independent of the extent of reaction. Assuming that **3** and **5** are primary products from **2** (**4** was stable under the reaction conditions), then the specificity noted with **1** may have been due partly to a steric effect. Nonetheless, the fact that the **3**:**5** ratio was not identical from **1** and **2** requires some stereospecificity in the alkyl shift.

However, more important than the stereochemical results is the alteration in the mechanism of the spiropentane rearrangement with **2** relative to that of **1** and to that of the isopropenylspiropentanes.[1] That the stereochemistry of the 4,5-dimethyl substitution is crucial derives from the observation that in benzene at 170° for 1 hr **1** reacts to the extent of 20% (to give **3**) while **2** gives 75% of **4**. Thus the relative rate of pyrolysis of **2** *vs.* **1** is 3.8. However, since little, if any, **4** was formed from **1**, the "abnormal" rearrangement of **2** to **4** is at least 100 times faster than that of **1** to **4**. Remarkably, *cis*-2,3-dimethyl-*cis*-1-chlorocyclopropane solvolyzes about 80 times faster than *trans*-2,3-dimethyl-1-chlorocyclopropane,[9c] a result entirely consistent with our results and proposed mechanism for conversion of **2** to **4**.[11]

Finally, it should be noted that the normal rearrangement of **1** to **3** was accelerated in acetonitrile solvent relative to benzene by at least a factor of ten. Thus, the dicyano substitution in the spiropentane system substantially increases the polarity of the transition state in the thermolysis. Most interesting to determine would be the overall stereochemistry of the spiropentane rearrangement (*i.e.*, retention or inversion at the migration terminus and the migrating group relative to the direction or rotation of what becomes the terminal carbon atom) as a function of substituent polarity. This work is in progress.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund for partial support of this work (2754-A1,4), and Professor Turro for samples of the *cis*- and *trans*-2,3-dimethylcyclobutanones.

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cis-2,3-dimethylcyclobutanone (220 MHz) showed: doublet at δ 1.02 (3 H, J = 7 Hz), doublet at 1.09 (3 H, J = 7 Hz), doublet of doublet of doublets at 2.36 (1 H, J = 16, 4, and 2 Hz), multiplet at 2.53 (1 H), and multiplet from 3.10 to 3.40 (2 H).

(11) A referee has suggested an alternative mechanism for the reaction of **2** in which initial C_4–C_5 cleavage occurs followed by migration of the dicyanomethylene group, and **2** would undergo this reaction faster than **1** "since *cis*-1,2-dimethylcyclopropanes are significantly higher in energy than trans ...." In fact, *cis*-1,2-dimethylcyclopropane is only 1.07 kcal/mol higher in enthalpy content than the trans compound, so the difference in reactions of **1** and **2** must be associated with the stereoelectronic nature of reaction pathways and not simply ground-state energy differences. M. C. Flowers and H. M. Frey, *Proc. Roy. Soc., Ser. A*, **257**, 122 (1960).

(12) Fellow of the Alfred P. Sloan Foundation, 1971–1973.

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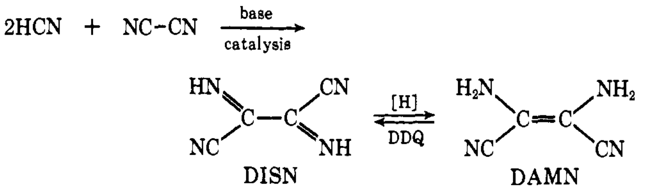
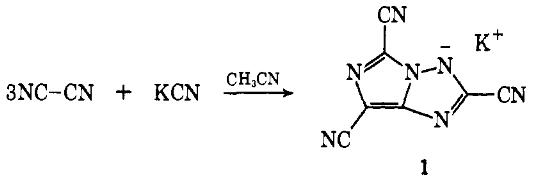
Hydrogen Cyanide Chemistry. I. Diiminosuccinonitrile

Sir:

Diiminosuccinonitrile (DISN), a new member of the cyanocarbon family, is prepared in high yield by base-catalyzed addition of hydrogen cyanide to cyanogen. A highly reactive polyfunctional intermediate, DISN is readily reduced to diaminomaleonitrile (DAMN), the well-known HCN tetramer;[1] the two-step reaction sequence provides the first high-yield synthesis of this versatile polyfunctional reagent.



