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# Chemistry of Diaminomaleonitrile. 4. Nitrile Hydration of the Schiff Bases[1]

Yozo Ohtsuka

*Sagami Chemical Research Center, 4-4-1 Nishi-Ohnuma, Sagamihara, Kanagawa 229, Japan*

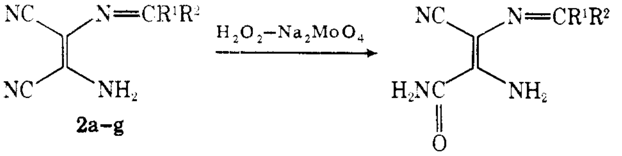
*Received July 19, 1978*

As a new transformation of diaminomaleonitrile (DAMN, **1**), nitrile hydration of DAMN Schiff base **2** was investigated. Open-chain amides **3a–g** were obtained by treatment of **2a–g** in ethanol with hydrogen peroxide and catalytic amounts of sodium molybdate. The structure **3** was determined on the basis of $^{13}$C NMR spectrometry of a number of maleonitrile derivatives. The hydration of Schiff bases **4a,b** gave pyrazine derivatives **5a,b**. Amide **3a** was converted into imidazole **6** by oxidation and **3a–g** were cyclized with alkali into pyrrolones **7a–g**.

In contrast to the well-studied reactions of the amino groups in diaminomaleonitrile (DAMN, **1**), the reaction involving its nitrile groups has been little explored. Hydration of the nitrile group(s) has been carried out along with[1,2] or after[3] the conversion of the amino groups into heterocyclic derivatives. Direct hydration of **1** with acids or bases tends to result in degraded compounds by elimination of hydrogen cyanide or ammonia.[3b,4] Oxidation of **1** produces diiminosuccinonitrile (DISN), which decomposes rapidly in contact with polar substances.[5]

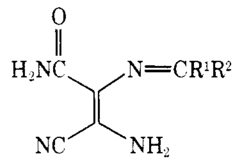
In the course of our study on DAMN derivatives, we have observed that DAMN Schiff bases **2** were more resistant than DAMN itself toward degradation reactions under several conditions. Oxidation of **2** with reagents, such as DISN and dichlorodicyanobenzoquinone (DDQ), is known to afford 2-substituted imidazole-4,5-dicarbonitrile.[6] The potential utility of nitrile reactions of the open-chain DAMN derivatives for synthesis of a wide variety of heterocyclic compounds has prompted us to study the nitrile hydration reaction of a series of Schiff bases **2a–g**.[3b,7]

**Reactions.** Preliminary examination of **2** showed that they underwent preferential cleavages of the azomethine linkages upon heating with acid or base. In experiments to effect mild and almost neutral hydration of the nitrile function in **2**, they were treated in alcohol solution with hydrogen peroxide. Among the results, a 37% yield of an amide product (**3a**) was isolated from **2a**. Then, it was found that the yield of the product could be increased when a catalytic amount of sodium molybdate[8] was added to the reaction mixture. The results of the reactions of a set of Schiff bases **2a–g** are summarized in Table I. Spectroscopic properties of the hydration products are shown in Tables II and III. The stereochemistry of the amide **3a–g** was assigned on the basis of $^{13}$C NMR spectrometry, which is separately described in the next section. Meticulous examinations of the hydration product mixtures revealed no trace of the alternative stereoisomers **3′**. In most cases, the reaction was complete within 18 h at room temperature, and prolonged reaction times (more than 24 h) or a higher temperature (at 40 °C) tended to result in the formation of oxamide. *p*-Nitrobenzylidenediaminomaleonitrile (**2e**) was incompletely converted to the amide under the conditions and the product **3e** was isolated by partial crystallizations from acetonitrile.



