June, 1989] © 1989 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 62, 1925—1929 (1989) 1925

Reactions of Sodium Salts of Tosylhydrazones of 2- and 3-Thiophenecarbaldehydes, 1-Methyl-2-pyrrolecarbaldehyde, and Furfural with Acrylonitrile

Katsuhiro Saito,* Tatsuji Sato, Hiraku Ishihara, and Kensuke Takahashi
Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466

(Received November 11, 1988)

Reactions of the sodium salts of tosylhydrazones of several heteroaromatic aldehydes with an equimolar amount of acrylonitrile afforded the corresponding cyclopropane derivatives as the major products accompanied by small amounts of pyrazole derivatives. On the other hand, reactions using ten-molar equivalents of acrylonitrile gave pyrazole derivatives as major products.

Much effort has been devoted to the investigation of the reactivities of tosylhydrazones which generate carbenes via diazo compounds. It is known that the reactivities of the diazo compounds or the carbenes are influenced by conjugation with unsaturated moieties.[1] Many papers have been published on the chemistry of tosylhydrazones conjugated with olefinic, aromatic, or carbonyl moieties, while detailed reports on the chemistry of tosylhydrazones conjugated with heterocyclic moieties have been relatively few.[2]

Previously, Shechter reported that the carbenes generated from the tosylhydrazones of furfural or thiophenecarbaldehyde inserted into the C-H bonds of alkanes or rearranged into unstable acetylene derivatives.[3] Maas[4] has documented the addition reactions of olefins with carbenes conjugated with furan, thiophene, or pyridine moieties to give cyclopropanes. The authors have investigated the reactivities of tosylhydrazones conjugated with heterocyclic moieties and reported 1,3 N-C migration of the tosyl group or nucleophilic and stereospecific additions of the carbenes generated from the tosylhydrazones.[5] As one part of our these studies, we investigated the reactions of tosylhydrazones conjugated with thiophene, pyrrole, and furan moieties with acrylonitrile. Here, the results are discussed.

Results and Discussion

The reaction of sodium salt of 2-thiophenecarbaldehyde tosylhydrazone (**1a**) with an equimolar amount of acrylonitrile (**2**) was carried out in anhydrous diglyme at 120 °C for 20 min. A thin-layer chromatographic separation and purification of the reaction mixture afforded a 1 : 1 mixture of *cis*-**3a** and *trans*-cyclopropane **4a** derivatives and a pyrazoline derivative **5a** in 65.0 and 9.1% yields, respectively. A similar reaction, but using ten-molar equivalents of **2**, afforded a pyrazoline derivative **6a** and a pyrazole derivative **7a** in 45.1 and 6.1% yields, respectively. A