The addition of nucleophiles to cyanogen is a well-known reaction.[2] The addition of cyanide ion to cyanogen was found in our laboratories to give the novel heterocyclic salt $C_7N_7^-K^+$ (**1**).[3] However, triethylamine catalyzes the addition of two molecules of hydrogen cyanide to cyanogen giving DISN in 96% yield. For example, 1.5 ml of dry Et_3N in 15 ml of CH_2Cl_2 was added dropwise over 45 min to a solution of 120 ml of CH_2Cl_2, 20 g (0.74 mol) of HCN, and 17.4 g (0.34 mol) of cyanogen at −40°. The reaction was mildly exothermic and DISN precipitated as the Et_3N was added. After 30 min the precipitated product was collected while still cold and washed with CH_2Cl_2 and ether to give 33.6 g (95%) of DISN as a fine tan powder of sufficient purity (ir and nmr nearly identical with recrystallized material) for synthetic use. Pure DISN is an air-stable white crystalline solid, mp 165–166° dec; sublimes 100° (1 mm). A good purification procedure is to dissolve DISN in hot ethyl acetate with "Darco" treatment, evaporate the solution to a slush, suction filter, and wash the solid with ether and dry in an inert atmosphere. DISN is moderately soluble in tetrahydrofuran, acetonitrile, and ethyl acetate, slightly soluble in ether, and insoluble in benzene and hydrocarbons. An analytical sample was recrystallized from acetonitrile: ir strong bands at 3240, 1630, 1265, and 932 cm^{-1}; a weak nitrile band at 2240 cm^{-1}; proton nmr (DMSO) δ 14.2 (major), 14.15, 12.90 (minor).



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

On the basis of the proton nmr and dipole moment of 1.59 D (*vs.* 7.8 D for DAMN), DISN is proposed to be primarily transoid in structure and to comprise an equilibrium 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.

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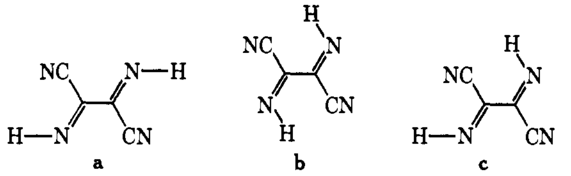
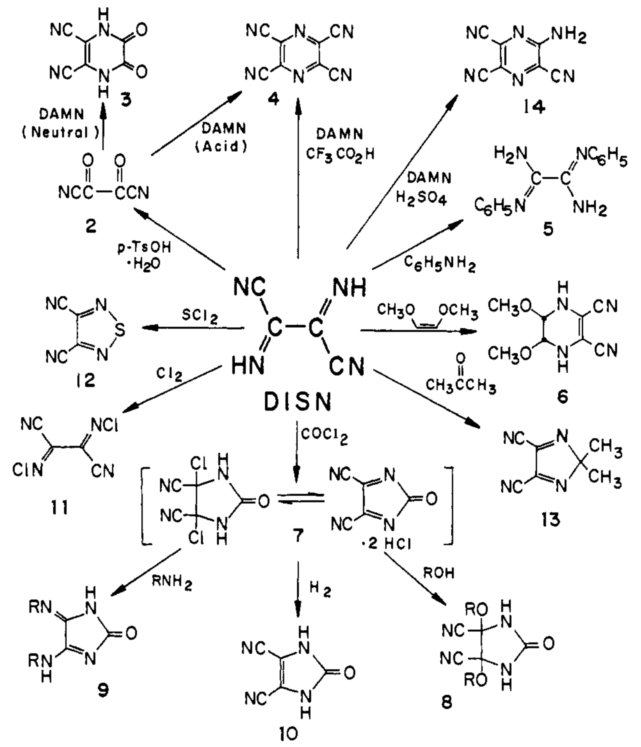
(1) H. Bredereck, G. Schmötzer, and E. Oehler, *Justus Liebigs Ann. Chem.*, **600**, 81 (1956); D. W. Woodward, U. S. Patent 2,499,441 (1950); *Chem. Abstr.*, **44**, 5898i (1950); P. S. Robertson and J. Vaughan, *J. Amer. Soc.*, **80**, 2691 (1958).

