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(15) Postdoctoral research associate, 1968–1971.

R. B. King,* A. Efraty[15]
Department of Chemistry, University of Georgia
Athens, Georgia 30601
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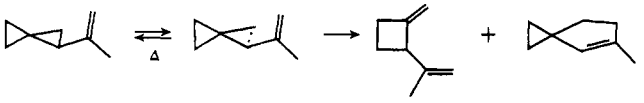
Stereochemistry of and Alteration in the Mechanism of the Spiropentane to Methylenecyclobutane Thermal Rearrangement by Polar Substituents

Sir:

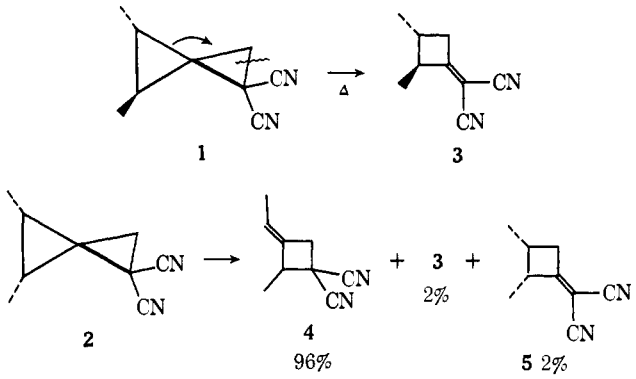
The thermal rearrangement of isopropenylspiropentanes to methylenecyclobutanes and spiro[2.4]hept-4-enes has been shown to proceed by initial reversible 1,2 (peripheral) bond fission followed by a vicinal alkyl shift to give the cyclobutanes.[1]

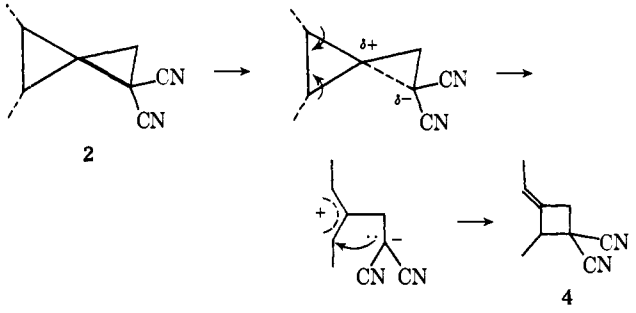


In an effort to examine the stereochemistry of the alkyl shift in a polarized diradical, *trans*- and *anti-cis*-dimethyl-1,1-dicyanospiropentane, **1** and **2**, respectively,[2] were prepared by addition of dicyanocarbene[3] to *trans*- and *cis*-2,3-dimethylmethylenecyclopropane, respectively.[4] Only one trans compound is possible (as an enantiomeric pair), but only one of the two possible cis compounds, presumably the anti material, was formed, possibly because of the steric effects.

Pyrolysis of **1** at 170° in the vapor phase or in benzene in sealed tubes gave a single product whose pmr was consistent with that of *trans*-2,3-dimethyldicyanomethylenecyclobutane (**3**).[5] This material can be formed by cleavage of what must be one of the weakest bonds in the system, namely, the 1,2 bond, followed by an alkyl shift with retention of stereochemistry of the migrating group.

However, when **2** was pyrolyzed under the same conditions, the major product was of an entirely different type, namely, 2-methyl-3-ethylidene-1,1-dicyanocyclobutane (**4**). There are two stereoisomers of **4**, syn and anti. Both were formed as a 1:1 mixture by cycloaddition of ethylidene malononitrile[6] to methylallene, and these were separated; in addition, two other compounds were formed in this cycloaddition whose pmr spectra were consistent with the *trans*- and *cis*-2,4-dimethyl-3-methylene-1,1-dicyanocyclobutanes. Significantly, only one of the isomers of **4** was produced upon pyrolysis of **2**. Pmr[7] would not allow assignment of stereochemistry although the ^{13}Cmr[8] could be interpreted in terms of the anti stereochemistry for the major rearrangement product from **2**. The pathway for formation of **4** from **2** is, most likely, initial fission of the 1,3 (radial) bond followed by fission of the 4,5 bond and recombination. Because of the high stereospecificity of this reaction, there is the suggestion that it resembles the cyclopropyl to allyl cation rearrangement *via* the appropriate disrotatory motions,[9] thus





Consistent with this interpretation is the direction of rotation of the methyl groups of the cyclopropane ring relative to the departing group[9] and the fact that the rearrangement is at least a factor of ten faster in acetonitrile as in benzene. However, the reaction of **1** to **3** was also dramatically faster in acetonitrile.