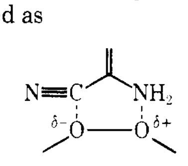
**2a–g** **3a–g**

a, $R^1$ = H; $R^2$ = Ph
b, $R^1$ = H; $R^2$ = 4-$CH_3C_6H_4$
c, $R^1$ = H; $R^2$ = 4-$CH_3OC_6H_4$
d, $R^1$ = H; $R^2$ = 9-anthranyl
e, $R^1$ = H; $R^2$ = 4-$NO_2C_6H_4$
f, $R^1$ = $CH_3$; $R^2$ = 4-$NO_2C_6H_4$
g, $R^1$ = $R^2$ = Ph



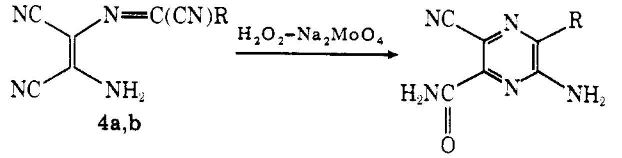
**3′**

The apparent regiospecificity of the hydration reaction may result from the interaction of the peroxy moiety with the $NH_2$ group in **2** illustrated as



Nitrile hydration by similar participation of $NH_2$ group has been observed previously by the reaction of carbonyl compounds with urea derivatives of **1**.[1]

Schiff bases **4a** and **4b**,[9] obtained from **1** with acetyl and benzoyl cyanide, respectively, were hydrated by the reagents under similar conditions and pyrazine derivatives **5a** and **5b**



**4a,b** **5a,b**

a, R = $CH_3$ b, R = Ph

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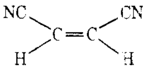
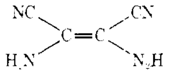
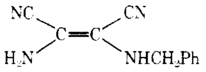
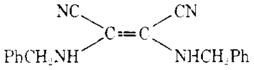
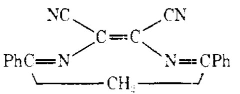
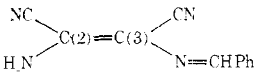
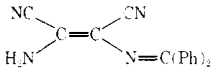
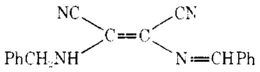
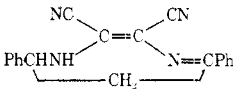
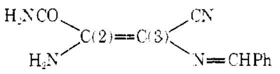
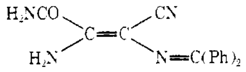
**Table I. 2-Amino-3-(aralkylideneamino)-3-cyanoacrylamides**

| compd[a] | $R^1$ | $R^2$ | % yield | mp, °C |
|---|---|---|---|---|
| **3a** | H | Ph | 81 | 197–199 dec[b] |
| **3b** | H | 4-$CH_3C_6H_4$ | 86 | 203–204 dec[c] |
| **3c** | H | 4-$CH_3OC_6H_4$ | 79 | 213–216 dec[b] |
| **3d** | H | 9-anthranyl | 95 | 177–179 dec[b] |
| **3e** | H | 4-$NO_2C_6H_4$ | 30 | 210–230 dec[b] |
| **3f** | $CH_3$ | 4-$NO_2C_6H_4$ | 62 | 200–203 dec[b] |
| **3g** | Ph | Ph | 36 | 183–185 dec[c] |

[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds listed in the table. [b,c] Recrystallization from [b] $CH_3CN$ or [c] EtOH.

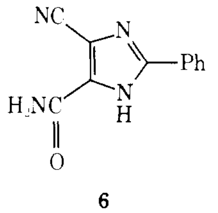
**Table II. $^{13}C$ Chemical Shifts for Olefinic Carbons in Maleonitrile Derivatives[a]**

| no. | compd | registry no. | C(2)[b] | C(3) |
|---|---|---|---|---|
| 1 |  | 928-53-0 | 119.63 | |
| 2 | <br>1 | 1187-42-4 | 106.23 | |
| 3 |  | 51802-03-0 | 108.26<br>107.78 | |
| 4 |  | 51802-04-1 | 109.72 | |
| 5 |  | 56984-07-7 | 123.28 | |
| 6 | <br>**2a** | | 126.93 | 102.70 |
| 7 | <br>**2g** | | 127.44 | 101.14 |
| 8 |  | 51802-24-5 | 128.13 | 103.24 |
| 9 |  | 51802-63-2 | 121.58 | 103.68 |
| 10 | <br>**3a** | | 152.11 | 92.70 |
| 11 | <br>**3g** | | 158.53 | 89.74 |

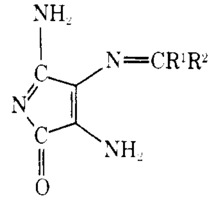
[a] Values (in $Me_2SO$) are in parts per million from $Me_4Si$ as an internal standard. [b] For the numbering see structures **2a** (no. 6) and **3a** (no. 10).

