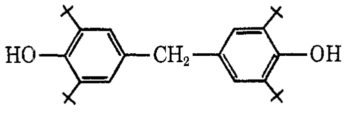
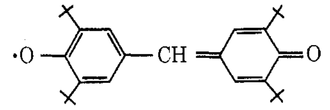
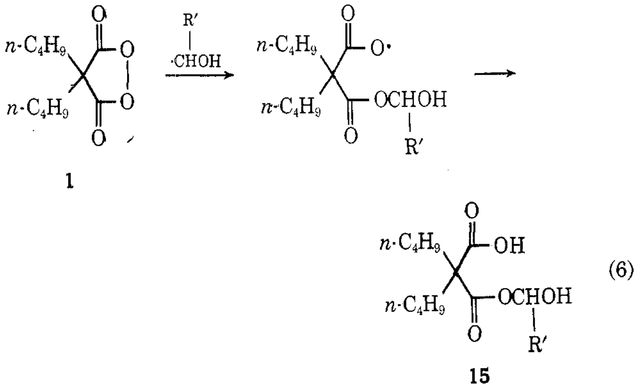


19



20

50% with **19** present. More important, no significant alteration in the yields of products **6** and **10** was observed (compare seventh and eighth entry in Table I). Therefore, chain propagation as shown in eq 6 to produce malonic acid **10** *via* loss of RCHO from **15** cannot be a major process, unless very short chain lengths are involved. To be more definite on this point, we would have liked to use galvinoxyl (**20**) as a radical counter, but unfortunately **20** is unstable in ethanol.[25]



Registry No.—**1**, 30842-78-5; dimethyl di-*n*-butylmalonate, 36602-11-6; methyl hydrogen di-*n*-butylmalonate, 36602-12-7; ethyl hydrogen di-*n*-butylmalonate, 36602-13-8; ethyl methyl di-*n*-butylmalonate, 36602-14-9; 2-*n*-butyl-2-methoxyhexanoic acid, 36602-15-0; methyl 2-*n*-butyl-2-methoxyhexanoate, 36602-16-1; methyl 2-*n*-butyl-2-hydroxyhexanoate, 36602-17-2; ethyl 2-*n*-butyl-2-methoxyhexanoate, 36622-57-8; 2-*n*-butyl-2-ethoxyhexanoic acid, 36602-18-3; methyl 2-*n*-butyl-2-ethoxyhexanoate, 36602-19-4; *cis*-2-butyl-2-hexanoic acid, 36602-20-7; *trans*-2-butyl-2-hexenoic acid, 36602-21-8; ethyl *cis*-2-*n*-butyl-2-hexenoate, 36602-22-9; ethyl *trans*-2-*n*-butyl-2-hexenoate, 36602-23-0; methyl *cis*-2-*n*-butyl-2-hexenoate, 36602-24-1; methyl *trans*-2-*n*-butyl-2-hexenoate, 36602-25-2.

Acknowledgments.—Financial support by the National Science Foundation, the Petroleum Research Fund of the American Chemical Society, and the A. P. Sloan Foundation and a Fullbright travel grant to R. Rucktäschel is gratefully appreciated.

Hydrogen Cyanide Chemistry. III. Synthesis of Diiminosuccinonitrile and Its Conversion to Diaminomaleonitrile[1]

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Contribution No. 1884 from the Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

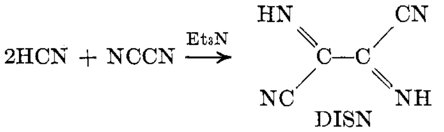
Received August 9, 1972

Diiminosuccinonitrile (DISN) is produced by base-catalyzed addition of hydrogen cyanide to cyanogen. Reduction of DISN yields diaminomaleonitrile (DAMN). Chlorination of DISN produces *N*-chlorodiiminosuccinonitrile or *N*,*N*′-dichlorodiiminosuccinonitrile.

