5-tosyl-1,2,4-triazole (3f) were prepared analogously to **2b** and **3b** from TosMIC and 3-pyridinediazonium chloride. No precipitate was formed by pouring the reaction mixture in the NaCl solution. Extraction with CH_2Cl_2 gave a black oil from which 20% of TosMIC was recovered by chromatography over a column of alumina with CH_2Cl_2. Continued chromatography with CH_2Cl_2 + 2% of MeOH gave a dark brown solid which was stirred with benzene to yield **2f**, mp 164–168° (11%). The mother liquor was concentrated and separated according to the procedure given for **2b** and **3b**, using CH_2Cl_2–Et_2O (1:1), giving the following. (1) A second crop of **2f**, mp 164–167° (4%, from benzene–pentane); the total yield of **2f** was 15% after correction for recovered TosMIC. Crystallization from EtOH gave an analytical sample: mp 168.5–174° (dimorphous); ir (Nujol) 1330 and 1145 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 9.07–8.97 (m, 1), 8.88–8.75 (m, 1), 8.72 (s, 1, H_5), 8.30–8.10 (m, 1), 7.70–~7.4 (m, 1); mass spectrum M^+ *m/e* 300. Anal. Calcd for $C_{14}H_{12}N_4O_2S$: C, 55.99; H, 4.03; N, 18.65; S, 10.67. Found: C, 55.8; H, 4.1; N, 18.4; S, 10.9. (2) **3f** (3%, based on recovered TosMIC), mp 124–127° (from benzene–pentane). An analytically pure sample was obtained after crystallization from benzene–pentane: mp 127–128°; ir (Nujol) 1340 and 1150 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 8.99–8.72 (m, 2), 8.13–7.90 (m + s, 2, H_3), 7.66–~7.4 (m, 1); mass spectrum M^+ *m/e* 300. Anal. Calcd for $C_{14}H_{12}N_4O_2S$: see **2f**. Found: C, 55.8; H, 4.1; N, 18.7; S, 10.5.

1-(α-Naphthyl)-3-tosyl-1,2,4-triazole (2g) was prepared analogously to **2a** from TosMIC and α-naphthalenediazonium tetrafluoroborate. A readily solidifying black oil was obtained, which was chromatographed over a column of alumina (benzene). The resulting brown solid was crystallized from benzene–pentane to give **2g**, mp 144–146.5° (38%). Two more crystallizations from benzene–pentane gave an analytically pure sample: mp 147.5–149.5°; ir (Nujol) 1330 and 1145 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 8.51 (s, 1, H_5), ca. 8.2–7.88 (m, 2), 7.77–~7.5 (m, 5); mass spectrum M^+ *m/e* 349. Anal. Calcd for $C_{19}H_{15}N_3O_2S$: C, 65.31; H, 4.33; N, 12.02; S, 9.18. Found: C, 65.0; H, 4.2; N, 12.2; S, 9.2.

***N*-Tosylmethyl-*p*-nitrobenzamide (6)** was prepared analogously to **2a** from TosMIC and *p*-nitrobenzenediazonium tetrafluoroborate. A dark brown solid was obtained, which was washed with CH_2Cl_2 and crystallized from acetone–pentane, yielding 39% of **6**, mp 211–213.5°. Further crystallization gave an analytical sample: mp 206.5–207° (slight dec); ir (Nujol) 1645 (C=O), 1545 and 1345 (NO_2), 1325 and 1130 cm^{-1} (SO_2); ^1H NMR (Me_2SO-d_6) δ ca. 10.0–9.7 (t, br, 1), 8.41, 8.26, 8.04, 7.90 (q, 4, J = 9 Hz), 4.94 (d, br, 2, J = 7 Hz); mass spectrum M^+ *m/e* 334. Anal. Calcd for $C_{15}H_{14}N_2O_5S$: C, 53.89; H, 4.22; N, 8.38; S, 9.59. Found: C, 53.8; H, 4.4; N, 8.4; S, 9.5. This compound was identical in all respects with a sample prepared independently by the procedure of Olijnsma et al.[19] for *N*-tosylmethylbenzamide; recrystallization of the crude product from acetone gave **6** in 62% yield, mp 203.5–204.5° (slight dec).

