1-Dimethylamino-1,3-dichloro-3-methylamino(*N*-2-ethylene)-trimethinium Chloride (7). *N*-Methylpyrrolidone (2.5 g, 25 mmol) and phosgene immonium chloride (8.1 g, 50 mmol) were refluxed in 50 ml of dry chloroform until all solid had dissolved. The solvent was then removed to give 6.01 g (98%) of 7 as a dense oil: nmr ($CDCl_3$) δ 4.39 (2 H, t, J = 10 Hz), 3.43 (9 H, s), 3.40 (2 H, t); uv (CH_2Cl_2) λ_{max} 381 nm (ϵ 5500).

3-(*N,N*-Dimethylcarbamoyl)-*N*-methyl-2-pyrrolidone. The cyanine 7 (6.00 g, 24.7 mmol) was dissolved in 20 ml of chloroform and stirred with 5 ml of water and an excess of $NaHCO_3$ for 1 hr. The organic phase was collected, dried over $MgSO_4$, and evaporated. Distillation gave 3.6 g (87%) of 7: bp 114° (0.5 mm); nmr ($CDCH_3$) δ 3.27 (3 H, s), 3.00 and 2.88 (6 H, 2 s), and a complex second-order pattern between 2.0 and 4.0 ppm (4 H); mass spectrum m/e 170 (M^+), 142, 126, 98.

General Procedure for Pyrazole Formation. The cyanine 6 (0.01 mol) and the hydrazine (0.011 mol) were combined in chloroform or dichloromethane (75 ml) and the reaction mixture was refluxed until the yellow color of the cyanine disappeared. The reaction mixture was filtered and the solvent was evaporated under reduced pressure. Aqueous potassium hydroxide (2 *N*) was added to liberate the free pyrazole, and the resulting mixture was extracted with dichloromethane (5 × 100 ml). The organic phase was dried (Na_2SO_4), the solvent was evaporated, and the crude pyrazole was purified either by crystallization or by molecular distillation; characteristics of the pyrazoles are given in Table I. The nmr spectra of all 1-substituted 3,5-bis(dimethylamino)pyrazoles had two six-proton singlets at 2.6–2.7 and 2.8–2.9 ppm; 4-unsubstituted compounds had a one-proton singlet at 5.2–5.3 ppm; peaks due to substituents were present at the expected positions in all spectra; all pyrazoles gave satisfactory analytical data (±0.3% for C and H or ±0.003 Daltons by mass spectrum). The general procedure above gave only poor yields of **9s**. For this reason **9s** was made by two alternate procedures:

Procedure 1. Methyl hydrazine (0.01 mol) in dioxane (50 ml) was slowly added to the phenoxycyanine 6 (R = OC_6H_5) (0.01 mol) in CH_2Cl_2 (25 ml) with stirring at −8°. The reaction mixture was stirred overnight, the precipitated salts were filtered off, and the organic solvent was evaporated under suction. The residue was dissolved in a minimal amount of water, and 2 *N* KOH was added to liberate the free pyrazole. The aqueous mixture was extracted with ether (5 × 100 ml), the ethereal solution was dried (Na_2SO_4), and the solvent was evaporated. The resulting residue was distilled horizontally to give 2.04 g (78%) of **9s**.

Procedure 2. The phenoxycyanine (0.01 mol) in $CHCl_3$ (50 ml) and *N,N*-dimethylhydrazine (0.02 mol) in $CHCl_3$ (25 ml) were combined slowly with stirring at 0°. After 1 hr the solution was refluxed until the yellow color of the cyanine disappeared. The dimethylhydrazine hydrochloride was filtered off and the solvent was evaporated under suction. The residue was dissolved in a minimal amount of water and 2 *N* KOH was added to liberate the free pyrazole. Further work-up was carried out as in procedure 1 to give 1.25 g (48%) of **9s**.

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Registry No.—4 (R = H), 127-19-5; 4 (R = CH_3), 758-96-3; 4 (R = C_2H_5), 760-79-2; 4 (R = C_6H_5), 18925-69-4; 4 (R = Cl), 2675-89-0; 4 (R = OCH_3), 4128-76-1; 4 (R = OC_2H_5), 24475-96-5; 4 [R = $OCH(CH_3)_2$], 50860-23-6; 4 (R = OC_6H_5), 10397-59-8; 4 (R = $OCOCH_3$), 13831-28-2; **5**, 33842-02-3; **7**, 50860-24-7; NH_2NHR' (R′ = CH_3), 60-34-4; NH_2NHR' (R′ = C_6H_5), 100-63-0; NH_2NHR' (R′ = $CO_2C_2H_5$), 4114-31-2; NH_2NHR' [R′ = 2,4-$(NO_2)_2C_6H_3$], 119-26-6; NH_2NHR' (R′ = $SO_2C_6H_5$), 80-17-1; NH_2NHR' (R′ = $SO_2C_2H_5$), 37984-88-6; NH_2NHR' (R′ = H), 302-01-2; *N*-methylpyrrolidone, 872-50-4; 3-(*N,N*-dimethylcarbamoyl)-*N*-methyl-2-pyrrolidone, 50932-75-7.