Hydrogen cyanide has considerable synthetic potential that has not been fully utilized because it is toxic and explosive, and thus many research workers are reluctant to use it. We believe that hydrogen cyanide will eventually become a major building block for heterocyclic synthesis and are thus engaged in research to exploit its chemistry. Indeed, hydrogen cyanide has been suggested as the basic material from which purines, present in all living matter as components of nucleic acids, arose in prebiotic times.[2] Adenine (HCN pentamer) is commercially produced by heating HCN to 120° in liquid ammonia[3] and caffeine is readily accessible from diaminomaleonitrile (HCN tetramer).[4] Some notable examples of other heterocyclic systems available by combination of HCN with other reagents are hydantoins,[5] imidazoles,[2] and *s*-triazines.[6]

Results and Discussion

Diiminosuccinonitrile (DISN) is formed quantitatively by base-catalyzed addition of hydrogen cyanide to cyanogen at −40°. DISN can also be prepared by passing chlorine into a toluene solution of HCN and trimethylamine at −15°.



DISN

$$4HCN + 2Me_3N + Cl_2 \longrightarrow DISN + 2Me_3NHCl$$

The first step in the formation of DISN is no doubt attack by cyanide ion on cyanogen. The resulting

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(1) Paper I: R. W. Begland, A. Cairncross, D. S. Donald, D. R. Hartter, W. A. Sheppard, and O. W. Webster, *J. Amer. Chem. Soc.*, **93**, 4953 (1971), reported this work in part in a preliminary communication. Presented at 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 16, 1971, Abstract ORGN 126.

(2) R. A. Sanchez, J. P. Ferris, and L. E. Orgel *J. Mol. Biol.*, **30**, 223 (1967); *Science*, **153**, 72 (1966), and references cited therein.

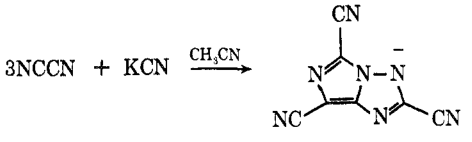
(3) H. Wakamatsu, Y. Yamada, T. Saito, I. Kumashiro, and T. Takenishi, *J. Org. Chem.*, **31**, 2035 (1966).

(4) D. W. Woodward, U. S. Patent 2,534,331 (1950); *Chem. Abstr.*, **45**, 5191 (1951).

(5) V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold, New York, N. Y., 1947.

(6) C. Grundmann, *Angew. Chem., Int. Ed., Engl.*, **2**, 309 (1963).

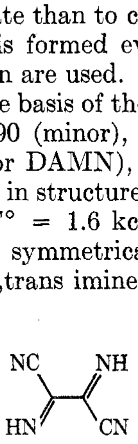
imino anion is quickly quenched by protonation. When protons are not available (aprotic solvent) cyanogen combines with cyanide to give the heterocyclic anion **1**.[7]



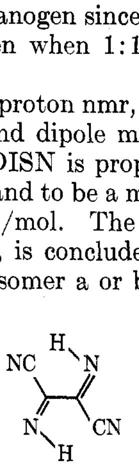
1

[A minor peak of m/e 182 ($C_7N_7^+$) is observed in the mass spectrum of DISN which could arise from traces of HC_7N_7, the conjugate acid of **1**.] A second mole of hydrogen cyanide adds to the initial adduct at a much faster rate than to cyanogen since only the 2:1 adduct, DISN, is formed even when 1:1 ratios of HCN and cyanogen are used.

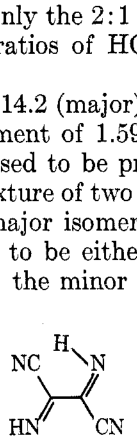
On the basis of the proton nmr, δ 14.2 (major), 14.15, and 12.90 (minor), and dipole moment of 1.59 D (*vs.* 7.8 D for DAMN), DISN is proposed to be primarily transoid in structure and to be a mixture of two isomers with $\Delta F° = 1.6$ kcal/mol. The major isomer, which must be symmetrical, is concluded to be either cis,cis or trans,trans imine isomer a or b; the minor constituent must be the unsymmetrical cis,trans isomer c. The succinonitrile structure is supported by the ^{13}C nmr, which shows only two types of carbon in a 1:1 ratio, 92.8 and 83.2 ppm upfield from $^{13}CS_2$.[8]



