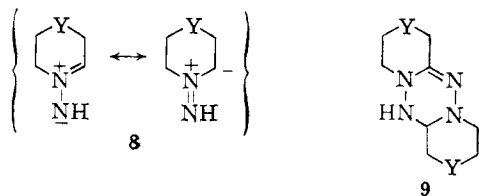


and hydrochloric acid into at least three compounds: the tetrazenes **6**, their tricyclic isomers **7**, and dehydro derivatives of **7** (**9**).¹⁰ In an experiment not designed



to optimize yields, morpholine gave 34% of **6**, 10% of **7**, and 6% of **9**.

Thus a comparison of the two series of reactions represented in Chart I allows little opportunity for doubt that diazenes are generated when Angeli's salt acts upon secondary amines in the presence of acids. Whether or not the unstable nitroxyl (HNO), a known decomposition product of Angeli's salt,¹¹ is the attacking species is not yet entirely clear. This and other aspects of the reaction will be investigated further in our laboratory.

Acknowledgment. The authors wish to express their gratitude to Dr. Ray S. Dewey (Merck Sharp and Dohme), who first acquainted them with Angeli's work on amines. They are indebted also to Mr. Richard W. Harrington for skillful technical assistance and to the National Science Foundation and the National Institutes of Health for financial support.

(10) At the turn of the century A. Angeli discovered that sodium nitrohydroxylamate transformed secondary aliphatic amines, and piperidine in particular, into the corresponding tetrazenes (A. Angeli, *Chem. Zentr.*, 71, II, 857 (1900)). Later he reported the isolation of three additional compounds from the reaction with piperidine: N-aminopiperidine and two crystalline substances which roughly corresponded in properties to **7** and **9** (Y = CH₂), but which he formulated incorrectly (A. Angeli and V. Castellana, *ibid.*, 76, I, 1260 (1905)). It is noteworthy that he considered the possibility of diazene intermediates at that time.

(11) Cf. P. A. S. Smith and G. E. Hein, *J. Am. Chem. Soc.*, 82, 5731 (1960), and references contained therein; J. Veprek-Siska, V. Pliska, F. Smirous, and F. Vesely, *Collection Czech. Chem. Commun.*, 24, 687 (1959).

(12) National Science Foundation Cooperative Fellow, 1963-1964.

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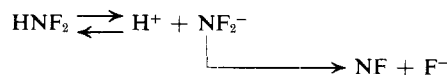
Evidence for the Difluoramide Anion

Sir:

Difluoramine, HNF₂, has been found to possess weak acid properties, and evidence has been obtained for the existence of the difluoramide anion, NF₂⁻. When HNF₂ became readily available by virtue of its direct synthesis,¹ an investigation of its dissociation was undertaken.

We have found the stability of HNF₂ in buffered aqueous solutions to decrease as pH or temperature increases, the principal decomposition products being N₂F₂ and N₂O. Furthermore, when the potentiometric titration of aqueous HNF₂ solutions with aqueous base was stopped short of the end point, the potentials drifted to lower pH. These results are consistent with the dissociation of HNF₂ and then relatively slow decomposition of the resulting anion.

(1) J. P. Freeman, A. Kennedy, and C. B. Colburn, *J. Am. Chem. Soc.*, 82, 5304 (1960).



The fluorazene formed in the anion decomposition would be the precursor of the N₂F₂ and N₂O isolated. Also, the postulated fluorazene has been shown to be the probable reactant in deamination reactions of difluoramine,² as well as a decomposition product of the electronically excited difluoramino free radical.³

Additional evidence for the difluoramide anion and its relative instability was provided by polarographic data. Difluoramine in aqueous solution undergoes a four-electron reduction at mercury electrodes at potentials more cathodic than -1.0 v. vs. s.c.e. It was expected that the reduction of NF₂⁻ would only occur at potentials beyond solvent reduction, while the reduction potential for undissociated HNF₂ was accurately predicted from a correlation of reduction potential with structure⁴ for a large number of difluoramino compounds. When base was added, the difluoramine reduction wave diminished and finally disappeared when base was in excess. If the solution was re-acidified rapidly, the wave reappeared but the diffusion current was somewhat diminished, the decrease in diffusion current being proportional to the time the solution stood before re-acidification.

A conductometric study of the dissociation of HNF₂ was carried out under carefully controlled conditions, but the results were inconclusive, since the data could also be explained by decomposition of less than 1% of the HNF₂ to fluoride. However, when conductometric titrations of aqueous HNF₂ solutions with NH₄OH solutions were performed rapidly, a distinct equivalence point was observed.

