.53; H, 7.32; N, 11.27%. Calcd for C_7H_9NO: C, 68.27; H, 7.37; N, 11.37%.

*Cyclization of N-(Chloro-t-butyl)propiolamide **2** to **5**.* A mixture of **2** (0.22 g, 1.4 mmol) and potassium hydroxide (0.13 g) in dry THF (10 ml) was refluxed under nitrogen atmosphere for 4 hr. The cooled mixture was treated with water and extracted with chloroform (10 ml×5). The work-up afforded **5** in 23.8% yield.

*Reaction of Cyanoacetylene with Hexylene Glycol (**6**).* A mixture of cyanoacetylene (1.3 g, 0.025 mol) and **6** (2.95 g, 0.025 mol) was added to stirred sulfuric acid (20 ml) over a period of ca. 10 min at room temperature; the temperature was raised up to *ca.* 50°C and stirring was continued for 1 day at room temperature. The mixture was poured onto ice-water and extracted with chloroform (80 ml×5) after being basified with 20% aqueous sodium hydroxide. The combined extracts were dried (Na_2SO_4) and evaporated to give a dark brownish residue which was distilled to afford 2-*ethynyl-4,4,6-trimethylethyl-5,6-dihydro-1,3-oxazine* **7**) (1.0 g, 26.5%); an analytical sample was obtained after recrystallization of the solidified distillate from *n*-hexane: bp 54—56°C (0.6 mmHg); mp 75—77°C; λ_{max}^{EtOH} 208 nm (ε 9250).

Found: C, 71.25; H, 8.80; N, 9.37%. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26%.

*Reaction of Chlorocyanoacetylene with **6**.* The reaction of chlorocyanoacetylene[15] with **6** under similar conditions to those described above gave 2-*chloroethynyl-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine* (**8**) (21.6%): bp 67—68°C (0.4 mmHg); n_D^{20} 1.5035; ν_{max}^{film} 2260 and 1638 cm^{-1}; λ_{max}^{EtOH} 222 nm (ε 10000); τ ($CDCl_3$) 5.80 (m, 1H, 6-H), 8.20 (m, 2H, CH_2), 8.68 (d, J=6.1 Hz, 3H, 6-CH_3), 8.78 (s, 6H, 4,4-$(CH_3)_2$); *m/e* 185 (M^+) and 187 (M+2) in 3 : 1 ratio.

Found: C, 58.01; H, 6.84; N, 7.31%. Calcd for $C_9H_{12}NOCl$: C, 58.21; H, 6.51; N, 7.54%.

*Reaction of Cyanoacetylene with 2,5-Dimethyl-2,5-hexanediol (**9**).* To a stirred sulfuric acid (20 ml) was added **9** (3.65 g, 0.025 mol) slowly below 5°C over a 1-hour period,

14) S. Murahashi, T. Takisawa, S. Kuroda, and S. Maikawa, *Nippon Kagaku Zasshi*, **77**, 1689 (1956); *Chem. Abstr.*, **53**, 5163f (1959).

15) E. Kloster-Jensen, *Acta Chem. Scand.*, **18**, 1629 (1964).

followed by addition of cyanoacetylene (1.3 g, 0.025 mol) over a period of 20 min under ice-cooling. After stirring was continued for 1 day at room temperature, the work-up and distillation afforded *2-ethynyl-5,5-dimethyl-3-isopropylidene-1-pyrroline* (**10**) (2.42 g, 60%) as an oil: bp 61—62°C (0.5 mmHg); n_D^{18} 1.5231; ν_{max}^{film} 3300, 3200, 2140, 1655, and 1640 cm^{-1}; λ_{max}^{MeOH} 267 nm (ε 11000), 223 (6900), and 208 (6100).

Found: C, 81.84; H, 9.65; N, 8.51%. Calcd for $C_{11}H_{15}N$: C, 81.93; H, 9.38; N, 8.69%.

Addition of cyanoacetylene to sulfuric acid, followed by that of **9** lowered the yield of **10** to 46%.

Reaction of Chlorocyanoacetylene with **9**. A similar reaction of chlorocyanoacetylene (2.2 g, 0.025 mol) with **9** (3.65 g, 0.025 mol) afforded crude *2-chloroethynyl-5,5-dimethyl-3-isopropylidene-1-pyrroline* (**11**) (5.0 g, quantitative) as a brownish oil which was characterized by spectral data (see Text) but it decomposed gradually on standing. Distillation under reduced pressure gave *2-(β,β-dichlorovinyl)-5,5-dimethyl-3-isopropylidene-1-pyrroline* (**12**) (7% from **9**) as an oil which solidified on standing. Recrystallization from *n*-hexane gave an analytically pure sample of **12**: bp 72—75°C (0.5 mmHg); mp 53—55°C; λ_{max}^{MeOH} 252 nm (ε 9000), infl. 231 and 223 nm.

Found: C, 57.12; H, 6.47; N, 5.85%. Calcd for $C_{11}H_{15}NCl_2$: C, 56.91; H, 6.51; N, 6.03%.