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Hydrogen Cyanide Chemistry. VII. Diiminosuccinonitrile Condensation with Diaminomaleonitrile[1]

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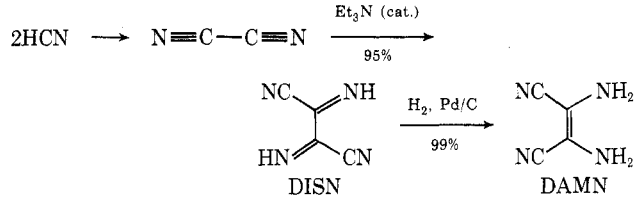
Diiminosuccinonitrile (DISN) condenses with diaminomaleonitrile (DAMN) to give tetracyanopyrazine, aminotricyanopyrazine, and 2,3-diamino-5,6-dicyanopyrazine. By choice of conditions any one of these tetrafunctional pyrazines can be the major product; linear 1:1 and 2:1 adducts are formed under other conditions and the 1:1 adduct can be cyclized to the pyrazines. DISN reacts with 1 mol of water to form an intermediate, probably iminooxalyl cyanide, which condenses with DAMN to give 2-amino-3-hydroxy-5,6-dicyanopyrazine. Two moles of water hydrolyze DISN to oxalyl cyanide, which condenses with DAMN to give tetracyanopyrazine under acidic conditions and 1,4,5,6-tetrahydro-5,6-dioxo-2,3-dicyanopyrazine under neutral conditions.

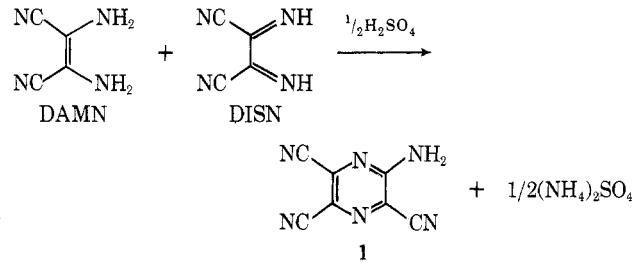
Diiminosuccinonitrile (DISN) and diaminomaleonitrile (DAMN) are now readily available research chemicals derived from hydrogen cyanide.[2] We have previously shown that nucleophiles displace either ammonia or hydrogen cyanide from DISN under varying conditions.[3] This behavior is further exemplified by the reactions of DISN with DAMN by which various tetrasubstituted pyrazines



and acyclic adducts can be selectively prepared in good yield.

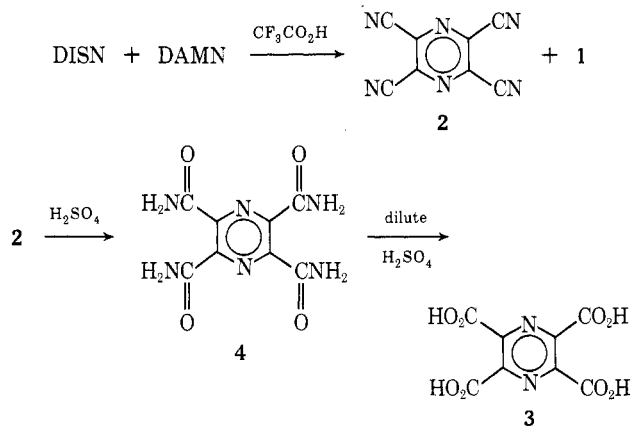
Results

When equimolar amounts of DISN and DAMN are mixed in tetrahydrofuran, no immediate reaction occurs. However, addition of 0.5 mol of sulfuric acid to this solution induces an exothermic reaction and ammonium sulfate precipitates. Filtration and removal of the solvent give aminotricyanopyrazine (1) as light-yellow crystals in 95% yield. Structure assignment of 1 is based on analysis, infrared and mass spectra, and its chemistry which will be discussed later. The *p*-toluenesulfonic acid salt of DAMN also reacts with DISN, giving 1 in good yield.