were obtained. The present method of partial hydration of *o*-dinitrile compounds was applied successfully to the preparation of 2-cyanopyrazine-3-carboxamide from pyrazine-2,3-dicarbonitrile.[10] Attempted hydration of *N,N'*-dibenzylidenediaminomaleonitrile[11] gave predominantly recovered starting material. *N'*-Acetyl[3b] and *N'*-benzyl[6] derivatives of **2a** gave soluble products and no rigorous attempt was made to isolate these compounds.

Oxidation of amide **3a** with DDQ or sodium hypochlorite gave 4(5)-cyano-2-phenylimidazole-5(4)-carboxamide (**6**) in a way analogous to the reactions of **2** into imidazoles.[6] Amides **3a–g** underwent ready cyclization with alkali (aqueous ammonia or sodium hydroxide) to give Schiff bases of 3,4,5-triamino-2*H*-pyrrol-2-one (**7a–g**). 2-Cyanobenzamide cyclizes similarly into phthalimidine.[12]



**6**

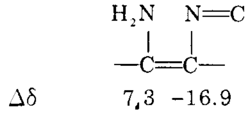


**7a–g**

($R^1$ and $R^2$ same as in **2a–g**)

**$^{13}C$ NMR Spectrometry.** Determination of stereochemistry in hydration products (differentiation of structure **3** from **3'**) was made on the basis of substituent effects on $^{13}C$ chemical shifts for olefinic carbons in maleonitrile derivatives shown in Table II.

Substituent effects of $NH_2$ and N=C(Ph) in the maleonitrile system were initially estimated from differences in chemical shifts for C(2,3) in symmetrically substituted (no. 2 and 5[13] in Table II) and in unsubstituted (no. 1) maleonitriles; $\Delta\delta = -13.4$ ppm for $NH_2$ and $\Delta\delta = 3.7$ for N=C(Ph).[14] Since the important substituent effect in unsaturated systems is that on the chemical shift of the $\beta$ carbon,[15] the assignments of C(2) and C(3) in Schiff bases (no. 6–8) were determined as shown in Table II. The values for substituent effects of $NH_2$ and N=C(Ph) were calculated more accurately using the data for C(2) and C(3) in Schiff base **2a** (no. 6) and that for C(2,3) in maleonitrile (no. 1).



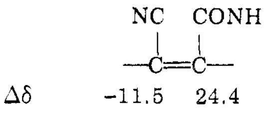
$$\begin{array}{ccc} & H_2N & N{=}C(Ph)- \\ & | & | \\ & -C & {=}C- \\ \Delta\delta & 7.3 & -16.9 \end{array}$$

I

The substituent effects of CN and $CONH_2$ were estimated from reported data[16] of cinnamonitrile and cinnamamide, where the shifts of 4-methoxystyrene were taken as a standard.[17]

| NCCH=CHPh | PhCH=CHCONH$_2$ |
|---|---|
| Δδ −14.9 13.8 | 3.4 10.6 |

From the additive relationship of substituent effects,[18] the values in olefin II were obtained as follows.



$$\begin{array}{ccc} & NC & CONH_2 \\ & | & | \\ & -C & {=}C- \\ \Delta\delta & -11.5 & 24.4 \end{array}$$

II

By combination of olefins I and II, it is now possible to estimate that the chemical shift differences in C(2) and C(3) will be greater in the order **3** (60.1 ppm, estimated) >**2** (~25 ppm, observed) >**3'** (11.7 ppm, estimated). The observed differences for hydration products (59.4 ppm for no. 10 and 68.8 ppm for no. 11) apparently fit for the structure **3**.

**Comparison of Spectral Data.** It is appropriate to correlate the spectral properties (Table III) of structures **2** and **3**, since such data are important in defining the structures of other products obtained from **1**.