Finally, it was determined that aqueous solutions of difluoramine can be oxidized easily both electrochemically and chemically. The electrooxidation at a rotating platinum working electrode was observed in this laboratory as early as June 1961, and is a one-electron process. The homogeneous oxidation with ferric ion yielded tetrafluorohydrazine, N₂F₄, of high purity. The rate of the oxidation with ferric ion decreased rapidly with decreasing pH, which supports the proposal that NF₂⁻ rather than undissociated HNF₂ is the species being oxidized. It is interesting to note that although N₂F₄ has been prepared by a number of methods,⁵ each of the published processes suffers from one or more of the disadvantages of low yield, difficultly separated product mixtures, or high temperature requirement. In addition to the simplicity and high purity of product obtained, the oxidation of NF₂⁻ is made even more attractive for the production of N₂F₄ by the relatively easy preparation of HNF₂ by aqueous fluorination of urea.⁶

Caution is advised in working with these compounds.

(2) C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *ibid.*, 85, 97 (1963).

(3) C. L. Bumgardner and M. Lustig, *Inorg. Chem.*, 2, 662 (1963).

(4) K. J. Martin, unpublished data.

(5) C. B. Colburn and A. Kennedy, *J. Am. Chem. Soc.*, 80, 5004 (1958); R. D. Dresdner, F. N. Tlumac, and J. A. Young, *J. Inorg. Nucl. Chem.*, 14, 299 (1960); *Chem. Eng. News*, 38, 85 (1960); J. W. Frazer, *J. Inorg. Nucl. Chem.*, 11, 166 (1959); S. I. Morrow, D. D. Perry, M. S. Cohen, and C. Schoenfelder, *J. Am. Chem. Soc.*, 82, 5301 (1960); E. A. Lawton and J. Q. Weber, *ibid.*, 81, 4755 (1959).

(6) E. A. Lawton, E. F. C. Cain, D. F. Sheehan, and M. Warner, *J. Inorg. Nucl. Chem.*, 17, 188 (1961); V. Grakauskas, Abstracts of 140th National Meeting of the American Society, Chicago, Ill., 1961.

N_2F_4 explodes on contact with air and combustible vapors, and HNF_2 has been known to explode on warming from temperatures below the melting point.

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Kenneth J. Martin

Rohm & Haas Company

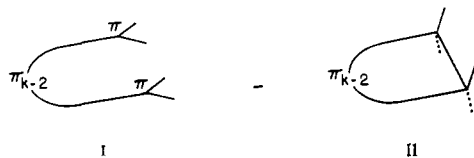
Redstone Arsenal Research Division, Huntsville, Alabama

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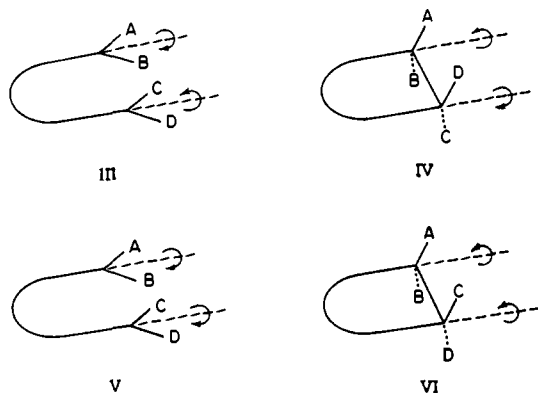
Stereochemistry of Electrocyclic Reactions

Sir:

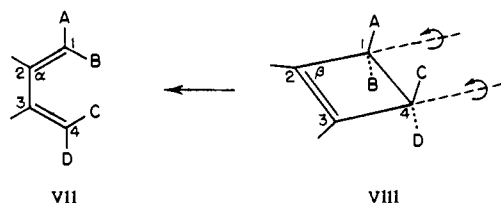
We define as *electrocyclic* transformations the formation of a single bond between the termini of a linear system containing k π -electrons ($I \rightarrow II$), and the



converse process. In such changes, fixed geometrical isomerism imposed upon the open-chain system is related to rigid tetrahedral isomerism in the cyclic array. *A priori*, this relationship might be *disrotatory* ($III \rightarrow IV$ or *vice versa*), or *conrotatory* ($V \rightarrow VI$, or

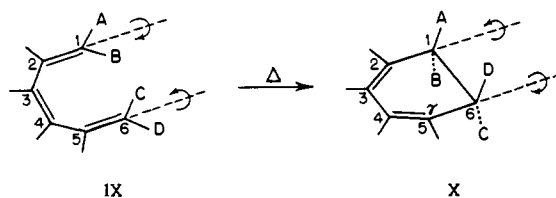


vice versa). In practice, transformations of this type have been brought about thermally, or photochemically, and *all known cases proceed in a highly stereospecific manner*. For example, the thermal isomerization of cyclobutenes is cleanly *conrotatory* ($VII \leftarrow VIII$).¹