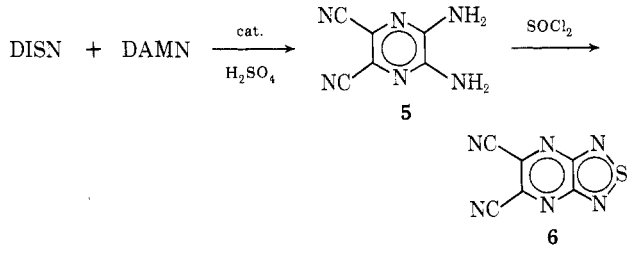
1

When a powdered mixture of DISN and DAMN is added to trifluoroacetic acid, an exothermic reaction occurs followed by precipitation of white crystals of tetracyanopyrazine (2) in 60% yield; by evaporation of the filtrate, a mixture of 1 and 2 is recovered in approximately 25% yield. The structure of tetracyanopyrazine (2) was confirmed by its hydrolysis to the known pyrazinetetracarboxylic acid (3).[4] Stepwise hydrolysis with concentrated sulfuric acid initially gave pyrazinetetracarboxamide (4) in over 90% yield followed by further hydrolysis to 3 in aqueous acid.



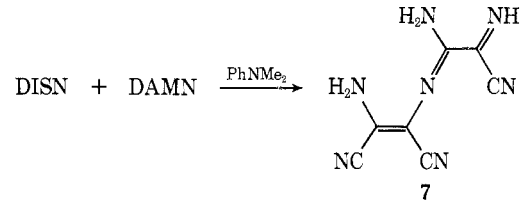
2 4 3

The addition of only a catalytic amount of sulfuric acid to an equimolar solution of DISN and DAMN in tetrahydrofuran or acetonitrile yields yet another new pyrazine. When the acid is added, an immediate exothermic reaction occurs and a yellow precipitate forms. Within the next 30 sec the precipitate redissolves, the reaction temperature again rises, and crystals begin to form. After 30 min the crystals are collected, giving 2,3-diamino-5,6-dicyanopyrazine (5) in 60–70% yield. The 2,3 orientation of the amino groups in 5 was confirmed by formation of 5,6-dicyano[1,2,5]thiadiazolo[3,4-*b*]pyrazine (6) upon treatment of 5 with thionyl chloride.

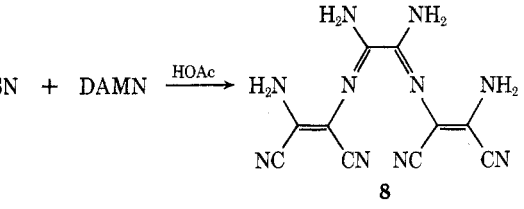


5 6

The condensation of DISN and DAMN using a basic catalyst such as *N,N*-dimethylaniline gives 1,4-diamino-1,2,5-tricyano-3,6-diazahexatriene (7) in 70% yield. Addition of acetic acid to a solution of DISN and DAMN in tetrahydrofuran also gives adduct 7; however, the major product from this reaction is a very insoluble 2:1 DAMN–DISN adduct which is thought to be 1,4,5,8-tetraamino-1,2,7,8-tetracyano-3,6-diazaoctatetraene (8).

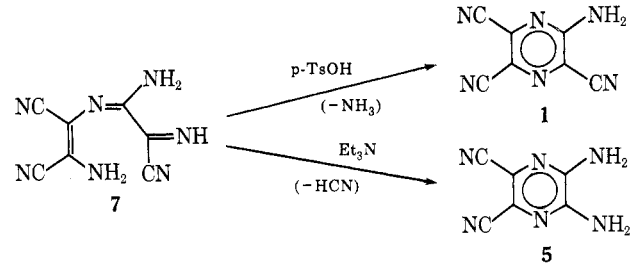


7



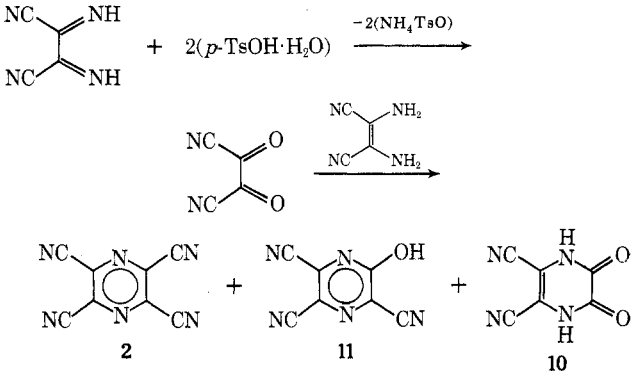
8

The structure of 7 was confirmed by its facile cyclization to two of the previously obtained pyrazines. Thus, treatment of 7 with 1 equiv of anhydrous *p*-toluenesulfonic acid gives 1 nearly quantitatively. Triethylamine, however, affords 2,3-diamino-5,6-dicyanopyrazine (5).