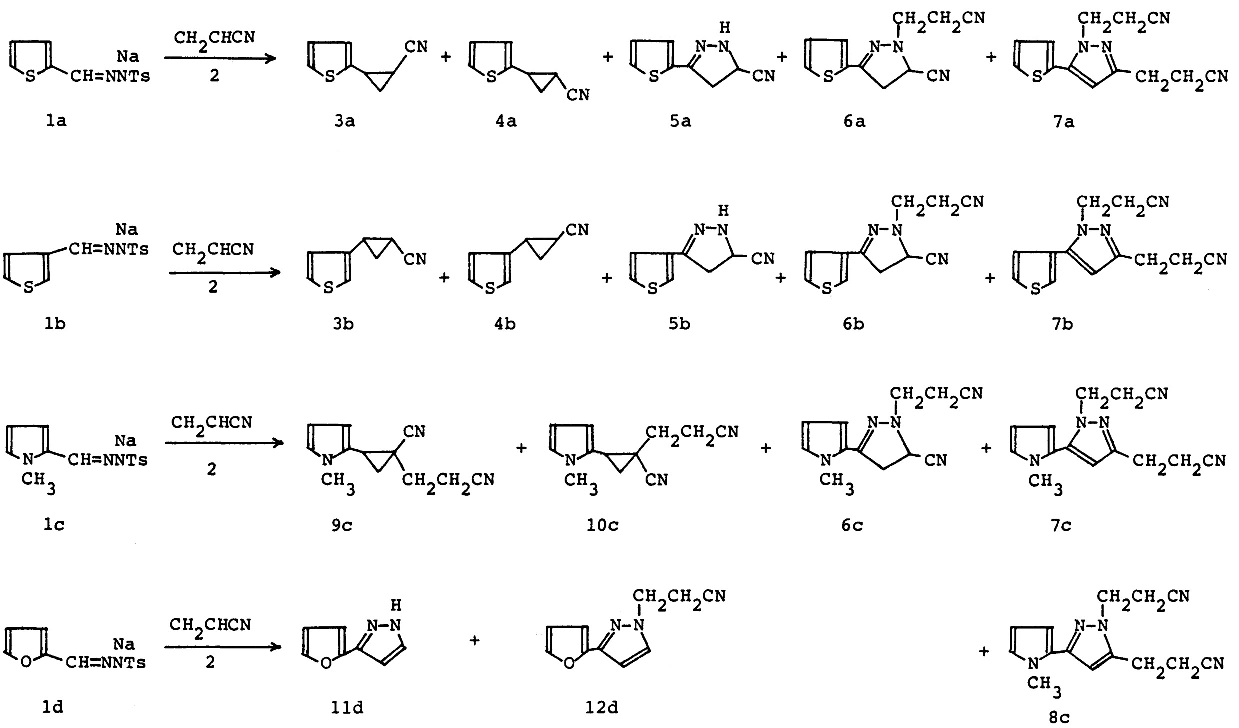


Fig. 1.

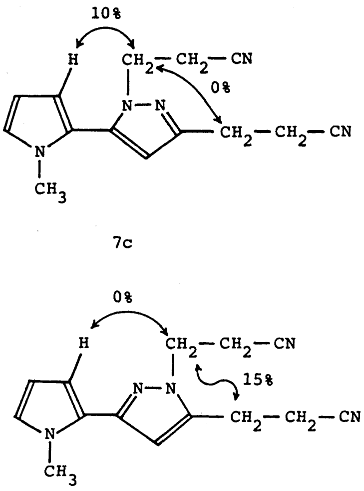
reaction with sodium salt of 3-thiophenecarbaldehyde tosylhydrazone (**1b**) gave almost the same result as mentioned above; a reaction of **1b** with an equimolar amount of **2** afforded a 1 : 1 mixture of cyclopropanes, **3b** and **4b**, and a pyrazoline derivative **5b** in 67.3 and 19.7% yields, respectively. A reaction of **1b** with ten-molar equivalents of **2** gave a pyrazoline derivative **6b** and a pyrazole derivative **7b** in 50.1 and 8.9% yields, respectively.

The same type of reaction using sodium salt of 1-methyl-2-pyrrolecarbaldehyde tosylhydrazone (**1c**) with an equimolar amount of **2** afforded no isolatable product. However, the employment of a large excess amount of acrylonitrile gave a better result, as follows. A reaction of **1c** with ten-molar equivalents of **2** yielded a cyclopropane derivative **9c**, a pyrazoline derivative **6c**, and pyrazole derivatives, **7c** and **8c**, in 6.5, 5.6, 3.1, and 4.9% yields, respectively. A reaction with twenty-molar equivalents of **2** promoted the product yields to give **9c**, **10c**, **6c**, **7c**, and **8c** in 18.8, 6.6, 18.6, 4.0, and 3.9% yields, respectively.

No cyclopropane derivatives were detected in the reaction of sodium salt of furfural tosylhydrazone (**1d**). A reaction of **1d** with an equimolar amount of **2** afforded pyrazole derivatives, **11d** and **12d**, each in 1.1% yield; these yields were improved by using ten-molar equivalents of **2** to 2.2 and 11.1%, respectively.

The structures of the products were deduced on the basis of their spectral properties and a comparison of the NMR spectra with those of the analogous compounds.6) The absorption maxima in the UV spectra of **5a**, **b** and **6a**, **b** (ca. 290 nm), which appear at longer wavelengths than those of **3a**, **b** and **4a**, **b** (238 nm) or thiophene (231 nm), show that these pyrazoline derivatives have double bonds conjugated with the heterocyclic moieties.