Also formed in the pyrolysis of **2** in the vapor phase were two minor products in a 1:1 ratio, representing no more than 4% of the total product. One of these was identical with **3** by nmr and vpc while the other had an nmr consistent with that of *cis*-2,3-dimethyldicyanomethylenecyclobutane (**5**).[10] The 3:5 ratio was

(1) J. J. Gajewski, *J. Amer. Chem. Soc.*, **92**, 3688 (1970).

(2) Both starting materials were collected by vpc and had *m/e* 146.085, calcd for $C_9H_{10}N_2$, 146.0844; nmr of **1** (220 MHz) multiplet with a symmetry plane from δ 1.10 to 1.4 (8 H), singlet at 2.05 (2 H); nmr of **2** (220 MHz) doublet at δ 1.11 (6 H, J = 6 Hz), symmetrical multiplet at 1.76 (2 H), singlet at 1.95 (2 H).

(3) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 1979 (1966).

(4) J. J. Gajewski, *ibid.*, 90, 7178 (1968).

(5) The pmr of **3** (220 MHz) showed: doublet at δ 1.26 (3 H, J = 7 Hz), doublet at 1.37 (3 H, J = 7 Hz), five-line multiplet with 7-Hz separation of lines at 2.14 (1 H), doublet of doublets at 2.60 (1 H, J = 18, 7 Hz), multiplet at 2.91 (1 H), and doublet of doublet of doublets at 3.22 (1 H, J = 18, 8, and 4 Hz); nominal mass 146. For reference, the pmr of *trans*-2,3-dimethylcyclobutanone (220 MHz) showed: doublet at δ 1.12 (3 H, J = 7 Hz), doublet at 1.34 (3 H, J = 7 Hz), five-line multiplet at 1.96 (1 H), doublet of doublet of doublets at 2.58 (1 H, J = 2, 8, and 17 Hz), multiplet at 2.79 (1 H), and doublet of doublet of doublets at 2.98 (1 H, J = 2, 8, and 16 Hz).

(6) Farbenfabriken Bayer Akt-Ges. British Patent 812,240 (1959); *Chem. Abstr.*, **53**, 15,648 (1959).

(7) Pmr of *anti*-**4** (220 MHz) showed: doublet at δ 1.42 (3 H, J = 7 Hz), doublet of quartets at 1.58 (3 H, J = 7 and 2 Hz), broad singlet at 3.34 (2 H), multiplet at 3.64 (1 H), and multiplet at 5.41 (1 H); nominal mass 146. Pmr of *syn*-**4** (220 MHz) showed: doublet at δ 1.53 (3 H, J = 7 Hz), doublet of quartets at 1.62 (3 H, J = 7 and 2 Hz), broad singlet at 3.30 (2 H), multiplet at 3.69 (1 H), and multiplet at 5.37 (1 H); nominal mass 146.

(8) The ring methylene carbon in the anti compound was at 154.7 ppm (relative to CS_2) while in the syn compound it occurred at 153.3 ppm. The ring methine carbon in the anti compound was at 144.4 ppm while in the syn compound it occurred at 145.0 ppm. The shielding effect of a γ substituent (the allylic methyl) appears to give rise to these shifts; B. V. Cheney and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 5319 (1967).

(9) (a) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *ibid.*, **87**, 4006 (1965); (b) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **87**, 4007 (1965); (c) P. von R. Schleyer, G. W. Van Dine, V. Schöllkopf, and J. Paust, *ibid.*, **88**, 2868 (1966).

(10) Pmr of **5** (220 MHz) showed: doublet at δ 1.15 (3 H, J = 7 Hz), doublet at 1.34 (3 H, J = 7 Hz), multiplet at 2.65 (2 H), multiplet at 3.25 (1 H), and multiplet at 3.50 (1 H). For reference, the pmr of

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.

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).

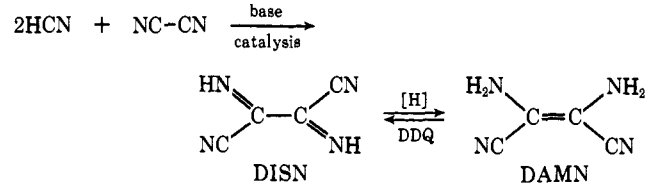
(12) Fellow of the Alfred P. Sloan Foundation, 1971–1973.

Joseph J. Gajewski,*[12] Leo T. Burka
Contribution No. 1982
Department of Chemistry, Indiana University
Bloomington, Indiana 47401
Received May 17, 1971

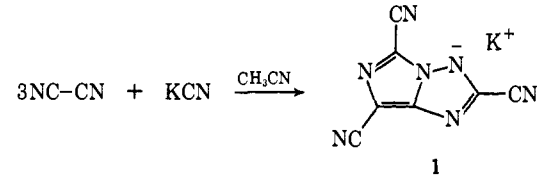
Hydrogen Cyanide Chemistry. I. Diiminosuccinonitrile

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, tri-



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ethylamine 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).

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 ΔF° = 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.

(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.