In IR spectra, Schiff bases **2** exhibit two nitrile bands at 2224–2230 cm$^{-1}$ (region 1) and 2184–2200 cm$^{-1}$ (region 2). The bands of nitrile in **3** are found in the region 2, while *N,N'*-dibenzylidenediaminomaleonitrile[11] shows the band at

**Table III. Electronic and IR Spectra of Schiff Bases 2 and Amides 3**

| | registry no. | 2 | | | registry no. | 3 | | |
|---|---|---|---|---|---|---|---|---|
| | | $\nu_{C\equiv N}$, cm$^{-1}$ [b] | | $\lambda_{max}$, nm (log $\epsilon$)[c] | | $\nu_{C=O}$ | $\nu_{C\equiv N}$ | $\lambda_{max}$ (log $\epsilon$) |
| **a**[a] | 56029-18-6 | 2224 | 2198 | 366 (4.44), 259 (4.17) | 68568-17-2 | 1692 | 2191 | 360 (4.49), 247 (4.29) |
| **b** | 66371-27-5 | 2230 | 2200 | 364 (4.01), 264 (4.21), 247 (4.01) | 68568-18-3 | 1691 | 2192 | 356 (4.36), 258 (4.12), 245 (4.11) |
| **c** | 59574-37-7 | 2224 | 2200 | 375 (4.45), 275 (4.08) | 68568-19-4 | 1689 | 2186 | 360 (4.40), 271 (4.10) |
| **d** | 66371-59-3 | 2230 | 2200 | 426 (4.42), 252 (4.98) | 68568-20-7 | 1688 | 2188 | 424 (3.98), 253.5 (4.57) |
| **e** | 59567-59-8 | 2230 | 2200 | 398 (4.35), 266 (4.05) | 68568-21-8 | 1692 | 2188 | 389 (3.70), 258 (3.41) |
| **f** | 55752-07-3 | 2224 | 2184 | 398 (4.22), 294 (4.26), 267 (4.25) | 68568-22-9 | 1698 | 2190 | 401 (3.75), 285 (3.81), 262 (3.83) |
| **g** | 55752-09-5 | 2220 | 2184 | 376 (3.99), 258.5 (4.04) | 68568-23-0 | 1678 | 2185 | 367 (3.98), 247.5 (4.09) |

[a] Substituents ($R^1$ and $R^2$) are identical with those in Table I. [b] KBr disks. [c] EtOH solutions.

2220 cm$^{-1}$ in the vicinity of the region 1. The band in the region 2 is normally characteristic of $\beta$-aminoacrylonitrile derivatives.[19] The bands in the regions 1 and 2 in the spectra of **2** may be attributable to the nitrile groups at C(2) and at C(3), respectively. The IR frequencies due to the C≡N and the C=O in **2** and **3** are relatively insensitive to substituents on the azomethine carbon ($R^1$ and $R^2$).

The electronic spectra of **2** have been explained by a major contribution of the $R^1R^2C$=NC=CCN conjugation.[7] Replacement of CN by $CONH_2$ causes a decrease of the conjugation (Table III). However, this difference is not extensive and total features of their spectra are determined chiefly by the substituents, $R^1$ and $R^2$.

**Comparison of Reactivity.** The reactivity of the $NH_2$ group in **3** was compared with those in **1** and its open-chain derivatives by the following reactions. (i) Aldehydes react with **1** or its benzyl derivatives under mild conditions (e.g., at room temperature with acid catalyst, see also in the Experimental Section) to give the Schiff bases.[6] The condensation with **2** proceeds under reflux in appropriate solvent with acid or base,[11] and **3** was recovered unchanged by our attempts to react with aldehydes under various conditions. (ii) Benzyldiaminomaleonitrile[1] and **1**[6] (without catalyst), and **2**[1] (with $NEt_3$ catalyst) react with RNCO at the $NH_2$ groups, while **3** was found to be inert to the reagent. (iii) Acetylation of **1** and **2** occurs at 50 °C[20] and at 136 °C,[3b] respectively. Under the latter conditions, **3** gave a mixture of the unchanged compound (~20%) and dark tarry products. These examples indicate the general reactivity **1** ≥ benzyldiaminomaleonitrile > **2** > **3**.

## Experimental Section

All melting points were measured on a hot-stage type Yanagimoto MP-21 (calibrated) apparatus and were uncorrected.