3-Hydroxy-1-phenyl-1,2,4-triazole (9). A powdered mixture of 1-phenyl-3-tosyl-1,2,4-triazole (**2c**, 450 mg, 1.51 mmol), NaOH (64 mg, 1.60 mmol), and KOH (136 mg, 2.43 mmol)[20] was heated for 10 min at 160°. The resulting brown solid was dissolved in 10 ml of an aqueous NaCl solution. After extraction with CH_2Cl_2 (10 ml), the solution was acidified to pH 1. The white precipitate was collected and stirred with CH_2Cl_2 (10 ml) to remove *p*-toluenesulfinic acid. The residual solid was collected, washed with water, and dried, yielding **9** (90 mg, 37%), mp 287° (subl). This compound was identical with an authentic sample, prepared by the method of Widman.[12a]

1-Phenyl-Δ²-1,2,4-triazolin-5-one (10) was prepared from **3c** analogously to the synthesis of **9**. The aqueous solution with the reaction product was neutralized with dilute sulfuric acid. Extraction with CH_2Cl_2 gave **10** as a white solid after removal of the solvent in 40% yield, after one recrystallization from Et_2O–pentane, mp 180.5–182.5°. Compound **10** has the same melting point (reported 182–184°,[21] 183–184° [22]) and the same characteristic ir and ^1H NMR data as reported previously.[22]

Registry No.—**1**, 39495-97-1; **2a**, 57428,35-0; **2b**, 57428-36-1; **2c**, 55860-44-1; **2d**, 57428-37-2; **2f**, 57428-38-3; **2g**, 57428-39-4; **3b**, 57428-40-7; **3c**, 57428-41-8; **3d**, 57428-42-9; **3f**, 57428-43-0; **5a**, 24564-52-1; **5b**, 4346-59-2; **5c**, 369-57-3; **5d**, 19262-73-8; **5e**, 456-27-9; **5f**, 35003-14-6; **5g**, 28912-93-8; **6**, 57428-44-1; **8**, 13423-60-4; **9**, 4231-68-9; **10**, 21434-16-2.

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Chemistry of Diaminomaleonitrile. I. Selective Preparations of Monoformyldiaminomaleonitrile and Imidazoles by Reaction with Formic Acid

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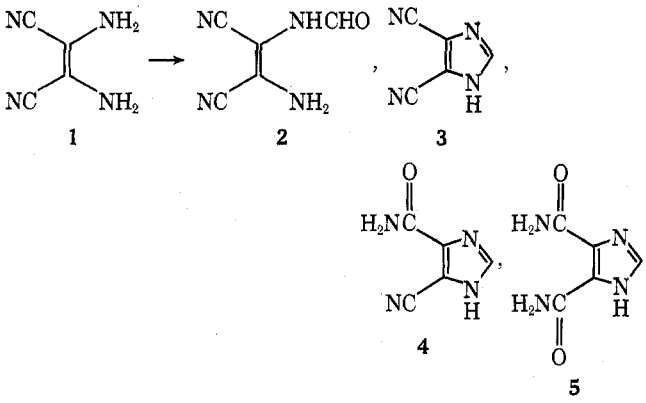
The reaction of diaminomaleonitrile (DAMN) and formic acid depends critically on the conditions under which the experiment is performed. Bredereck and Schmötzer[1] have reported the reaction of DAMN in anhydrous formic acid under mild conditions (<35°C, within 5 min) to give monoformyldiaminomaleonitrile in 50% yield. This reaction is accompanied by formation of tarry materials; an intractable black syrup is obtained after prolonged reaction times or at higher reaction temperatures. On the other hand, heating a heterogeneous mixture consisting of DAMN, formic acid, and xylene gives a fair yield (61%) of 4(5)-cyanoimidazole-5(4)-carboxamide (**4**)[2] with little tar formation.

We have examined the reaction in several solvents and found that monoformyldiaminomaleonitrile (**2**), 4,5-dicya-

noimidazole (3), 4(5)-cyanoimidazole-5(4)-carboxamide (4), and imidazole-4,5-dicarboxamide (5) can each be selectively prepared from DAMN (1) and formic acid by choice of reaction conditions.



Formic acid and 1 can be mixed at room temperature without tar formation as a stirred suspension in an inert medium. On heating the mixture in benzene, a 95% yield of crude 2 was obtained. Cyclohexane, carbon tetrachloride, and petroleum ether (immiscible with formic acid) can be used as the medium to give a similar result. The reaction was greatly retarded and a major part of 1 was recovered when solvents such as ethyl ether, ethanol, and chloroform (miscible with formic acid) were used.

Cyclization of 2 by heating in an inert medium appears to be a slow reaction. For example, refluxing 2 for 3 days in dry xylene with continuous separation of water gave only a 37% yield of 3. The presence of a small amount of water in the medium gave a mixture of 3 and 4. The reaction was facilitated in glycol ethers. Thus, 2 in diglyme gave 3 in 89% yield after 18 hr of refluxing. 3 was also prepared from 1 and formic acid in diglyme in 76% yield after 6 hr of refluxing. Similar results were obtained in diethyl carbitol. In glycol ethers, the presence of a small amount of water did not increase the formation of 4 and solvents can be used without any prior purifications to give a high selectivity for the formation of 3.