The structures of **7c** and **8c** were deduced by measurements of the nuclear overhauser effect in their NMR spectra, as follws. Irradiation of the methylene protons of the *N*-substituted cyanoethyl group of **7c** caused a 10% growth of the signal of the 3-position proton of the pyrrole ring, though the peak of the other cyanoethyl group showed no change, as shown in Fig. 2. On the other hand, a corresponding irradiation of **8c** resulted in a 15% enhancement of the peak of the other cyanoethyl moiety but did not effect on the ring protons. The structures of **7a** and **7b** were assigned on the basis of a comparison of their ^{1}H NMR and ^{13}C NMR spectra with those of **7c** and **8c**.



7c

8c

Fig. 2.

The stereochemistries of **9c** and **10c** are not clear, but considering the steric size of cyanoethyl and cyano groups, the major product **9c** is thought to have a pyrrole group and a cyanoethyl group as a trans-configuration, as shown in the figure.

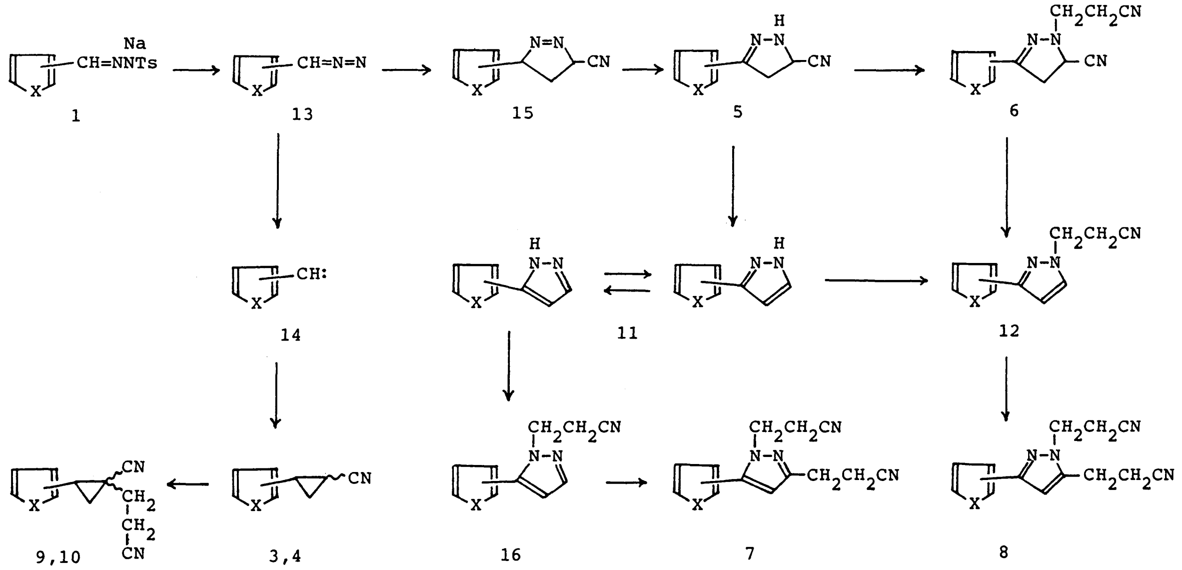


Fig. 3.

The reaction is considered to proceed as follows.[7] The thermolysis of **1** generates the diazo compound **13**, which further decomposes to carbene **14**, and adds to **2** to give **3** and **4**.[8] The cyclopropane derivatives, **9** and **10**, are considered to be formed through reactions of **3** and **4** with **2**. A 1,3-dipolar addition of **13** to **2** gives **5** via an intermediate **15**. An aromatization of **5**, leaving hydrogen cyanide, forms **11**. A nucleophilic attack of **5** to **2** can give **6**, which then aromatizes to **12** leaving hydrogen cyanide. The pyrazole derivatives **7** and **8** are considered to be derived through **11** and **12**, respectively.

There is a possibility of the formation of cyclopropane derivatives (**3**, **4**) from **15** via a loss of nitrogen. In order to examine this possibility, a reaction of **1b** with ten-molar equivalents of **2** was carried out in a five-fold diluted concentration. The products were a 38.0% yield of **6b** and a 21.3% yield of **7b**; no cyclopropane derivatives were detected at all. This fact shows that the cyclopropane derivatives were formed via a reaction of carbene **14** but not via **15**.

In the presence of an excess amount of acrylonitrile, the diazo compound **13** reacts with acrylonitrile to give pyrazoline- or pyrazole-type products. If there is no such excess amount of acrylonitrile, **13** further decomposes to the carbene to give cyclopropane-type products.