**Spectra.** Infrared spectra (KBr disks) and electronic spectra (ethanol solution) were recorded on a Hitachi EPI-G3 and a Hitachi 323 spectrometer, respectively. Mass spectra were taken on a Hitachi RMU-6E mass spectrometer. $^1$H NMR spectra were measured in $Me_2SO$-$d_6$ solutions on a Varian HA-100 spectrometer. $^{13}$C NMR spectra were recorded on a Varian XL-100 spectrometer equipped for pulsed Fourier transform (FT) operation. This instrument was controlled with a Nicolet TT-100 computer system. In most cases, the spectra were determined for 700 mg/3 mL of $Me_2SO$-$d_6$ solutions containing 10 mg of $Cr(acac)_3$ and chemical shifts were reported in parts per million downfield from the internal standard $Me_4Si$. The olefinic signals shown in Table II were readily distinguished from the rest of the signals by chemical shift considerations and signal multiplicities from off-resonance decoupling experiments or from coupled spectra.

**Materials.** Diaminomaleonitrile (DAMN, **1**) was purchased from Nippon Soda Company, Ltd. (grade A; 98% purity). Maleonitrile was prepared from maleamide by the dehydration with phosphorus oxychloride.[21] *N*-Benzyldiaminomaleonitrile, *N,N'*-dibenzyldiaminomaleonitrile, *N*-benzyl-*N'*-benzylidenediaminomaleonitrile, and 6,7-dihydro-5,7-diphenyl-1*H*-1,4-diazepine-2,3-dicarbonitrile were prepared from **1** after the procedure reported by Begland et al.[6] *N,N'*-Dibenzylidenediaminomaleonitrile[11] was prepared from benzylidenediaminomaleonitrile (**2a**) and benzaldehyde with piperidine and purified by sublimation [160–165 °C (3 mm)] to give a yellow powder, mp 168–177 °C dec. The preparation of 5,7-diphenyl-1*H*-1,4-diazepine-2,3-dicarbonitrile and the Schiff bases of **2f** and **2g** were described in a previous paper.[9] For the preparation of the Schiff bases **2a–e**, a simple and convenient procedure has been developed in our laboratory (partly contributed by Dr. T. Kojima).

**General Procedure for Preparation of Schiff Bases 2.** To a solution of 10.8 g of **1** and the equimolar weight of aldehyde in 25 mL of dimethyl sulfoxide were added 3 drops of concentrated $H_2SO_4$. After stirring at room temperature for 15 min to 1 h, the reaction mixture was poured into ten volumes of ice–water. The mixture was thoroughly stirred and then kept standing for 1–2 h. Filtration and washing with methanol gave the product. Workup as above and recrystallization from the appropriate solvent gave: **2a**, mp 193–195 °C dec (lit.[3b] mp 191 °C), in a 92% yield; **2c**, mp 225–228 °C dec (lit.[3b] mp 227 °C dec), in a 97% yield; **2e**, mp 257–258 °C dec (lit.[7] mp 258–258.5 °C), in an almost quantitative yield. Similarly, **2b**, mp 228–231 °C dec (recrystallization from acetone), and **2d**, mp 217 °C dec (from acetonitrile-methanol), were obtained with 92 and 99% yield, respectively, and these compounds were identified by microanalyses and spectroscopic properties (Table III). This procedure is generally applicable to the condensation of other aldehydes and satisfactory results can be obtained by the reaction of crude **1** which tends to give a dark tarry mixture on heating.

**General Procedure for Hydration of 2 to Give Amides 3.** An aqueous solution of sodium molybdate (50 mL, 0.5% w/w) and 25 mL of 30% aqueous hydrogen peroxide were added to a stirred suspension (or solution) of 30 mmol of **2** in 600 mL of ethanol. On stirring at room temperature, the product was gradually precipitated. Filtration after 18 h and washing with water gave **3**. A small amount of a second crop was obtained from the filtrate after standing in a refrigerator. The results for each compound are shown in Tables I–III. Additional data for 2-amino-3-(benzylideneamino)-3-cyanoacrylamide (**3a**): $^1$H NMR $\delta$ 7.70–7.77 and 8.25–8.35 (m, total 5, Ph), 8.50 (s, 1, =CH–), and exchangeable broad peaks (NH) at 7.65, 8.10, and 8.21; $^{13}$C NMR $\delta$ 115.16 (C≡N); MS *m/e* (rel intensities) 214 (56, $M^+$), 213 (34), 196 (27), 170 (8), 142 (22), and 137 (100). Careful examination of the product mixtures obtained as the second crops and as the evaporated residues of crystallization mother liquids indicated no trace of the isomers **3'**.