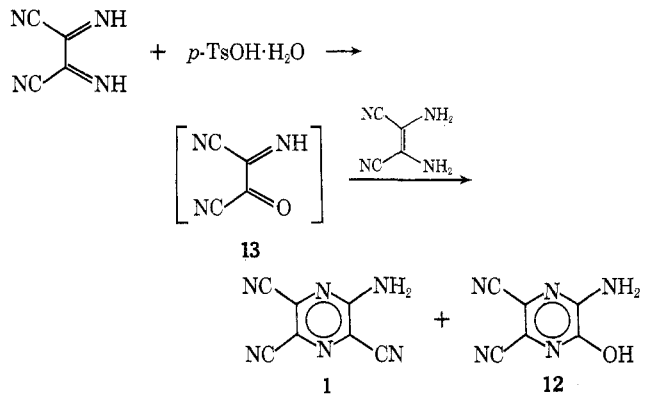
7 1 5

In addition to the compounds obtained by the direct condensation of DISN with DAMN, we have isolated three other pyrazines when water is added to the DISN prior to the addition of DAMN. Addition of 2 equiv of *p*-toluenesulfonic acid monohydrate to a solution of DISN in THF forms oxalyl cyanide (9).[3] If DAMN is added to this solution, the isolated products are tetracyanopyrazine (2, 25%), 2,3-dioxo-1,2,3,4-tetrahydro-5,6-dicyanopyrazine[5] (10, 34%), and hydroxytricyanopyrazine (11, 5%).



2 11 10

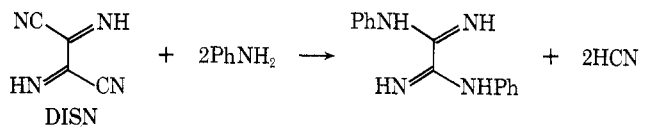
Addition of 1 equiv of *p*-toluenesulfonic acid monohydrate to a solution of DISN, followed by addition of DAMN, yields aminotricyanopyrazine (**1**, 31%) and 2-amino-3-hydroxy-5,6-dicyanopyrazine (**12**, 22%). Although we were unable to isolate α-iminooxalyl cyanide (**13**), we feel that it must be the initially formed intermediate in this reaction.



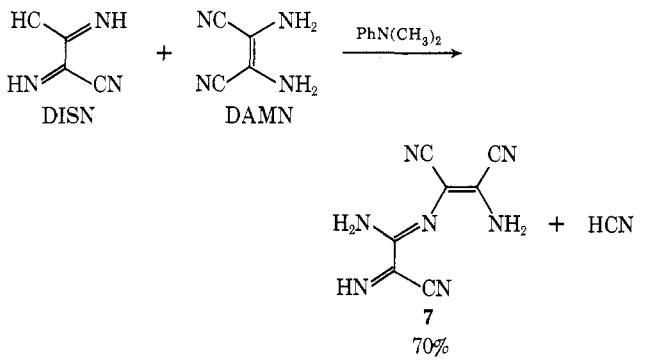
Discussion

The condensation of DISN with *o*-phenylenediamine to give amino- and cyano-substituted quinoxalines was reported in a previous paper in the series.[3] The condensation of DISN with DAMN is analogous and has been examined more thoroughly, especially with regard to the control of product formation under acid catalysis. A detailed mechanistic interpretation is not possible without extensive experimental investigation, but the control achieved through acid catalysis can be rationalized in the following way.

Under neutral or basic conditions DISN reacts with amines with cyanide displacement,[3] as shown, for example, with aniline.

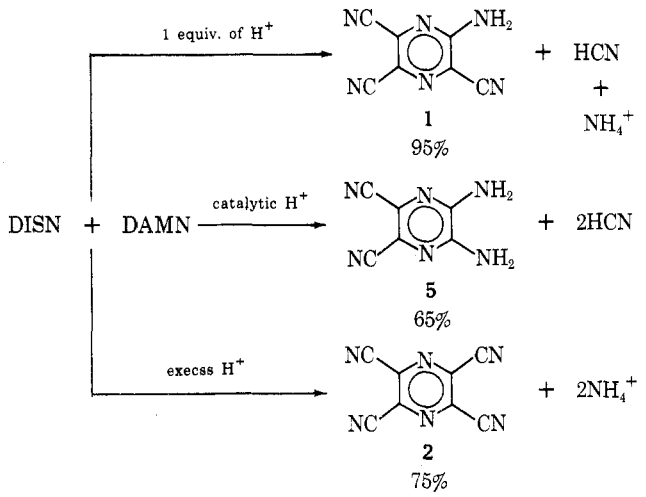


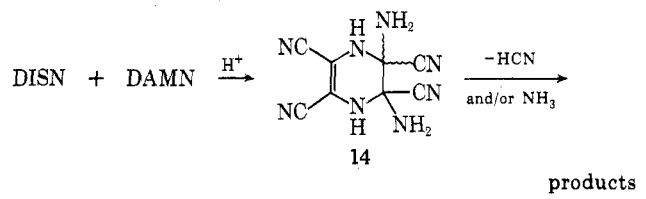
Attack by the weakly basic amine groups of DAMN is very slow under neutral conditions but is mildly base catalyzed by bases such as tertiary amines which are compatible with DISN.