(2) T. K. Brotherton and J. W. Lynn, *Chem. Rev.*, **59**, 841 (1959).

(3) O. W. Webster, U. S. Patent 3,093,653 (1963); *Chem. Abstr.*, **59**, 11507b (1963); D. W. Wiley, E. P. Blanchard, and O. W. Webster, Third Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 1968, Abstract H70.





Further proof of structure was obtained by reduction of DISN to DAMN under a variety of conditions. For example, DISN in tetrahydrofuran containing Pd on carbon catalyst was quantitatively hydrogenated in a Parr apparatus. DAMN is oxidized to DISN by dichlorodicyanobenzoquinone (DDQ).

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.*

When heated in water, DISN hydrolyzes to oxalic acid. However, controlled hydrolysis (carried out by the addition of 2 equiv of *p*-toluenesulfonic acid monohydrate to a solution of DISN in tetrahydrofuran) gives oxalyl cyanide (**2**).[4] Oxalyl cyanide can be isolated under anhydrous conditions by sublimation directly from the reaction mixture at 50° (0.5 mm) as a crystalline white solid: mp 61–62°; ir 2230 and 1735 cm^{-1}; mass spectrum 108, 82, 54, and 26. Due to the rapid hydrolysis of **2**, it is usually used in subsequent reactions without isolation. The addition of diaminomaleonitrile (DAMN) to a solution of oxalyl cyanide in tetrahydrofuran gives 2,3-dioxo-5,6-dicyano-1,2,3,4-tetrahydropyrazine (**3**).[5] However, if the *p*-toluenesulfonic acid salt of DAMN is added to oxalyl cyanide the product is tetracyanopyrazine (**4**): mp 274–276°; ir 2250, 1180, and 1160 cm^{-1}.

Nucleophiles normally displace the nitrile groups of DISN; for example, aniline gives diphenyloxamidine (**5**).[6]

DISN undergoes a $2 + 4$ cycloaddition reaction with electron-rich olefins; for example, the addition of *cis*-1,2-dimethoxyethylene to a solution of DISN in acetonitrile gives an exothermic reaction resulting in the formation of 2,3-dimethoxy-5,6-dicyano-1,2,3,4-tetrahydropyrazine (**6**) in 76% yield, mp 159–162°; ir 3370, 3240, 2210, and 1610 cm^{-1}. Pyrazine **6** is formed with complete retention of stereochemistry. Various other reaction paths are found with other types of unsaturated hydrocarbons.[7]

The reaction of DISN with phosgene at $-20°$ in tetrahydrofuran gives in high yield the new 4,5-dichloro-4,5-dicyano-2-imidazolidone (**7**) which is relatively unstable if not kept in solution. This adduct **7** in solution readily adds certain nucleophiles, such as alcohols, to give compound **8** (R = allyl, 82% yield; mp 150–151°), but also behaves like DISN to undergo nucleophilic substitution of the nitrile groups, such as with amines to give imidazolone **9** (R = isopropyl; 10% yield; mp 232–233°; ir 3155, 3050, 1740, 1703, 1628 cm^{-1}). Compound **7** is readily hydrogenated over Pd on carbon in a Parr apparatus at room temperature to the corresponding 4,5-dicyano-2-imidazolone (**10**).[8]

The addition of excess chlorine to an acetonitrile solution of DISN at -40 to $-20°$ over a 2-hr period gives a quantitative yield of *N,N′*-dichlorodiiminosuccinonitrile (**11**) as white crystals from chloroform: mp 164.5–165.5°; ir 2240, 1540, and 1015 cm^{-1}. DISN reacts with sulfur dichloride[9] in methylene chloride at room temperature to give in 93% yield dicyano-1,2,5-thiadiazole (**12**).[10]

DISN condenses with DAMN to give linear or heterocyclic products depending on the conditions; for example, if 1 equiv of sulfuric acid is added to a solution of DISN and DAMN in tetrahydrofuran, aminotricyanopyrazine (**14**) (mp 300° dec; ir 3420, 3340, 3230, 2240, 1630, and 1550 cm^{-1}) is obtained in 95% yield. However, if DISN and DAMN are combined in trifluoroacetic acid, then tetracyanopyrazine (**4**) is the major product (59% yield). DISN also condenses with low molecular weight ketones to give the new family of dicyanoisoimidazoles. For example, by refluxing a solution of DISN in acetone containing catalytic amounts of oxalic acid and DAMN along with molecular sieves, isoimidazole **13** is obtained in 65% yield: mp 139–140°; ir 2250, 1600, and 1540 cm^{-1}.