**6-Amino-3-cyano-5-methylpyrazine-2-carboxamide (5a).** From 1.59 g (10 mmol) of *N*-(1-cyanoethylidene)diaminomaleonitrile (**4a**),[9] 16 mL of 0.5% aqueous sodium molybdate, and 8 mL of 30% aqueous $H_2O_2$ in 200 mL of ethanol, there was obtained 1.10 g (a 62% yield) of pale yellow powder by the general procedure for **3**. Recrystallization from 66% (v/v) aqueous ethanol gave the analytical sample: mp >300 °C; IR 2220 (C≡N), 1695 cm$^{-1}$ (C=O); MS *m/e* 178 (32), 177 (100, $M^+$), 160 (8), 134 (52), 122 (16), 107 (63).

Anal. Calcd for $C_7H_7N_5O$: C, 47.46; H, 3.98; N, 39.53. Found: C, 47.22; H, 3.79; N, 39.44.

**6-Amino-3-cyano-5-phenylpyrazine-2-carboxamide (5b).** From 0.7 g (3 mmol) of *N*-($\alpha$-cyanobenzylidene)diaminomaleonitrile (**4b**),[9] there was obtained as above 0.5 g (a 69% yield) of gray powder. Recrystallization from 80% (v/v) aqueous methanol gave pale yellow crystals: mp >300 °C; IR 2220 (C≡N), 1680 cm$^{-1}$ (C=O); MS *m/e* 240 (20), 239 (100, $M^+$), 221 (12), 196 (20), 169 (16).

Anal. Calcd for $C_{12}H_9N_5O$: C, 60.24; H, 3.79; N, 29.28. Found: C, 60.03; H, 3.68; N, 29.11.

**Oxidation of 3a to Imidazole 6. Method A.** A solution of 1 g of **3a** and 1 g of dichlorodicyanobenzoquinone (DDQ) in 30 mL of acetonitrile was heated under reflux for 17 h. Then, the reaction mixture was cooled to room temperature and the resulting crystals were collected by filtration and washed with ethyl ether. Recrystallization from 50% (v/v) aqueous ethanol gave 0.7 g of 4(5)-cyano-2-phenylimidazole-5(4)-carboxamide (**6**) as colorless crystals: mp ~305 °C; $^1$H NMR $\delta$ 7.8–7.9 and 8.3–8.4 (m, total 5, Ph), 8.08 (br peak, NH); MS *m/e* 212 (80, $M^+$), 195 (100); IR 2210 ($C\equiv N$), 1660 $cm^{-1}$ ($C=O$).

Anal. Calcd for $C_{11}H_8N_4O$: C, 62.25; H, 3.80; N, 26.40. Found: C, 62.13; H, 3.75; N, 26.37.

**Method B.** To an ice-cooled solution of 0.7 g of $Cl_2$ in 40 mL of 0.2 N aqueous NaOH was added portionwise 0.5 g of **3a.** Stirring was continued for 1 h on cooling and for an additional 1 h at 50 °C. The resulting precipitates were filtered, washed with water and ethanol, and dried to give 0.2 g of white powder, which was identical (IR) with the above product (**6**). The same compound (1.2 g) was obtained from 2-phenylimidazole-4,5-dicarbonitrile[6] (2 g) with stirring at room temperature for 5 h in a mixture of 1 N aqueous NaOH (10 mL) and 30% aqueous $H_2O_2$ (2 mL).

**General Procedure for Cyclization of 3 into 7.** Amide **3a** (20 mmol) was stirred in 90 mL of 28% aqueous ammonia at room temperature for 3 h. Filtration and washing with water gave the product in almost quantitative yield. The reaction with aqueous NaOH also gave the same product, but was accompanied by some decomposition. 4-(Benzylideneamino)-3,5-diamino-2*H*-pyrrol-2-one (**7a**): mp 243–247 °C dec (from ethanol); IR 1748 $cm^{-1}$ ($C=O$); $^1H$ NMR $\delta$ 8.87 (s, 1, $=CH-$), 7.46–7.52 and 7.92–8.02 (m, total 5, Ph), and broad peaks (**NH**) at 7.1 and 8.9; MS *m/e* 214 (30), 111 (92), 83 (100).