The condensation of DISN and DAMN is strongly acid catalyzed, presumably because of protonation of DISN. In addition, an acidic medium promotes the loss of ammonia from the intermediates. This latter effect has provided a means for controlling the reaction so that any one of the three possible pyrazines **1**, **2**, and **5** can be made the major product.

These three sets of reaction conditions undoubtedly influence not only the overall outcome of the reaction, but also the sequence of events leading to products in such a way that no one unifying mechanism can be written. The discussion is greatly simplified, however, by assuming that the cyclic intermediate **14** is formed rapidly under acid catalysis. However, ammonia and/or hydrogen cyanide could be lost from acyclic intermediates that can cyclize to pyrazine products. Various acid-base equilibria are obviously involved and the amount of acid present would have significant influence on equilibria.





In the case of the reaction utilizing a catalytic amount of acid which produces mainly 2,3-diamino-5,6-dicyanopyrazine by loss of 2 mol of hydrogen cyanide, the primary function of the acid is to catalyze the addition of the amino groups of DAMN to DISN.

Even at this low acid concentration some loss of ammonia occurs, leading to aminotricyanopyrazine **1**. In this acid-catalyzed case presumably the small amount of acid would be consumed when ammonia is eliminated so that cyclization must occur before loss of ammonia (note that ammonium salts do not catalyze the condensation of DISN and DAMN); however, this does not rule out acyclic intermediates which have lost hydrogen cyanide.

The reaction of DAMN with oxalyl cyanide and α-iminooxalyl cyanide can be rationalized in a manner analogous to the DISN reactions, but with these more reactive and less basic compounds the catalytic role of the acid in the initial addition is less important. Also acid has less effect in influencing loss of water from the intermediates as compared to the loss of ammonia in the DISN reactions.

Experimental Section

The infrared spectra were obtained on a Perkin-Elmer Model 21 spectrometer, the uv spectra on a Cary Model 14, and the mass spectra on a Du Pont CEC 21-110B high-resolution double-focusing instrument. All reactions were conducted under nitrogen.

2-Amino-3,5,6-tricyanopyrazine (1). To a vigorously stirred solution of 10.0 g (0.0095 mol) of DISN and 10.0 g (0.093 mol) of DAMN in 200 ml of THF at 30° was added all at once 3.7 g (0.068 equiv) of sulfuric acid. The temperature rose immediately to 55° and a precipitate of $(NH_4)_2SO_4$ formed. The reaction mixture was stirred for 18 hr, filtered, and stripped to dryness, and the resulting solid was washed with ether to give 15.0 g (95.5%) of **1** as a yellow powder. Recrystallization from chloroform gave light-yel-

low needles: mp 225° dec; ir (KBr) 3420, 3340, 3230, 2240, 1630, 1550, and 1480 cm^{-1}; uv (CH_3CN) 207 nm (ϵ 17,000), 225 (11,300), 285 (21,300), 375 (6700); mass spectrum m/e 170.0338 (calcd m/e 170.0341).

Anal. Calcd for $C_7H_2N_6$: C, 49.41; H, 1.19, N, 49.40. Found: C, 49.48, 49.78; H, 1.49, 1.30; N, 49.20, 49.48.

Tetracyanopyrazine (2). A powdered mixture of 64.2 g (0.60 mol) of DISN and 64.8 g (0.60 mol) of DAMN was added in portions over 20 min to 900 ml of trifluoroacetic acid. The temperature rose from 27° to 48° during the addition. The resulting mixture was warmed to 70° and filtered to give 63.8 g (59%) of tetracyanopyrazine (as a white powder) after washing with 30 ml of CF_3CO_2H and 2 × 300 ml of water. Removal of the CF_3CO_2H from the filtrate gave, after washing with water, 26.9 g of a mixture of **1** and **2**. Recrystallization of **2** from benzene gave white plates: mp 274–276°; ir (KBr) 2250, 1175, and 1158 cm^{-1}; uv (CH_3CN) 213 nm (ϵ 34,500), 253 (13,300), 295 (6900), 302 (7050), 313 sh (5500); mass spectrum m/e 180.0172 (calcd m/e 180.0184).

Anal. Calcd for C_8N_6: C, 53.33; N, 46.67. Found: C, 53.14; N, 46.80

Pyrazinetetracarboxamide (4). Tetracyanopyrazine (660 mg, 3.66 mmol) was stirred in 10 ml of concentrated H_2SO_4 for 3 days, then poured into ice water. The precipitated white tetramide, **4**, was washed with water and acetone, collected, and dried, 920 mg (99%), mp 390–391° dec. Recrystallization of the product from water gave colorless prisms: mp 390–391° dec; ir (KBr) 3490, 3290, 3200, 1690, 1613, and 1595 cm^{-1}; uv (H_2O) 223 nm (ϵ 11,800), 282 (8250), 325 sh (890).