It has been reported that in a reaction of **1** with stilbene, dimethyl fumarate, dimethyl maleate, or styrene derivatives, neither pyrazoline nor pyrazole derivatives were detected; only cyclopropane derivatives were afforded.[5] The difference between the abovementioned result and the present result can be considered to be attributable to the high reactivity of acrylonitrile to diazo compounds.

The product yields of the reaction of **1d** were poor. One of the reasons for this phenomenon is considered to be the liability of the furyl ring to ring opening. Shechter reported that the ring in carbene **14d** can very easily be opened and rearranged to a very unstable acetylene derivative.[3] In the present reaction, **1d** is thought to generate the unreactive diazo compound **13d**, which then forms carbene; it then decomposes to resinous materials via an unstable acetylene derivative.

Experimental

Melting points were recorded on a Yanagimoto Micro Melting Point Apparatus and are uncorrected. NMR spectra were measured with a Varian XL 200 or a Hitachi R-20B spectrometer with tetramethylsilane as an internal standard. UV and IR spectra were measured with Hitachi 220A and JASCO A-102 spectrometers, respectively. Mass spectra were measured with a Hitachi M-52 or a JMS-DX300 spectrometer. Wako gel B5F was used for thin-layer chromatography. Diglyme was distilled from calcium hydride and stored on Molecular Sieves 3A 1/16.

Reaction of 1a with an Equimolar Amount of 2. A typical reaction procedure: To a solution of **1a** (2.80 g, 10 mmol) in anhydrous diglyme (30 ml) was added sodium hydride (50% in mineral oil, 0.72 g, 15 mmol). After the evolution of hydrogen gas had ceased **2** (0.53 g, 10 mmol) was added. The mixture was then heated at 120 °C for 20 min to evolve a nitrogen gas (170 ml, 76%). The reaction mixture was poured into water and extracted with diethyl ether. The ether was washed with water and brine and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator and the residue was subjected to thin-layer chromatography on silica gel by using chloroform as a developing solvent to give an oily mixture of **3a** and **4a** (970 mg, 65.0%, R_f=0.70) and crystals **5a** (169 mg, 9.1%, R_f=0.24).

3a or 4a: Found: m/z 149.0279. Calcd for C_8H_7NS: M, 149.0299. MS m/z (rel intensity): 149 (M^+, 100) and 121 (40). IR (oil): 2240 cm^{-1}. UV (EtOH): 238 nm (log ε, 3.78). ^1H NMR ($CDCl_3$) δ=1.38 (m, 1H), 1.53 (m, 2H), 2.72 (m, 1H), 6.84 (m, 1H), 6.91 (m, 1H), and 7.12 (m, 1H).

4a or 3a: Found: m/z 149.0311. Calcd for C_8H_7NS: M, 149.0299. MS m/z (rel intensity): 149 (M^+, 100) and 121 (48). IR (oil): 2240 cm^{-1}. UV (EtOH): 238 nm (log ε, 3.78). ^1H NMR ($CDCl_3$) δ=1.42 (m, 2H), 1.70 (m, 1H), 2.52 (m, 1H), 6.93 (m, 2H), and 7.18 (m, 1H).

5a: Mp 53—54 °C. Found: m/z 177.0322. Calcd for $C_8H_7N_3S$: M, 177.0335. MS m/z (rel intensity): 177 (M^+, 100), 143 (35), and 121 (15). IR (KBr): 2230 cm^{-1}. UV (EtOH): 285 nm (log ε, 3.99). ^1H NMR ($CDCl_3$) δ=2.99 (dd, 1H, J=18 and 10 Hz), 3.34 (dd, 1H, J=18 and 12 Hz), 5.31 (dd, 1H, J=18 and 10 Hz), 6.60 (s, 1H), 7.02 (m, 2H), and 7.31 (m, 1H).

Reaction of 1a with Ten-Molar Equivalents of 2. A mixture of **1a** (2.50 g, 9 mmol), sodium hydride (50%, 0.65 g, 14 mmol), and **2** (4.78 g, 90 mmol) in diglyme (30 ml) was heated at 130 °C for 1 h to evolve nitrogen gas (100 ml, 45%). The reaction mixture was treated as usual by using benzene-diethyl ether 6:4 as a developing solvent to give crystals **6a** (926 mg, 45.1%, R_f=0.60) and an oil **7a** (140 mg, 6.1%, R_f=0.37).