Many derived products of DISN have been converted to useful intermediates for a variety of potential applications; for example, tetracyanopyrazine is converted *via* pyrazinetetracarboxylic acid to pyrazinetetracarboxylic acid dianhydride for use in preparation of polyimides.[11] In forthcoming publications we will

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[4] Satisfactory analyses were obtained on all new compounds and appropriate spectra were used to confirm structures.

[5] H. Bredereck and G. Schmötzer, *Justus Liebigs Ann. Chem.*, **600**, 95 (1956).

[6] Reported prepared by addition of aniline to cyanogen: A. W. Hofmann, *ibid.*, **66**, 129 (1848).

[7] Under study by Dr. T. Fukunaga of this laboratory.

[8] Reported prepared from DAMN and phosgene: D. W. Woodward, U. S. Patent 2,534,332 (1950); *Chem. Abstr.*, **45**, 5191 (1951).

[9] We thank Dr. F. N. Jones for this experiment.

[10] M. Carmack, D. Shew, and L. M. Weinstock, U. S. Patent 2,990,408 and 2,990,409 (1961); *Chem. Abstr.*, **56**, 4775 (1962).

[11] (a) W. M. Edwards, U. S. Patent 3,179,634 (1965); (b) S. S. Hirsch, *J. Polym. Sci., Part A-1*, **7**, 15 (1969).

describe extensive chemistry based on novel derivatives from hydrogen cyanide chemistry, particularly with DISN as the key intermediate.

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Influence of Remote Functional Groups in the Chemical Ionization Mass Spectra of Long-Chain Compounds

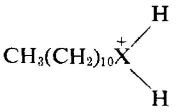
Sir:

It has been previously demonstrated that the interaction between remote functional groups or atoms in long-chain compounds can lead to major effects in their electron ionization mass spectra.[1] These effects were originally recognized as being due to winding or coiling of the conformationally mobile long chains[2,3] and have more recently been associated with such factors as transition-state ring size,[4] stabilization by charge exchange,[1c] sites of localized activation,[5] and internal solvation by the alkyl chain.[1a,6]

In view of the fundamentally different nature of ions produced by chemical ionization,[7] we have sought to identify the occurrence of remote group participation in the spectra of suitable long-chain models. For these purposes the chemical ionization spectra of monofunctional compounds **1a–c** have been recorded using methane reagent gas, and compared with those of the corresponding bifunctional analogs **2a–c**.[8] Our spectra of **1a** and **1c** are similar to those of 1-decanol and 1-octylamine previously reported.[10] As shown in Table I, the abundances of protonated molecular ions $(M + H)^+$ from the **1** series (ion a) reflect increased stabilization, and therefore less rapid fragmentation, in the order N > S > O, in analogy to the same general order found on electron ionization.[11] The stability of $(M + H)^+$ from **1a** is sufficiently low that no peak is observed,[10] a relatively unusual occurrence for molecules which contain a heteroatom. Earlier studies using the less energetic reagent gas isobutane have shown that the tendency to form $(M + H)^+$ from monofunctional alcohols further decreases with increasing chain length, and no peak is observed with chain lengths greater than C_5.[12]

$CH_3(CH_2)_9XH$ **1** $\qquad HX(CH_2)_{10}XH$ **2**

a, X = O
b, X = S
c, X = NH



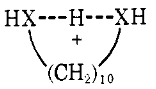
a

Table I. Abundance of $(M + H)^+$ in the Methane Chemical Ionization Mass Spectra of **1** and **2**

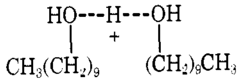
Compound	% rel int	% $\Sigma_{60}{}^a$
1-Decanol (**1a**)	0.0	0.0
1-Decanethiol (**1b**)	90	23
1-Decylamine (**1c**)	100	73
1,10-Decanediol (**2a**)	59	14
1,10-Decanedithiol (**2b**)	100	51
1,10-Decanediamine (**2c**)	100	88

[a] Excluded from calculation were (i) peaks below *m/e* 60, to avoid contributions from reagent gas, and (ii) peaks representing adduct ions arising from unrelated processes, such as $(M + C_2H_5)^+$.