Anal. Calcd for $C_8H_8O_4N_6$: C, 38.10; H, 3.20; N, 33.30. Found: C, 37.83; H, 3.34; N, 33.40.

Pyrazinetetracarboxylic Acid (3). Pyrazinetetracarboxamide **4** was heated at reflux in 5 *N* sulfuric acid for 2 days, giving a 91.4% yield of pyrazinetetracarboxylic acid (**3**), mp 198–199° dec.[6]

The tetramethyl ester of **3** was prepared, mp 181.5–182.8° (lit.[8] mp 184°).

2,3-Diamino-5,6-dicyanopyrazine (5). To a solution of 70 g (0.66 mol) of DISN and 60 g (0.55 mol) of DAMN in 1500 of acetonitrile partially immersed in a water bath at 25° was added (all at once) 2.5 ml of concentrated sulfuric acid. The pot temperature rose immediately to 36° and a yellow precipitate formed. Over the next 30 sec the precipitate redissolved, the temperature rose to 44°, and crystals of **5** began to form. The reaction temperature dropped to 30° over 10 min, the solution was then stirred for 30 min and cooled to −10°, and the solid was collected by filtration and washed with a little CH_3CN to give 71 g of crude product. This solid was washed with 200 ml of water to remove $(NH_4)_2SO_4$, rinsed with CH_3CN, and dried in a vacuum oven at 100° to give 63 g (71%) of **5** as a light tan powder. Recrystallization from acetonitrile gave white plates: mp 332° dec; ir (KBr) 3460, 3400, 3320, 3160, 2230, 1675, 1630, 1560, 1520, and 1505 cm^{-1}; uv (CH_3CN) 227 nm (ϵ 25,050), 317 (17,450); mass spectrum m/e 160.0502 (calcd m/e 160.0497).

Anal. Calcd for $C_6H_4N_6$: C, 45.00; H, 2.52; N, 52.48. Found: C, 45.06; H, 2.32; N, 52.35.

5,6-Dicyano[1,2,5]thiadiazolo[3,4-*b*]pyrazine (6). A solution of 16.0 g (0.10 mol) of **5** and 21.6 ml (0.328 mol) of $SOCl_2$ in 500 ml of CH_3CN was heated at gentle reflux for 22 hr. The resulting orange solution was evaporated at reduced pressure, leaving 18.7 g of crude **6** which was recrystallized from CH_3CN, 16.8 g (89.5%), as yellow prisms: mp 268° dec: ir (KBr) 2235, 1520, 900–800 cm^{-1}; uv (CH_3CN) 213 nm (ϵ 24,900), 335 (18,500), 342 (20,200), 348 (21,800).

Anal. Calcd for C_6N_6S: C, 38.29; N, 44.66. Found: C, 38.26; N, 44.80.

3,6-Diamino-2,5,6-tricyano-1,4-diaza-1,3,5-hexatriene (7). To a 3-l., three-necked flask equipped with a condenser, mechanical stirrer, and addition funnel was added 6.0 g (5.55 mmol) of DAMN and 2.0 ml of *N,N*-dimethylaniline in 400 ml of acetonitrile. The solution was brought to reflux under nitrogen with stirring and dropwise addition of 300 ml of an acetonitrile solution containing 8.0 g (7.5 mmol) of DISN was begun. The addition required 2.25 hr. After refluxing overnight 50 g of SilicAR was added and the slurry was evaporated to dryness. The dry solid was washed repeatedly with diethyl ether, which removed 5.75 g (55%) of tan solid. Recrystallization from acetonitrile gave **7** as yellow crystals: mp 204° dec; ir (KBr) 3460, 3320, 3260, 2240, 2200, 1650, 1620, 1605, 1590, 1560 cm^{-1}; uv (CH_3CN) 295 nm (ϵ 13,400), 385 (12,800); nmr (DMSO-d_6) δ 6.55 (broad singlet, 2 H), 7.30 (broad singlet, 2 H), 13.85 (singlet, 1 H); mass spectrum m/e 187.0610 (calcd m/e 187.0606).

Anal. Calcd for $C_7H_5N_7$: C, 44.92; H, 2.69; N, 52.39. Found: C, 44.97; H, 2.60; N, 52.10.

2,3-Diamino-5,6-dicyanopyrazine (5) *via* Cyclization of 7. A solution of 5.75 g (3.1 mmol) of **7** and 2 ml of triethylamine in 300 ml of acetonitrile was refluxed for 20 hr. SilicAR (50 g) was added and the solution was evaporated to dryness. The dry solid was washed repeatedly with diethyl ether, which removed 1.73 g (35%) of **5**, identified by its infrared spectrum.