6a: Mp 90—91 °C. Found: m/z 230.0620. Calcd for $C_{11}H_{10}N_4S$: M, 230.0626. MS m/z (rel intensity): 230 (M^+, 85), 189 (100), and 163 (26). IR (KBr): 2260 and 2220 cm^{-1}. UV (EtOH): 291 nm (log ε, 3.99). ^1H NMR ($CDCl_3$) δ=2.71 (t, 2H, J=7 Hz), 3.03 (dd, 1H, J=18 and 12Hz), 3.36 (m, 3H), 5.00 (dd, 1H, J=12 and 11 Hz), 7.02 (m, 1H), 7.24 (m, 1H), and 7.37 (m, 1H).

7a: Found: m/z 256.0774. Calcd for $C_{13}H_{12}N_4S$: M, 256.0728. MS m/z (rel intensity): 256 (M^+, 100), 215 (69), and 202 (47). IR (oil): 2243 cm^{-1}. ^1H NMR ($CDCl_3$) δ=2.91 (m, 6H), 4.35 (t, 2H, J=7 Hz), 6.24 (s, 1H), 7.36 (m, 1H), and 7.43 (m, 2H). ^{13}C NMR ($CDCl_3$) δ=17.0, 18.7, 24.4, 44.7, 106.7, 116.9, 119.4, 127.6, 127.9, 128.1, 129.6, 138.0, and 149.4.

Reaction of 1b with an Equimolar Amount of 2. A mixture of **1b** (2.80 g, 10 mmol), sodium hydride (50%, 0.72 g, 15 mmol), and **2** (0.53 g, 10 mmol) in diglyme (30 ml) was heated at 120 °C for 20 min to evolve nitrogen gas (98 ml, 44%). The usual work up using chloroform as a developing solvent gave a mixture of **3b** and **4b** (1004 mg, 67.3%, R_f=0.65) and an oil **5b** (349 mg, 19.7%, R_f=0.30).

Mixture of 3b and 4b: Found: m/z 149.0312. Calcd for C_8H_7NS: M, 149.0299. MS m/z (rel intensity): 149 (M^+, 100) and 121 (45). IR (oil): 2240 cm^{-1}. UV (EtOH): 238 nm (log ε, 3.72). ^1H NMR ($CDCl_3$) δ=1.2—1.8 (m, 3H), 2.3—2.8 (m, 1H), and 6.7—7.4 (m, 3H).

5b: Found: m/z 177.0348. Calcd for C_8H_7NS: M, 177.0335. MS m/z (rel intensity): 177 (M^+, 1), 148 (100), and 122 (46). IR (oil): 2230 cm^{-1}. UV (EtOH): 282 nm (log ε, 3.85). ^{1}H NMR ($CDCl_3$) δ=2.90 (dd, 1H, J=18 and 10 Hz), 3.31 (dd, 1H, J=18 and 12 Hz), 5.16 (dd, 1H, J=18 and 10 Hz), 6.63 (s, 1H), 7.04 (m, 1H), and 7.32 (m, 2H).

Reaction of 1b with Ten-Molar Equivalents of 2. A mixture of **1b** (2.52 g, 9 mmol), sodium hydride (50%, 0.65 g, 14 mmol), and **2** (4.78 g, 90 mmol) in diglyme (30 ml) was heated at 130 °C for 20 min to evolve nitrogen gas (90 ml, 45%). The reaction mixture was treated as usual by using chloroform-diethyl ether 8 : 2 as a developing solvent to give crystals **6b** (2070 mg, 50.1%, R_f=0.70) and an oil **7b** (202 mg, 8.9%, R_f=0.33).

6b: Mp 108—109 °C. Found: m/z 230.0625. Calcd for $C_{11}H_{10}N_4S$: M, 230.0626. MS m/z (rel intensity): 230 (M^+, 74), 189 (100), 163 (21). IR (KBr): 2250 and 2230 cm^{-1}. UV (EtOH): 291 nm (log ε, 4.05). ^{1}H NMR ($CDCl_3$) δ=2.65 (m, 2H), 2.97 (dd, 1H, J=18 and 13 Hz), 3.30 (m, 3H), 4.87 (dd, 1H, J=13 and 11 Hz), 7.16 (m, 1H), and 7.42 (m, 2H).