Anal. Calcd for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.71; N, 26.16. Found: C, 61.64; H, 4.74; N, 25.89.

Similarly, amides **3b–g** were applied to the cyclization reaction to give 4-$R^1R^2C=N-$ derivatives of 3,5-diamino-2*H*-pyrrol-2-one [compound number ($R^1$, $R^2$), % yield, decomposition point[22] (recrystallization solvent)]: **7b** (H, 4-$CH_3C_6H_4$), 97, 257–259 °C (MeOH); **7c** (H, 4-$CH_3OC_6H_4$), 94, ~230 °C ($Me_2NCHO$ + $CH_3CN$); **7d** (H, 9-anthranyl), 86, ~205 °C (MeOH); **7e** (H, 4-$NO_2C_6C_6H_4$), 97, 238–242 °C (MeOH); **7f** ($CH_3$, 4-$NO_2C_6H_4$), 97, 250–255 °C (MeOH); **7g** (Ph, Ph), 94, 200–201 °C ($CH_3CN$). These compounds were identified by both consistent results of spectral properties and microanalyses.

**Acknowledgment.** The author thanks Messrs. M. Aiba, H. Watanabe, and Miss E. Tohma for their help in carrying out of the experiments. He also wishes to thank Dr. T. Kojima and Mr. K. Sato for helpful discussion and measurement of $^{13}C$ NMR spectra.

**Registry No.**—**4a,** 57443-97-7; **4b,** 57444-00-5; **5a,** 68568-24-1; **5b,** 68568-25-2; **6,** 68568-26-3; **7a,** 68568-27-4; **7b,** 68568-28-5; **7c,** 68568-29-6; **7d,** 68568-30-9; **7e,** 68568-31-0; **7f,** 68568-32-1; **7g,** 68568-33-2; benzaldehyde, 100-52-7; *p*-tolualdehyde, 104-87-0; *p*-anisaldehyde, 123-11-5; 9-anthracenecarboxaldehyde, 642-31-9; *p*-nitrobenzaldehyde, 555-16-8; 4′-nitroacetophenone, 100-19-6; benzophenone, 119-61-9; 2-phenylimidazole-4,5-dicarbonitrile, 50847-06-8.

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# Reactions of Thiirene 1,1-Dioxides with α-Metalated Nitriles

Yasuo Yoshida, Mitsuo Komatsu,* Yoshiki Ohshiro, and Toshio Agawa

*Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565, Japan*

*Received September 6, 1978*

Reactions of thiirene 1,1-dioxides with α-metalated nitriles are described. 2,3-Dimethylthiirene 1,1-dioxide (**1a**) was found to act as an ambident electrophile to afford two types of sulfur-containing cyclic products, sulfolenes **3** and **7**, in moderate yields when the metalated nitriles have no α-hydrogen atom. The former (**3**) arose from nucleophilic attack of the aryl-substituted carbanions to the ring carbon of **1a**, and the latter (**7**) arose from the attack of an alkyl-substituted carbanion to the sulfur atom. When nitriles bear an α-hydrogen atom, acyclic products were obtained. On the other hand, 2,3-diphenylthiirene 1,1-dioxide suffered only one type of nucleophilic attack to the ring carbon atom. They gave sulfinate salts **9**, which can easily be converted to sulfolenes **10**, in good yields. The whole reactions are quite sensitive to the substituents of the thiirenes and nitriles.

Thiirenes are one of the 3-heterocyclopropenes which have been of great interest for many chemists, not only because of their highly strained structures but also because of their antiaromaticity.[1-3] While no thiirenes have been isolated, a few thiirene 1,1-dioxides have been prepared[4-6] and studied from both structural and theoretical points of view. The structure of the compounds was determined by X-ray crystallographic analysis,[7] and molecular orbital calculations showed weak conjugation between the ethylenic and sulfonyl groups.[1-3] However, chemical properties of thiirene 1,1-dioxides have not yet been well studied and only a few reactions have been reported on 2,3-diphenylthiirene 1,1-diox-