a



b



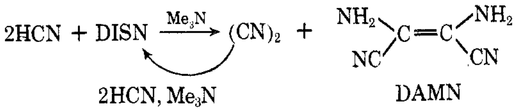
c

DISN has an oral toxicity ALD 90 mg/kg in rats. It causes severe irritation on contact with rabbit eyes and permanent damage is prevented only by immediate flushing with water. It causes mild skin and nose irritation. Also, since DISN produces hydrogen cyanide when wet or in contact with hydroxylic solvent, we strongly *caution that it be handled only in well-ventilated areas with adequate protection.*

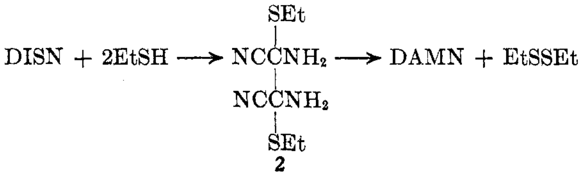
Dry samples of DISN are quite stable when stored in the dark but discolor slowly when exposed to light. In water, DISN slowly decomposes ($t_{1/2}$ about 2 weeks at ambient conditions). DISN decomposes more rapidly in dilute acid or base and in concentrated acid or base nearly instantly. Acid hydrolysis produces oxalic acid, ammonium salts, and hydrogen cyanide. Basic hydrolysis gives mainly tars.

Pure DISN is a stable white solid, mp 165–166°. However, if crude DISN in contact with solvent and basic catalyst is allowed to warm to room temperature before filtering, it decomposes extensively. This temperature effect may explain why DISN has not been previously reported. If excess hydrogen cyanide is present and the reaction mixture is warmed to room temperature, a modest amount of diaminomaleonitrile (DAMN, previously called HCN tetramer)[9] is produced as well as insoluble polymeric products. Since under comparable conditions the polymerization of HCN to DAMN is very slow, the DAMN must be produced by reduction of DISN with HCN. Cyanogen, the expected product from oxidation of HCN, would add HCN under the reaction conditions to give more DISN.

Up to 3 equiv of DAMN per 1 equiv of cyanogen have been obtained in the base-cyanogen-catalyzed tetramerization of HCN to DAMN at 0°.[10] About 30% of the product is an insoluble dark polymer.



DISN is reduced to DAMN quantitatively by hydrogen over palladium on carbon and in good yields by a number of chemical reducing agents, such as hydrogen sulfide, sodium borohydride, lithium aluminum hydride, phenylhydrazine, hydroquinone, and ethanethiol. In the last case an intermediate **2** can be isolated. On



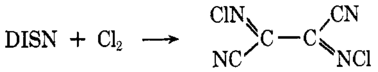
$$\text{DISN} + 2\text{EtSH} \longrightarrow \begin{array}{c}\text{SEt}\\ | \\ \text{NCCNH}_2\\ | \\ \text{NCCNH}_2\\ | \\ \text{SEt}\end{array} \longrightarrow \text{DAMN} + \text{EtSSEt}$$

2

standing it slowly generates DAMN and diethyl disulfide. Dichlorodicyanobenzoquinone oxidizes DAMN to DISN.

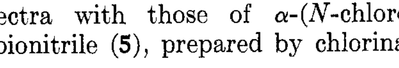
The reduction of DISN confirms its structure and provides the first high-yield synthesis of DAMN. Previously DAMN was obtained by the polymerization of HCN[11] or indirectly from 1-cyanoformamide p-toluenesulfonylhydrazone[12] and from aminomalononitrile p-toluenesulfonate.[13]

DISN is chlorinated quantitatively at −30° to give N,N'-dichlorodiiminosuccinonitrile (**3**), a white solid,