7b: Found: m/z 256.0763. Calcd for $C_{13}H_{12}N_4S$: M, 256.0782. MS m/z (rel intensity): 256 (M^+, 93), 215 (83), and 202 (100). IR (oil): 2240 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.74 (t, 2H, J=7 Hz), 2.95 (m, 4H), 4.34 (t, 2H, J=6 Hz), 6.22 (s, 1H), 7.19 (m, 1H), and 7.45 (m, 2H). ^{13}C NMR ($CDCl_3$) δ=17.0, 18.7, 24.4, 44.6, 105.6, 117.1, 119.4, 124.9, 127.0, 127.8, 129.7, 140.4, and 149.4.

Reaction of 1c with Ten-Molar Equivalents of 2. A mixture of **1c** (2.77 g, 10 mmol), sodium hydride (50%, 0.66 g, 14 mmol), and **2** (5.31 g, 10 mmol) in diglyme (50 ml) was heated at 95 °C for 25 min to evolve nitrogen gas (180 ml, 80%). The usual work up using benzene-diethyl ether 7 : 3 as a developing solvent gave oils **9c** (130 mg, 6.5%, R_f=0.45), **6c** (126 mg, 5.6%, R_f=0.36), **7c** (78 mg, 3.1%, R_f=0.60), and **8c** (125 mg, 4.9%, R_f=0.55).

6c: Found: m/z 227.1178. Calcd for $C_{12}H_{13}N_5$: M, 227.1170. MS m/z (rel intensity): 227 (M^+, 19), 226 (100), 158 (90), and 145 (48). IR (oil): 2250 and 2220 cm^{-1}. UV (EtOH): 290 nm (log ε, 3.96). ^{1}H NMR ($CDCl_3$) δ=2.62 (ddd, 1H, J=17, 6, and 6 Hz), 2.71 (ddd, 1H, J=17, 8, and 6 Hz), 3.01 (dd, 1H, J=17 and 14 Hz), 3.27 (ddd, 1H, J=13, 6, and 6 Hz), 3.28 (dd, 1H, J=17 and 12 Hz), 3.35 (ddd, 1H, J=13, 8, and 6 Hz), 3.63 (s, 3H), 4.79 (dd, 1H, J=14 and 12 Hz), 6.08 (dd, 1H, J=4 and 3 Hz), 6.16 (dd, 1H, J=4 and 2 Hz), and 6.66 (dd, 1H, J=3 and 2 Hz).

7c: Found: m/z 253.1348. Calcd for $C_{14}H_{15}N_5$: M, 253.1327. MS m/z (rel intensity): 253 (M^+, 100), 213 (53), 200 (49), and 173 (26). IR (oil): 2265 cm^{-1}. UV (EtOH): 253 nm (log ε, 3.96). ^{1}H NMR ($CDCl_3$) δ=2.73 (t, 2H, J=7 Hz), 2.85 (t, 2H, J=7 Hz), 2.99 (t, 2H, J=7 Hz), 3.54 (s, 3H), 4.29 (t, 2H, J=7 Hz), 6.19 (s, 1H), 6.21 (dd, 1H, J=4 and 3 Hz), 6.25 (dd, 1H, J=4 and 2 Hz), and 6.69 (dd, 1H, J=3 and 2 Hz). ^{13}C NMR ($CDCl_3$) δ=17.0, 18.8, 24.4, 34.5, 44.3, 106.6, 108.1, 111.4, 117.1, 119.5, 120.7, 124.5, 136.5, and 149.2.

8c: Found: m/z 253.1355. Calcd for $C_{14}H_{15}N_5$: M, 253.1326. MS m/z (rel intensity): 253 (M^+, 21), 252 (100), 212 (55), 200 (52), and 173 (33). IR (oil): 2265 and 2210 cm^{-1}. UV (EtOH): 271 nm (log ε, 4.12). ^{1}H NMR ($CDCl_3$) δ=2.58 (t, 2H, J=7 Hz), 2.83 (t, 2H, J=6 Hz), 2.86 (t, 2H, J=7 Hz), 3.83 (s, 3H), 4.13 (t, 2H, J=6 Hz), 6.10 (dd, 1H, J=4 and 3 Hz), 6.21 (s, 1H), 6.36 (dd, 1H, J=4 and 3 Hz), and 6.62 (dd, 1H, J=3 and 2 Hz). ^{13}C NMR ($CDCl_3$) δ=16.9, 18.8, 21.2, 36.3, 44.0, 103.4, 107.6, 108.8, 117.7, 118.8, 124.4, 126.3, 140.0, and 145.8.