A one-step and selective preparation of 4 from 1 and formic acid[2] was reinvestigated at the temperatures between 115 (in toluene) and 170°C (in phenetol). 4 was obtained in 69–77% yield. When these reaction mixtures were heated at around 80°C, 2 was obtained. Refluxing 2 and formic acid in xylene gave a similar yield of 4 to that from 1 and formic acid, but 2 and other acids (*p*-toluenesulfonic acid, propionic acid, and sulfuric acid) gave considerable tar formations with small amounts of 3 and 4.

It was found that 5 was prepared directly either from 2 or from 1 and formic acid by heating in formamide at around 200°C for 1 hr in 65 or 90% yield, respectively. A brief examination using other high boiling point solvents gave unsuccessful results.

The present preparations are simpler and may be more economical than previous preparations of 3,[3,4] 4, and 5,[5] which are important intermediates for the synthesis of 4-amino-5-cyanoimidazole[5,6] or purine derivatives.[4,7] Typical experiments are shown in the Experimental Section.

Experimental Section

All compounds obtained here were identified from elemental analysis, mass spectra, and comparisons of their ir spectra with those of authentic samples prepared by known procedures.

Monoformyldiaminomaleonitrile (2). Anhydrous formic acid (16 ml) was added to a suspension of 1 (10 g) in dry benzene (200 ml). After stirring at room temperature for 30 min, the mixture was refluxed for 15 min. Filtration, washing with ethyl ether, and removal of volatile materials[8] gave brown crystals (12 g, 95% yield), of which the ir spectrum was almost identical with that of an authentic sample of 2.[1] Recrystallization from water gave a pure specimen, mp 182–184°C.[9]

4,5-Dicyanoimidazole (3). Method A. From 1 and Formic Acid. To a solution of 1 (2.8 g) in diglyme (120 ml) was added formic acid (4 ml). The mixture was stirred for 30 min at room temperature and then refluxed for 6 hr. The reaction mixture was evaporated under reduced pressure and the residual solids were dissolved in ethyl ether (150 ml). After separation of undissolved solids (a mixture of 1 and 2 identified from ir) by filtration, the ether solution was concentrated to give 3 (mp 176°C)[4] with 76% yield (2.2 g).[11]

Method B. From 2. 2 (2.0 g) was refluxed in dry diglyme (100 ml) for 18 hr and treated as above to give 89% yield of 3 (1.55 g). A small quantity of 2 was recovered as undissolved dark solids in ether.

4(5)-Cyanoimidazole-5(4)-carboxamide (4). Method A. From 1 and Formic Acid. A mixture of 1 (4 g), formic acid (4 ml), and xylene (150 ml) was stirred for 30 min at room temperature and then refluxed for 6 hr. The resulting dark solids (adhering to the walls of the vessel) were gathered, washed with ethyl ether, and extracted repeatedly with hot water. Concentration of the aqueous solution gave 4[5] (mp 273°C) with 77% yield (3.9 g). From the residue of the extraction, 5 was obtained (2.2%, yield, 0.12 g) by extraction with a larger quantity of water.

Method B. From 2. A mixture of 2 (1.36 g), formic acid (concentration 80%, 1.5 ml) and xylene (120 ml) was treated as in method A to give a 71% yield of 4 (0.97 g).

Imidazole-4,5-dicarboxamide (5). Method A. From 1 and Formic Acid. In an open vessel, 1 (4 g) and formic acid (5 ml, concentration 99%) in formamide (140 ml) were stirred for 30 min at room temperature and then heated at 200°C (bath temperature) for 1 hr. The reaction mixture was allowed to cool and the resulting solid (4.35 g) was separated by filtration. Another crop (1.25 g) was obtained by concentration of the filtrate under reduced pressure. The combined crude product was washed with ethanol and dissolved in hot 10% aqueous sodium carbonate. Charcoal treatment and neutralization with hydrochloric acid gave 5 (mp 300°C)[5] with 91% yield (5.2 g).

Method B. From 2. 2 (1.36 g) was heated at approximately 200°C for 2 hr in formamide (100 ml) as in method A, giving 5 in 65% yield (1.0 g). When 2 in formamide was heated at 180°C for 30 min, 4 was obtained with 42% yield.

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Registry No.—1, 1187-42-4; 2, 53144-01-7; 3, 1122-28-7; 4, 5372-23-6; 5, 83-39-6; formic acid, 64-18-6.

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