3

mp 164.5–165.5°. Under similar conditions DAMN gives **3** in about 50% yield. Its structure was assigned on the basis of a comparison of its infrared and ultraviolet spectra with those of α-(N-chloroimino)trichloropropionitrile (**5**), prepared by chlorination of α-iminotrichloropropionitrile,[14] and the fact that it contains positive chlorine. Equimolar quantities of DISN



$$\underset{\mathbf{4}}{\text{CCl}_3\overset{\overset{\text{NH}}{\|}}{\text{C}}\text{—CN}} + \text{Cl}_2 \longrightarrow \underset{\mathbf{5}}{\text{CCl}_3\text{—}\overset{\overset{\text{N—Cl}}{\|}}{\text{C}}\text{—CN}}$$

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[7] O. W. Webster, U. S. Patent 3,093,653 (1963); D. W. Wiley, E. P. Blanchard, and O. W. Webster 3rd Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 1968, Abstract H70.

[8] We thank Professor J. D. Roberts of California Institute of Technology for this measurement.

[9] Other HCN tetramers are diaminofumaronitrile[2] and 4-amino-5-cyanoimidazole.[2]

[10] Sanchez, *et al.*, ref 2, mention that cyanogen and other substances increase the rate of polymerization of aqueous hydrogen cyanide.

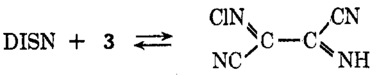
[11] R. P. Linstead, E. G. Noble, and J. M. Wright *J. Chem. Soc.*, 911 (1937); H. Bredereck, G. Schmötzer, and E. Oehler, *Justus Liebigs Ann. Chem.*, **600**, 81 (1956); D. W. Woodward, U. S. Patents 2,499,441 and 2,534,322 (2950); *Chem. Abstr.*, **44**, 5898*i* (1950); **45**, 5191 (1951); T. Okada and N. Asai, German Patent Application 2,022,243 (1970).

[12] R. E. Moser, J. M. Fritsch, T. L. Westman, R. M. Kliss, and C. N. Matthews, *J. Amer. Chem. Soc.*, **89**, 5673 (1967).

[13] J. P. Ferris and R. A. Sanchez *Org. Syn.*, **48**, 60 (1969).

[14] H. Zima, German Patent 1,053,500 (1959).

and **3** in refluxing MeCN disproportionate to *N*-chlorodiiminosuccinonitrile (**6**). This reaction is proba-



6

bly reversible since **3** and DISN can still be isolated after long reaction times.

DISN has proved to be a versatile intermediate, particularly for synthesis of heterocyclic compounds.[1] The extensive chemistry of DISN and its derivatives will be described in subsequent papers.[15]

Experimental Section

The infrared spectra were obtained on a Perkin-Elmer Model 21 spectrometer, the uv on a Cary Model 14, the nmr on a Varian A-60, and the mass spectra on a Du Pont CEC 21-110B high-resolution double-focusing instrument. Hydrogen cyanide was commercial grade inhibited with sulfuric acid and SO_2. The cyanogen was obtained from Matheson Gas Products, Inc., and contained up to 3% cyanogen chloride. All reactions were conducted under nitrogen in solvents dried over a molecular sieve.

Synthesis of Diiminosuccinonitrile (DISN). A. From Cyanogen and HCN.—A solution of 1800 ml of CH_2Cl_2, 320 g (11.85 mol) of HCN, and 294 g (5.65 mol) of cyanogen was cooled to −40°, and with moderate stirring, a solution of 25 ml (0.167 mol) of dry Et_3N in 75 ml of CH_2Cl_2 was added dropwise. After 25 ml of the catalyst solution was added, the reaction became exothermic and the initial precipitation of DISN was observed. During catalyst addition, the reaction solution was maintained at −45 to −40°. (*Caution*—If the temperature is maintained at below −45°, hydrogen cyanide crystallizes and the reaction proceeds at a much slower rate with the danger that solid HCN will be collected on the filter rather than DISN. Also, for large-scale reactions, a circulating cooling bath was used which could be quickly cooled to −80° in case the reaction temperature rose above −20°.)