Reaction of **7** *with Diazomethane.* Treatment of **7** (151 mg, 1.00 mmol) with a large excess of ethereal diazomethane at room temperature for 1 day, followed by removal of excess diazomethane and the solvent afforded a solid residue (153 mg) which was recrystallized from *n*-hexane–dichloromethane to give *4,4,6-trimethyl-2-(4-*H*-pyrazolyl)-2,6-dihydro-1,3-oxazine* (**13**) (81 mg, 42%) as colorless crystals: mp 169—172°C; ν_{max}^{KBr} 3160, 1660, 1640, and 1580 cm^{-1}; λ_{max}^{EtOH} 220 (ε 13200); τ ($CDCl_3$) −1.75 (s, 1H, NH), 2.15 (s, 2H, 3′-H and 5′-H in the pyrazole ring), 5.75 (m, 1H, 6-H), 8.05 (m, 2H, CH_2), 8.65 (d, J=6.0 Hz, 3H, 6-CH_3), and 8.72 (s, 6H, 4,4-$(CH_3)_2$); *m/e* 193 (M^+).

Found: C, 62.32; H, 7.85; N, 21.88%. Calcd for $C_{10}H_{15}N_3C$: C, 62.15; H, 7.82; N, 21.75%.

Purification of the mother liquor on a silica gel column eluting with $CHCl_3$–MeOH afforded *4,4,6-trimethyl-2-(3-*1H*-pyrazolyl)-5,6-dihydro-1,3-oxazine* (**14**) (72 mg, 40%) as a semi-solid material: ν_{max}^{film} 3160, 1660, 1640, and 1560 cm^{-1}; λ_{max}^{MeOH} 224 nm (ε 12000); τ ($CDCl_3$) −0.92 (s, 1H, NH), 2.48 and 3.38 (each d, J=1.9 Hz, each 1H, CH=CH), 5.70 (m, 1H, 6-H), 8.05 (m, 2H, CH_2), 8.57 (d, J=6.01 Hz, 3H, 6-CH_3), and 8.67 (s, 6H, 4,4-$(CH_3)_2$); *m/e* 193 (M^+).

Found: C, 62.26; H, 7.63; N, 21.83%. Calcd for $C_{10}H_{15}N_3O$: C, 62.15; H, 7.82; N, 21.75%.

Reaction of **8** *with Diazomethane.* Treatment of **8** (186 mg, 1.00 mmol) with excess diazomethane in ether at room temperature for 1 day gave a solid product after removal of the solvent, which on recrystallization from *n*-hexane–dichloromethane afforded *4,4,6-trimethyl-2-[3-(4-chloro-1-methyl)pyrazolyl]-5,6-dihydro-1,3-oxazine* (**15**) (126 mg, 52.1 %) as colorless crystals: mp 78—80°C; ν_{max}^{KBr} 1660 and 1650 cm^{-1}; λ_{max}^{EtOH} 224 nm (ε 10200).

Found: C, 55.10; H, 6.79; N, 17.09%. Calcd for $C_{11}H_{16}N_3OCl$: C, 54.65; H, 6.67; N, 17.38%.

Reaction of 10 *with Diazomethane.* A similar treatment of **10** (161 mg, 1.00 mmol) with excess diazomethane for 1 day afforded *5,5-dimethyl-2-(3-1*H*-pyrazolyl)-3-isopropylidene-1-pyrroline* (**16**) (130 mg, 63.9%) as crystals after recrystallization from ether–*n*-hexane: mp 133—135°C; ν_{max}^{KBr} 3160, 1655, 1585, and 1545 cm^{-1}; λ_{max}^{MeOH} 252 nm (ε 10000); τ ($CDCl_3$) 0.02 (s, 1H, NH), 2.52 and 3.55 (each d, J=1.9 Hz, each 1H, CH=CH), 7.45 (q, J=1.65 Hz, 2H, CH_2), 8.28 (s, 3H, C^bH_3), 8.32 (t, J=1.65 Hz, 3H, C^aH_3), and 8.68 (s, 6H, 5,5-$(CH_3)_2$(; *m/e* 203 (M^+).

Found: C, 70.96; H, 8.38; N, 20.67%. Calcd for $C_{12}H_{17}N_3$: C, 70.90; H, 8.43; N, 20.67%.

Reaction of **11** *with Diazomethane.* A similar treatment of crude **11** with excess diazomethane in ether followed by purification on a neutral alumina column eluting with $CHCl_3$–MeOH afforded *5,5-dimethyl-2-[3-(4-chloro-1-methyl)pyrazolyl]-3-isopropylidene-1-pyrroline* (**17**) (16% from **9**) as a semi-solid: ν_{max}^{film} 1650, 1590, and 1540 cm^{-1}; λ_{max}^{MeOH} 250 nm (ε 6800); τ ($CDCl_3$) 2.63 (s, 1H, C=CH), 6.12 (s, 3H, NCH_3), 7.45 (q, J=1.7 Hz, 2H, CH_2), 8.19 (s, 3H, C^bH_3), 8.45 (t, J=1.7 Hz, 3H, C^aH_3), and 8.65 (s, 6H, 5,5-$(CH_3)_2$); *m/e* 252 (M^+) and 254 (M+2) in 3 : 1 ratio.

Found: C, 62.32; H, 6.92; N, 16.68%. Calcd for $C_{13}H_{18}N_3Cl$: C, 62.02; H, 6.92; N, 16.68%.