9c: Found: m/z 199.1084. Calcd for $C_{12}H_{13}N_3$: M, 199.1108. MS m/z (rel intensity): 199 (M^+, 19), 198 (35), and 158 (100). IR (oil): 2240 and 2220 cm^{-1}. UV (EtOH): 225 nm (log ε, 4.01). ^{1}H NMR ($CDCl_3$) δ=1.43 (dd, 1H, J=9 and 6 Hz), 1.71 (dd, 1H, J=7 and 6 Hz), 1.82 (dd, 1H, J=15 and 7 Hz), 2.05 (dd, 1H, J=15 and 7 Hz), 2.21 (dd, 1H, J=4 and 3 Hz), 6.04 (dd, 1H, J=4 and 2 Hz), and 6.64 (dd, J=3 and 2 Hz).

Reaction of 1c with Twenty-Molar Equivalents of 2. A mixture of **1c** (2.77 g, 10 mmol), sodium hydride (50%, 0.66 g, 14 mmol), and **2** (10.62 g, 200 mmol) in diglyme (50 ml) was heated at 100 °C for 10 min to evolve nitrogen gas (195 ml, 87%). The same treatment as above gave oils **9c** (374 mg, 18.8%), **10c** (131 mg, 6.6%), **6c** (423 mg, 18.6%), **7c** (101 mg, 4.0%), and **8c** (98 mg, 3.9%).

10c: Found: m/z 199.1094. Calcd for $C_{12}H_{13}N_3$: M, 199.1108. MS m/z (rel intensity): 199 (M^+, 23), 159 (100), and 145 (31). IR (oil): 2230 cm^{-1}. UV (EtOH): 227 nm (log ε, 3.84). ^{1}H NMR ($CDCl_3$) δ=1.38 (m, 2H), 1.79 (m, 2H), 2.43 (m, 2H), 2.62 (dd, 1H, J=10 and 7 Hz), 3.62 (s, 3H), 5.83 (dd, 1H, J=4 and 3 Hz), 6.01 (dd, 1H, J=4 and 2 Hz), and 6.63 (dd, 1H, J=3 and 2 Hz).

Reaction of 1d with an Equimolar Amount of 2. A mixture of **1d** (7.89 g, 30 mmol), sodium hydride (50%, 2.16 g, 45 mmol), and **2** (1.59 g, 30 mmol) in diglyme (70 ml) was heated at 90 °C for 20 min to evolve nitrogen gas (600 ml, 89%). The usual work up using benzene-diethyl ether 1 : 1 as a developing solvent gave oils **11d** (45 mg, 1.1%, R_f=0.38) and **12d** (61 mg, 1.1%, R_f=0.25).

11d: Found: m/z 134.0467. Calcd for $C_7H_6N_2O$: M, 134.0480. MS m/z (rel intensity): 134 (M^+, 100), 115 (25), and 105 (53). IR (oil): 3140 cm^{-1}. UV (EtOH): 262 nm (log ε, 4.08). ^{1}H NMR ($CDCl_3$) δ=6.46 (dd, 1H, J=3 and 2 Hz), 6.54 (d, 1H, J=2 Hz), 6.65 (dd, 1H, J=3 and 1 Hz), 7.26 (s, 1H), 7.45 (dd, 1H, J=2 and 1 Hz), and 7.62 (d, 1H, J=2 Hz).

12d: Found: m/z 184.0740. Calcd for $C_{10}H_9N_3O$: M, 187.0746. MS m/z (rel intensity): 187 (M^+, 79), 147 (100), and 119 (26). IR (oil): 2240 cm^{-1}. UV (EtOH): 266 nm (log ε, 4.58). ^{1}H NMR ($CDCl_3$) δ=2.98 (t, 2H, J=7 Hz), 4.41 (t, 2H, J=7 Hz), 6.47 (dd, 1H, J=3 and 2 Hz), 6.50 (d, 1H, J=2 Hz), 6.66 (dd, 1H, J=3 and 1 Hz), 7.46 (dd, 1H, J=2 and 1 Hz), and 7.50 (d, 1H, J=2 Hz).