After the addition was complete (2 hr), the precipitated product was collected while cold and washed with 1 l. each of cold CH_2Cl_2 and ether. On drying under N_2, there remained 577 g of a fine tan DISN (96% yield). The product obtained in this manner is sufficiently pure for most synthetic purposes.

For further purification DISN was dissolved in hot ethyl acetate, and the solution was treated with Darco and then evaporated to a slush. The slush was filtered and the solid DISN was washed with ether and dried in an inert atmosphere. An analytical sample was recrystallized from acetonitrile: mp 165–166°; sublimation point 100° (0.1 mm); crystal structure, orthorhombic, a = 7.83 Å, b = 9.80 Å, c = 6.71 Å, space group *Pcab;* uv max (MeCN) 292 nm (ϵ 280); ir (KBr) 3280, 2670, 2354, 2256, 1905, 1617, 1402, 1267, 1111, 932 cm^{-1}; nmr (DMSO) δ 14.2 (s) (major isomer), 14.15 (s) and 12.90 (s) (minor isomer); ^{13}C nmr δ 92.8, 83.2 ppm upfield from $^{13}CS_2$; dipole moment (dioxane) 1.59 D; mass spectrum m/e 26, 27, 52, 53, 79, 105; polarography no oxidation up to 2.3 V (*vs.* hydrogen, rotating Pt electrode), irreversible reduction at −1.45 V (*vs.* hydrogen, dropping Hg electrode); thermogravimetric analysis 5% weight loss at 194°, 50% at 202°; heat of combustion, 5090 cal/g; solubility (25°), acetone 21, DMAC 5.9, THF 21, MeCN 18, ether 1.5 g/100 ml; differential thermal analysis, endotherm 164°, exotherm 183°.

Anal. Calcd for $C_4H_2N_4$: C, 45.3; H, 1.9; N, 52.8. Found: C, 45.6; H, 2.1; N, 52.5.

B. From HCN and Cl_2.—To a solution of 306 ml (8.00 mol) of hydrogen cyanide, 387 ml (4.00 mol) of trimethylamine, and 2.5 l. of toluene at −20° was added 145 g (2.04 mol) of chlorine over 40 min. The mixture was stirred for 0.5 hr at −15° and filtered. The precipitate was washed with toluene, then twice with 500 ml of ice water, and air dried. There remained 135 g of diiminosuccinonitrile (65%) characterized by its infrared spectrum.

C. From Oxidation of Diaminomaleonitrile.—A solution of 3.24 g (0.03 mol) of DAMN in 75 ml of CH_3CN was treated with 6.78 g (0.03 mol) of dichlorodicyanobenzoquinone at room temperature. After 0.5 hr the reaction mixture was filtered to give 6.53 g of dichlorodicyanohydroquinone. On evaporation of the filtrate there remained 3.32 g of DISN containing a trace of dichlorodicyanohydroquinone (ir).

Synthesis of Diaminomaleonitrile (DAMN). A. Reduction of Diiminosuccinonitrile (DISN). Hydrogen.—In a 3-gallon autoclave equipped with a stirrer and cooling coils were placed 13 g of 10% Pd/C catalyst (Engelhardt), 760 g of DISN, and 2 gallons of THF.

The autoclave was closed, stirred, briefly evacuated, cooled, and pressured with 150 psi of hydrogen and then by small stages to 1500 psi so that the temperature was not allowed to exceed 35°. The reaction is exothermic; so it was necessary to stop temporarily at 1000 or 1500 psi. After the pressure drop ended (1–3 hr), the reaction was stirred for 1 hr at 1500 psi, 25–35°. The autoclave was immediately vented and flushed with nitrogen. The product was siphoned and the autoclave was rinsed with 1.5 l. of THF. The reaction solution from five runs was concentrated to give 3.68 kg (95%) of DAMN. This product was golden brown and was suitable for most reactions. For purification 200 g of DAMN was added to a boiling mixture of 2 l. of water and 160 g of carbon black. After 8–10 min the mixture was filtered quickly through a preheated thin Celite bed into a flask containing 1.6 kg of ice stirred and cooled in an ice bath. The filter cake was washed with 400 ml of boiling water. After the ice had melted, the DAMN (140 g) was collected on a filter and dried over P_2O_5 (0.1 mm). Two recrystallizations gave white DAMN.