Aminotricyanopyrazine (1) from the Acid-Catalyzed Cyclization of 3,6-Diamino-2,5,6-tricyano-1,4-diaza-1,3,5-hexatriene (7). The water of hydration was removed from 0.505 g (2.66 mmol) of *p*-toluenesulfonic acid monohydrate by azeotropic distillation in 3 ml of benzene. The dry benzene solution was diluted with 10 ml of anhydrous tetrahydrofuran and 0.500 g (2.66 mmol) of **7** was added. After stirring at room temperature for 45 min the slurry was filtered and the collected solid was washed with tetrahydrofuran and dried, yielding 0.50 g (2.64 mmol) of the ammonium salt of *p*-toluenesulfonic acid. Evaporation of the filtrate to dryness gave the theoretical amount of **1**, identified by its infrared spectrum.

1,4,5,8-Tetraamino-1,2,7,8-tetracyano-3,6-diazaoctatetraene (8). A solution containing 5.0 g of DISN, 5.0 g of DAMN, and 10 ml of glacial acetric acid in 100 ml of tetrahydrofuran was stirred at room temperature for 18 hr. Removal of the solvent and collection of the resulting product with an ether rinse gave a dark powder. This material was slurried with 500 ml of acetonitrile and filtered to give 4.35 g (69.5%) of crude **8**. Tetraamine **8** is very insoluble in most organic solvents and can be recrystallized only with considerable product loss by dissolution in dimethylformamide, treatment with Darco, and reprecipitation with water to give a yellow-brown powder: mp 249° dec; ir (KBr) 3410, 3305, 3175, 2250, 2200, 1610, 1510 cm^{-1}; uv (CH_3CN) 235 nm (ϵ 10,450), 292 (13,200), 362 (21,800); mass spectrum m/e 268; m/e for $M^+ - HCN$ 241.0825 (calcd m/e for $C_9H_7N_9$ 241.0825).

Anal. Calcd for $C_{10}H_8N_{10}$: C, 44.77; H, 3.00; N, 52.22. Found: C, 45.22; H, 3.15; N, 52.07.

Reaction of DAMN with Oxalyl Cyanide. To a stirred solution of 40.0 g (0.376 mol) of DISN in 600 ml of THF under N_2 was added dropwise at room temperature (1.5-hr addition) a solution of 152 g (0.80 mol) of *p*-toluenesulfonic acid monohydrate in 500 ml of THF. Stirring at room temperature was continued for 2 hr. The precipitated ammonium tosylate was then removed by filtering the solution under N_2 into another flask. To the orange-colored filtrate was added 20 g (0.185 mol) of powdered DAMN (15 min) followed by stirring at 50° for 3 days. The solution was filtered (removing additional $^+NH_4OTs^-$) and preabsorbed on 150 g of SilicAR CC7 which was subsequently chromatographed on another 300 g of SilicAR. Elution with benzene removed crude tetracyanopyrazine, which was recrystallized twice from benzene, giving 8.47 g (25.4%) of white leaflets, mp 274–276. Elution with $CHCl_3$ gave a dark, viscous oil which solidified on standing overnight and was recrystallized from benzene, affording 1.62 g (5.1%) of hydroxytricyanopyrazine (**11**) as tan prisms, mp 165–168°. Ether removed the known dioxopyrazine **10**, which was recrystallized from water, yielding 10.28 g (34.2%) of white needles, mp 278° (lit.[5] mp 270° dec). Spectral data of **11** follow: ir (KBr) 3160, 2260, 1690, 1560, and 1545 cm^{-1}; uv (CH_3CN) 206 nm (ϵ 17,900), 257 (9850), 300 (5200), 328 (7400), 385 (1760); mass spectrum m/e 171.0170 (calcd m/e 171.0181).

Anal. Calcd for C_7HON_5: C, 49.12; H, 0.59; N, 40.93. Found: C, 48.91; H, 0.60; N, 41.41.

Reaction of DAMN with α-Iminooxalyl Cyanide. To a stirred solution of 21.2 g (0.20 mol) of DISN in 400 ml of CH_3CN–ether (50:50) under N_2 was added dropwise at room temperature (1-hr addition) a solution of 37.0 g (0.20 mol) of *p*-toluenesulfonic acid monohydrate in 400 ml of CH_3CN–ether (50:50). Stirring at room temperature was continued for an additional 1 hr and the reaction mixture was filtered under N_2 into another flask. Powdered DAMN (10.8 g, 0.10 mol) was added to the filtrate (10 min) and this solution was stirred at 50° for 3 days, filtered, preabsorbed on 100 g of SilicAR CC7, and chromatographed. Elution with $CHCl_3$ removed **1**, which has recrystallized from $CHCl_3$, giving 5.36 g (31.5%) of light-yellow needles, mp 225° dec. Elution with CH_3CN gave an orange solid which was recrystallized from acetone, yielding **12** as pale-yellow needles: 3.58 g (22.2%); mp 300° dec; ir (KBr) 3430, 3340, 2780, 2270, 1685, 1625, 1595, and 1530 cm^{-1}; uv (CH_3CN) 225 nm (ϵ 14,400), 313 (16,600), 324 (17,500), 338 (10,700); mass spectrum m/e 160.0330 (calcd m/e 160.0338).