Reaction of 1d with Ten-Molar Equivalents of 2. A mixture of **1d** (2.64 g, 10 mmol), sodium hydride (50%, 0.66 g, 14 mmol), and **2** (5.31 g, 100 mmol) in diglyme (30 ml) was heated from 90 °C to 160 °C in a period of 50 min. No nitrogen gas was evolved. The usual work up using benzene-diethyl ether 1 : 9 as a developing solvent gave oils **11d** (29 mg, 2.2%, R_f=0.55) and **12d** (208 mg, 11.1%, R_f=0.46).

Reaction of 1a with Ten-Molar Equivalents of 2 in Diluted Conditions. A mixture of **1a** (2.80 g, 10 mmol), sodium hydride (50%, 0.72 g, 15 mmol), and 2 (5.3 g, 100 mmol) in diglyme (150 ml) was heated at 140 °C for 25 min to evolve nitrogen gas (70 ml, 31%). The reaction mixture was chromatographed on silica gel to give **6a** (873 mg, 38.0%, benzene-diethyl ether 8 : 2) and **7a** (545 mg, 21.3%, benzene-diethyl ether 1 : 1).

References

1) W. Kirms, "Carbene Chemistry," Academic Press (1964); J. Hine, "Divalent Carbon," Ronald Press (1964); W.

R. Bambord and T. S. Stevens, *J. Chem. Soc.*, **1952**, 4735; W. M. Jones and C. L. Ennis, *J. Am. Chem. Soc.*, **89**, 3069 (1967); K. Saito, T. Toda, and T. Mukai, *Bull. Chem. Soc. Jpn.*, **57**, 1567 (1984); K. Saito, *ibid.*, **60**, 2105 (1987); K. Saito and H. Ishihara, *ibid.*, **60**, 4447 (1987).

2) R. Huisgen, *Angew. Chem.*, **75**, 604 (1963); E. Ciganek, *ibid.*, **78**, 1979 (1966); W. J. Lenoble, Tatsukami, H. F. Morris, *J. Am. Chem. Soc.*, **92**, 5681 (1970); M. Jones, Jr., W. J. Baron, and Y. H. Shen, *ibid.*, **92**, 4745 (1970).

3) R. V. Hoffman and H. Shechter, *J. Am. Chem. Soc.*, **93**, 5940 (1971); R. V. Hoffman, G. G. Orphanide, and H. Shechter, *ibid.*, **100**, 7934 (1978); R. V. Hoffman and H. Shechter, *ibid.*, **100**, 7937 (1978).

4) G. Maas and C. Hummel, *Chem. Ber.*, **113**, 3679 (1980).

5) K. Saito and H. Ishihara, *Heterocycles*, **24**, 1291 (1986); *idem, ibid.*, **26**, 1891 (1987); K. Saito, H. Ishihara, T. Murase, Y. Horie, and E. Maekawa, *Bull. Chem. Soc. Jpn.*, **60**, 4317 (1987); K. Saito, H. Ishihara, and K. Takahashi, *Heterocycles*, **27**, 1141 (1988).

6) N. S. Bacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "NMR Spectra Catalog," The National Press (1985); C. J. Powchert and J. R. Campbell, "The Aldrich Library of NMR Spectra," Aldrich Chemical Company Inc. (1974); A. R. Katritzky, "Handbook of Heterocyclic Chemistry," Pergamon Press (1985).

7) K. Bowden and M. J. Price, *J. Chem. Soc. B*, **1970**, 1466; E. K. Launio and T. G. Frey, *J. Org. Chem.*, **36**, 345 (1971); K. Saito, *Bull. Chem. Soc. Jpn.*, **60**, 2105 (1987).

8) The referee suggested a possibility of an existence of the following diazo intermediate. We are indebted to the referee for this suggestion.

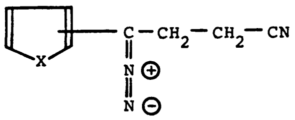


Fig. 4.