DAMN produced by reduction of DISN was identical with that produced by other methods:[9] mp 184° dec; sublimation point 120° (0.1 mm); crystal structure, no molecular symmetry, a = 6.44 Å, b = 18.24 Å, c = 5.22 Å, space group $P2_1/c$; uv max (H_2O) 295 nm (ϵ 12,000), uv (EtOH) 300 (14,000); ir 3300–3500 (three bands), 2213, 2165, 1647, 1623 cm^{-1}; nmr (DMSO) δ 5.26; ^{13}C nmr δ 75.2 and 85.4 ppm upfield from $^{13}CS_2$; dipole moment, 7.8 D; mass spectrum m/e 52, 53, 54, 55, 81, 108; pK_b 2.18; toxicity, ALD 450 mg/kg in rats; TGA, 5% weight loss at 209°, 50% weight loss at 637°; DTA, endotherm 182°, exotherm 204°; heat of combustion, 5230 cal/g; density 1.29 g/cc; dielectric constant 4.5; conductivity $\rho > 3 \times 10^{10}$ ohm-cm; solubility (25°), acetone 15, DMAC 39, water 0.5, THF 14, MeCN 7, EtOAc 3.6, ether 0.4, MeOH 6.1, EtOH 3.6, isopropyl alcohol 2.6, dioxane 9.6, water (100°) 15 g/100 ml.

H_2S.—A stream of hydrogen sulfide gas was bubbled through a slurry of 10.0 g of DISN in 100 ml of methylene chloride for 0.5 hr. The reaction mixture was concentrated to dryness and the residue was extracted with CS_2 to remove sulfur. DAMN (8.6 g, 84%) remained and was identified by its infrared spectrum.

2,3-Diamino-2,3-bis(ethylthio)succinonitrile (2).—A solution of 2.0 g of DISN, 4 ml of ethanethiol, and 20 ml of methylene chloride was stirred at 26° for 15 min and was then refluxed for 30 min. Petroleum ether (bp 30–60°) (75 ml) was added and the mixture was filtered to give 0.9 g (43%) of DAMN. On standing 1.0 g of **2** (23%) crystallized from the filtrate. An analytical sample was recrystsllized from ether: mp 104–106°; ir (KBr) 3376, 3320, 1630 ($-NH_2$), 2985, 2935, and 2875 (CH), 2248 (CN), 1379 cm^{-1} (CCH_3); nmr (acetone-d_6) δ 1.34 (t, 6), 3.02 (q + broad absorption, 8); mass spectrum m/e 230.

Anal. Calcd for $C_8H_{14}N_4S_2$: C, 41.7; H, 6.1; N, 24.3. Found: C, 41.8; H, 6.0; N, 24.3.

$NaBH_4$.—To a stirred solution of 3.0 g (0.028 mol) of DISN in 50 ml of methanol at −20° was added 1.0 g (0.026 mol) of $NaBH_4$ in small portions. The resulting solution was warmed to room temperature and poured into a flask containing 200 ml of water. Approximately 75 ml of solvent was removed on a rotary evaporator and the remaining aqueous solution was extracted with two 300-ml portions of ethyl acetate. The combined organic layers were dried over $MgSO_4$ and the solvent was removed to give 2.4 g (79%) of light tan DAMN, identified by its infrared spectrum.

Lithium Aluminum Hydride.—To a slurry of 1.52 go of $LiAlH_4$ in 100 ml of dry ether was added 2.0 g (0.019 mol) of diiminosuccinonitrile in 200 ml of ether. After the addition was completed, the excess $LiAlH_4$ was destroyed with water and 20% NaOH. The resulting dark colored solution was filtered and the ether was removed to give 0.31 g (15%) of diaminomaleonitrile.