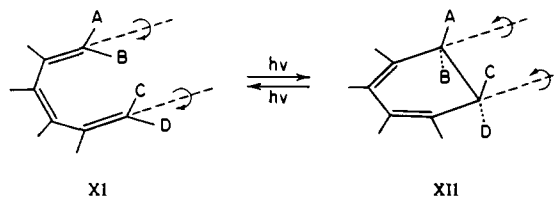


By contrast, the thermal cyclization of hexatrienes is uniquely *disrotatory* ($IX \rightarrow X$)²; this case is the more

(1) *cis*-3,4-Dicarbomethoxycyclobut-1-ene: E. Vogel, *Ann.*, **615**, 14 (1958). *cis*- and *trans*-1,2,3,4-tetramethylcyclobut-1-enes: R. Criegee and K. Noll, *ibid.*, **627**, 1 (1959). W. Adam [*Chem Ber*, **97**, 1811 (1964)] describes several cases and cites others which proceed stereospecifically, but whose products are of as yet undetermined configuration.

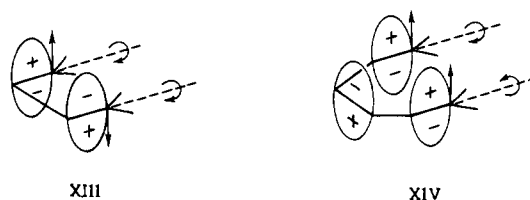


striking in view of the fact that factors of steric demand and angle strain clearly suggest that a *conrotatory* process should be followed.³ Finally, the stereospecific *conrotatory* process ($XI \rightarrow XII$) is observed when



hexatrienes are subjected to photochemical cyclization to cyclohexadienes, and *vice versa*.⁴

It is the purpose of this communication to suggest that the steric course of electrocyclic transformations is determined by the symmetry of the highest occupied molecular orbital of the open-chain partner in these changes.⁵ Thus, in an open-chain system containing $4n$ π -electrons, the symmetry of the highest occupied ground-state orbital is such that a bonding interaction between the termini *must involve overlap between orbital envelopes on opposite faces of the system*, and this can only be achieved in a *conrotatory* process (cf. XIII). Conversely, in open systems containing $4n + 2$ π -electrons, terminal bonding interaction within ground-state molecules *requires overlap of orbital envelopes on the same face of the system*, attainable only by *disrotatory* displacements (cf. XIV). On



the other hand, promotion of an electron to the first excited state leads to a reversal of terminal symmetry relationships in the orbitals mainly involved in bond redistribution, with the consequence that a system which undergoes a thermally induced *disrotatory*

(2) Precalciferol \rightarrow pyro- and isopyrociferols: E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, **16**, 146 (1961). *trans,cis,trans*-1,6-dimethylhexa-1,3,5-triene \rightarrow *cis*-1,2-dimethylcyclohexa-3,5-diene; *trans,cis,cis*-1,6-dimethylhexa-1,3,5-triene \rightarrow *trans*-1,2-dimethylcyclohexa-3,5-diene: E. Vogel, E. Marvell, private communications.

(3) Cf. K. E. Lewis and H. Steiner [*J. Chem. Soc.*, 3080 (1964)], who do not even consider the *disrotatory* course which is in fact very probably followed in the thermal cyclization of hexa-1-*cis*-3,5-triene itself.

(4) Precalciferol \rightleftharpoons ergosterol, tachysterol \rightarrow lumisterol \rightarrow precalciferol: E. Havinga, R. J. de Kock, and M. P. Rappoldt, *Tetrahedron*, **11**, 276 (1960); and E. Havinga and J. L. M. A. Schlatmann, ref. 2. *trans,cis,trans*-1,6-Dimethylhexa-1,3,5-triene \rightleftharpoons *trans*-1,2-dimethylcyclohexa-3,5-diene: G. J. Fonken, *Tetrahedron Letters*, 549 (1962).

(5) Professor L. J. Oosterhoff (Leiden) clearly deserves credit for having first put forward the suggestion that orbital symmetries might play a role in determining the course of the stereochemical phenomena attendant upon triene cyclizations (private communication to Professor Havinga, quoted in E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, **16**, 151 (1961)). The suggestion was described so succinctly that it has received no currency, and it has not been generalized to include other cases.