Anal. Calcd for $C_6H_3ON_5$: C, 44.72; H, 1.88; N, 43.47. Found: C, 44.66; H, 1.93; N, 43.75.

Registry No.—1, 33420-45-0; 2, 33420-37-0; 3, 43193-60-8; 4, 22051-80-5; 5, 36023-58-2; 6, 50921-36-3; 7, 36023-60-6; 8, 36023-59-3; 9, 36086-83-6; 11, 36023-63-9; 12, 36023-62-8; 13, 41245-87-8; DISN, 28321-79-1; DAMN, 1187-42-4.

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Synthesis of Adamantane Derivatives. XXV.[1] Synthesis and Reactions of 1- and 2-Adamantyl Isocyanides

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1- (4) and 2-adamantyl isocyanide (11) were prepared by the reactions of the corresponding amines with dichlorocarbene using a phase-transfer method and/or by dehydration of *N*-1-adamantylformamide. 4 was very stable in the atmosphere while 11 was converted rapidly to *N*-2-adamantylformamide (13) by the atmospheric moisture. Some simple derivatives of 4 and 11 such as 1-(1-adamantyl)- (5) and 1-(2-adamantyl)tetrazole (12), 1-(1-adamantyl)-2,4-dithioxo-1,2,3,4-tetrahydrotriazine (6), and *N*-adamantyl-*N'*-pentamethyleneformamidine (7) were prepared. Thermal rearrangements of 4 and 11 to the corresponding nitriles 8 and 14 were compared with that of *tert*-butyl isocyanide. The relative rate of the rearrangement for gas phase at 200° was 1.0:0.22:0.24 for *t*-BuNC, 4, and 11. The rate of the rearrangement of 4 in diglyme at 200° was 11 times faster than that of 11 and the formation of considerable amounts of adamantane was observed.

Adamantyl isocyanides have not been described in the extensive literature on adamantane chemistry.[2,3] This paper describes the facile preparation of 1- and 2-adamantyl isocyanides and some of their fundamental chemical and thermal behaviors.

Results and Discussion

Preparation and Properties of 1- and 2-Adamantyl Isocyanides. 1-Adamantyl isocyanide (4) was prepared in 61% yield by dehydration with triphenylphosphine–carbon tetrachloride–triethylamine[4] of *N*-1-adamantylformamide (2), which was obtained by the Ritter reaction on 1-adamantanecarboxylic acid (1b)[5] or 1-adamantyl bromide (1a), and/or by heating 1a in formamide. It was also prepared by the Hofmann carbylamine reaction of 1-adamantanamine (3) in 40% yield by using a 3-molar excess of dichlorocarbene, which was generated from $CHCl_3$ and *t*-BuOK in *n*-hexane.[6] The yield of 4 was improved up to 54% in the carbylamine reaction by using benzyltriethylammonium chloride, a phase-transfer catalyst.[7,8] 1-Adamantyl isocyanide (4) formed colorless crystals, mp 185–186°, and had no foul odor but a rather fragrant one. The structure was indicated by ir (KBr) absorption at 2150 cm^{-1} ($\nu_{N=C}$), mass spectral ion peaks at *m/e* (rel intensity) 161 (M^+, 5), 135 (95), and 41 (100), and nmr ($CDCl_3$) signals at δ 3.30–1.85 (broad s, 9 H) and 1.80–1.56 (unsymmetrical s, 6 H).

2-Adamantyl isocyanide (11) was prepared by the carbylamine reaction of 2-adamantanamine (10). *N*-2-Adamantylformamide (13) was not chosen as the starting material because it was not obtained by the conventional formylation of 10 with formic acid. The yield of 11 in the carbylamine reaction was raised from 40% to 76% by application of the phase-transfer technique[7] (50% aqueous KOH–C_6H_6–benzyltriethylammonium chloride). Colorless crystals of 11 were obtained, mp 186–188°, having a similar odor to 4 and ir (KBr) absorption at 2140 cm^{-1} ($\nu_{N=C}$), mass spectral ion peaks at *m/e* (rel intensity) 161 (M^+, 34), 135 (94), and 106 (100), and nmr ($CDCl_3$) signals at δ 3.41 (broad s, 1 H) and 2.35–1.30 (m, 14 H).

The 1 isomer 4 was very stable and was largely recovered even after stirring in $CHCl_3$–H_2O in the presence of a catalytic amount of sulfuric acid for 3 days at room temperature. In contrast the 2 isomer 11 was very sensitive to atmospheric moisture and was converted rapidly to formamide 13.

Both 4 and 11 afforded the corresponding 1-substituted tetrazole derivatives 5 and 12 in 92 and 54% yields, re-

Scheme I