Phenylhydrazine.—To a solution of 5.3 g (0.05 mol) of diiminosuccinonitrile in 100 ml of ethanol and 50 ml of acetonitrile

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(15) Paper IV: R. W. Begland and D. R. Hartter, *J. Org. Chem.*, **37**, 4136 (1972).

at 0° was added dropwise 10.8 g (0.10 mol) of phenylhydrazine in 50 ml of ethanol. The solution was allowed to warm to 25°, stirred for 1 hr, and stripped to dryness. The resulting solid was washed with ether and dried to give 3.3 g (61%) of diaminomaleonitrile.

Hydroquinone.—To a solution of 1.06 g (10 mmol) of DISN in 20 ml of CH_3CN was added 1.10 g (10 mmol) of hydroquinone. After 24 hr 230 mg of quinone was isolated by filtration. On evaporation of the filtrate there remained 1.86 g of a mixture of DAMN, DISN, hydroquinone, and quinone (ir).

B. **From Cyanogen-Catalyzed Tetramerization of HCN.**—A solution of 100 ml (70 g) of HCN and 300 ml of toluene was maintained at −15 to −10°. Trimethylamine (11 ml) was condensed into the solution and then 14 g of cyanogen was introduced over 5 hr. The solution turned black and 77 g of DAMN and higher polymers of HCN precipitated. DAMN (59 g, 84%) was isolated by extraction with tetrahydrofuran and precipitation with petroleum ether. Although dark colored, its infrared spectrum was identical with that of DAMN prepared by reduction of DISN. This represents a catalyst turnover number of approximately 2. A catalyst turnover number of 3 was obtained when DISN was used in place of cyanogen.

N,N'-**Dichlorodiiminosuccinonitrile** (**3**).—A solution of 16.75 g of DISN in 250 ml of MeCN was cooled to −40° and about 100 ml of liquid Cl_2 (excess) was added. The mixture was stirred at −20° for 2 hr, and was then concentrated to dryness (the excess chlorine was trapped in aqueous NaOH). There remained 27.4 g of **3** (97%). Recrystallization from $CHCl_3$ gave 21.0 g of **3**: mp 164.5-165.5°; uv max 258 nm (ϵ 18,200), sh 300 (278); ir 2238 (C≡N), 1545 (C=N), 1013, 225 cm^{-1}; molecular weight (bp benzene) 175°.

Anal. Calcd for $C_4N_4Cl_2$: C, 27.5; N, 32.0; Cl, 40.5. Found C, 27.2; N, 32.0; Cl, 40.5.

α-N-**Chloroiminotrichloropropionitrile** (**5**)—A 15.0-g (88 mmol) portion of **4** in 100 ml of CH_2Cl_2 [uv max 264 nm (ϵ 178); ir 3250 (NH), 1631 (C=N), 2270 cm^{-1} (C≡N)] was mixed with 20 ml of liquid Cl_2 at −30°. After 2 hr at −20° the solution was concentrated and the residue was distilled to give 15.2 g of **5**: bp 42° (3.5 mm); uv max 231 nm (ϵ 5860), sh 283 (97); ir 2233 (CN), 1572 (C=N), 841, 782, 710 cm^{-1}; mol wt (fp benzene) 206.

Anal. Calcd for $C_3N_2Cl_4$: C, 17.5; N, 13.6; Cl, 68.9. Found C, 17.7; N, 13.6; Cl, 68.6.

N-**Chlorodiiminosuccinonitrile** (**6**).—A solution of 5.30 g (50 mmol) of DISN and 8.70 g (50 mmol) of **3** in 200 ml of CH_3CN was heated at reflux under N_2 for 24 hr. The product was preabsorbed on "SilicAR CC7" and chromatographed. Elution with CCl_4 removed 0.30 g of **3** while benzene-$CHCl_3$ (1:1) removed 3.50 g of **6** which was subsequently sublimed: white crystals; 2.50 g (35.7%); mp 120–122°; ir 3280 (NH), 2260 (CN), 1610 (C—NH), 1560 cm^{-1} (C=NCl); mol wt (fp benzene) 142.