By contrast, the presence of a second heteroatom at the opposite end of the chain produces marked enhancement of $(M + H)^+$, as indicated by comparisons of **1** *vs.* **2** in Table I. We attribute the increased stabilities of $(M + H)^+$ from the **2** series to proton sharing by the heteroatoms (ion b).

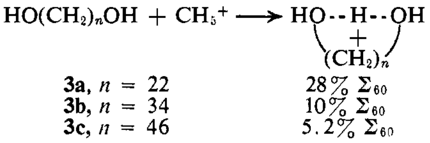


b



c

The same effect is achieved by operating at high partial pressures of **1a**, which, in parallel to the behavior of CH_3OH,[13] permits formation of clusters of the type $(CH_3(CH_2)_9OH)_nH^+$, where, however, n = 2 and 3 but not 1. The stabilized complex shown schematically as c is therefore analogous to ion b, and points to a degree of similarity between ion–molecule reactions and those occurring between the termini of long chains.[14] As the alkyl chain is lengthened (**3a–c**), $(M + H)^+$ still accounts for a significant portion of the total ion current,[15] implying the existence of cyclic ions containing up to 49 members.



Hydride abstraction leading to $(M - H)^+$ is significant in the spectra of **1a**,[10] **2a**, and **3**. In **1a**, the α-carbon has been postulated[10] as the point of ab-

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(1) For leading references see (a) S. Meyerson and L. C. Leitch, *J. Amer. Chem. Soc.*, **93**, 2244 (1971); (b) E. White, V, and J. A. McCloskey, *J. Org. Chem.*, **35**, 4241 (1970); (c) J. Diekman, J. B. Thompson, and C. Djerassi, *ibid.*, **34**, 3147 (1969); (d) G. H. Draffan, R. N. Stillwell, and J. A. McCloskey, *Org. Mass Spectrom.*, **1**, 669 (1968); (c) R. Brandt and C. Djerassi, *Helv. Chim. Acta*, **51**, 1750 (1968).

(2) R. Ryhage and E. Stenhagen, *J. Lipid Res.*, **1**, 361 (1960).

(3) J. A. McCloskey and M. J. McClelland, *J. Amer. Chem. Soc.*, **87**, 5090 (1965).

(4) For example, H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, pp 179–180.

(5) For example, S. Meyerson and L. C. Leitch, *J. Amer. Chem. Soc.*, **88**, 56 (1966); A. Caspar, G. Teller, and R. E. Wolff, *Org. Mass Spectrom.*, **3**, 1351 (1970).

(6) P. Bommer and K. Biemann, *Annu. Rev. Phys. Chem.*, **16**, 481 (1965).

(7) F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1968).

(8) Determined on a CEC 21-110B instrument, modified as previously described:[9] P_{CH_4}, 0.4 Torr; ion source temperatures, 120–150°; accelerating voltage, 8 kV; repeller field, 0–30 V/cm.

(9) I. Dzidic, D. M. Desiderio, M. S. Wilson, P. F. Crain, and J. A. McCloskey, *Anal. Chem.*, in press.

(10) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 2621 (1966).

(11) K. Biemann, "Mass Spectrometry," McGraw-Hill, New York, N. Y., 1962, p 87.

(12) F. H. Field, *J. Amer. Chem. Soc.*, **92**, 2672 (1970).

(13) M. S. B. Munson, *ibid.*, **87**, 5313 (1965).

(14) This similarity was first pointed out to us in the case of electron ionization spectra of α,ω-bis(trimethylsilyl) ethers, by Dr. F. H. Field (personal communication, Jan 1970).

(15) Compounds **3a**, **3b**, and **3c** were introduced by direct probe, at ion source temperatures of 180, 220, and 250°, respectively.