Anal. Calcd for C_4HN_4Cl: C, 34.2; H, 0.7; N, 39.9; Cl, 25.2. Found: C, 34.4; H, 1.0; N, 40.0; Cl, 25.4.

Registry No.—**2**, 36601-97-5; **3**, 33420-44-9; **5**, 36601-99-7; **6**, 36602-00-3; HCN, 74-90-8; DISN, 28321-79-1; DAMN, 1187-42-4.

Hydrogen Cyanide Chemistry. IV. Diiminosuccinonitrile Reactions with Nucleophiles, Acyl Halides, and Carbonyl Compounds[1]

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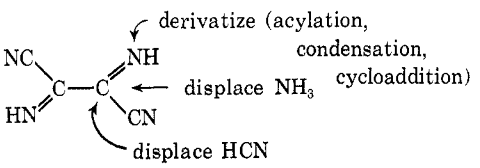
Received August 9, 1972

The reactions of diiminosuccinonitrile (DISN) with nucleophiles, acyl halides, and carbonyl compounds are described. Nucleophiles such as water, alcohols, and amines add to DISN giving products which result from displacement of either hydrogen cyanide or ammonia. Phosgene reacts with DISN to give a reactive imidazolidone from which several new polyfunctional derivatives have been prepared. Isoimidazoles, pyrazines, and oxazoles have been obtained by condensation of DISN with various ketones. Upon heating, some of these 2,2-dialkylisoimidazoles undergo a 1,5 shift of an alkyl group from carbon to nitrogen resulting in 1,2-dialkylimidazole formation.

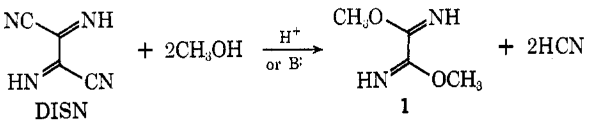
Diiminosuccinonitrile (DISN), recently prepared in our laboratory by reaction of hydrogen cyanide with cyanogen,[2] has proven to be a valuable intermediate for the preparation of many polyfunctional heterocyclic and acyclic compounds. In this paper we describe the basic reactions of DISN which occur at either the carbon or nitrogen of the imine bonds.



DISN

Nucleophiles react with DISN giving products which result from displacement of either hydrogen cyanide or ammonia. For example, under neutral or basic reaction conditions the cyano groups are usually displaced while under acidic conditions loss of ammonia is the predominant process. Derivatization of the imine nitrogen occurs with a variety of reagents. Reactive halogen compounds such as sulfur dichloride, phosgene, and chlorine readily add to the imines of DISN; carbonyl compounds condense with DISN yielding isoimidazoles and pyrazines; and olefins react with DISN giving aziridines and tetrahydropyrazines.[3]

Reaction with Nucleophiles.—DISN behaves much like benzoyl cyanide in reactions with alcohols and aromatic amines. Thus, treatment of DISN with methanol under acid or base catalysis results in attack of the imine carbon by alcohol and loss of hydrogen cyanide. The dialkyl oxaldiimidate (**1**) thus formed can also be prepared by reaction of cyanogen with methanol.[4] In a similar manner aniline adds to DISN giving diphenyloxamidine (**2**).[5]



DISN 1

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[1] Paper III: O. W. Webster, D. R. Hartter, R. W. Begland, W. A. Sheppard, and A. Cairncross, *J. Org. Chem.*, **37**, 4133 (1972).

[2] R. W. Begland, A. Cairncross, D. S. Donald, D. R. Hartter, W. A. Sheppard, and O. W. Webster, *J. Amer. Chem. Soc.* **93**, 4953 (1971).

[3] T. Fukunaga, *ibid.*, **94**, 3242 (1972).

[4] K. Brotherton and J. W. Lynn, *Chem. Rev.*, **59**, 841 (1959).

[5] Prepared by addition of aniline to cyanogen: A. W. Hofmann, *Justus Liebigs Ann. Chem.*, **66**, 130 (1848).