

$\text{N}_2\text{F}_4$  explodes on contact with air and combustible vapors, and  $\text{HNF}_2$  has been known to explode on warming from temperatures below the melting point.

**Acknowledgment.** This work was carried out under Army Ordnance Contract DA-01-021 ORD-11909, funded by the Advanced Research Projects Agency in 1960-1962.

Kenneth J. Martin

Rohm & Haas Company

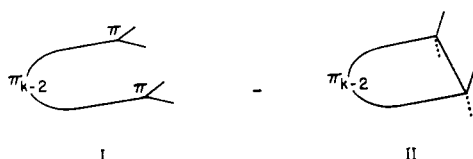
Redstone Arsenal Research Division, Huntsville, Alabama

Received November 2, 1964

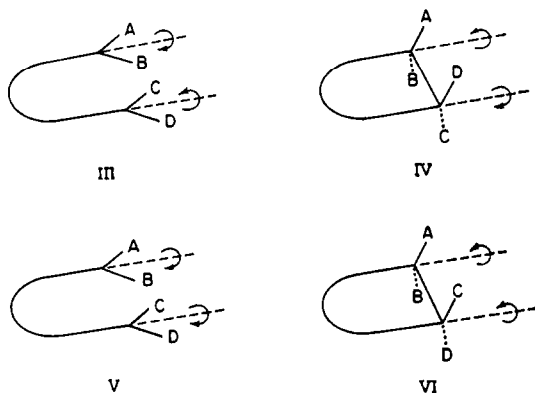
## Stereochemistry of Electrocyclic Reactions

Sir:

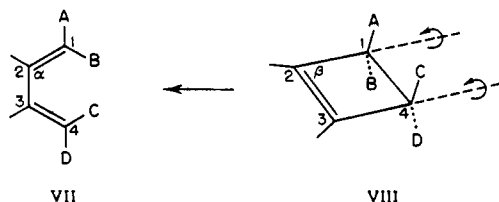
We define as *electrocyclic* transformations the formation of a single bond between the termini of a linear system containing  $k$   $\pi$ -electrons ( $\text{I} \rightarrow \text{II}$ ), and the



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* ( $\text{III} \rightarrow \text{IV}$  or *vice versa*), or *conrotatory* ( $\text{V} \rightarrow \text{VI}$ , or

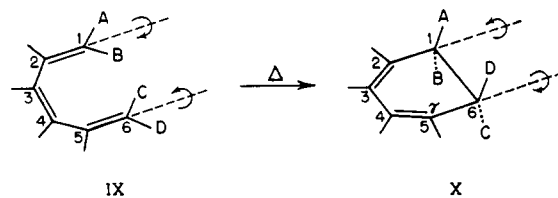


*vice versa*). In practice, transformations of this type have been brought about thermally, or photochemically, and all known cases proceed in a highly stereospecific manner. For example, the thermal isomerization of cyclobutenes is cleanly *conrotatory* ( $\text{VII} \leftarrow \text{VIII}$ ).<sup>1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

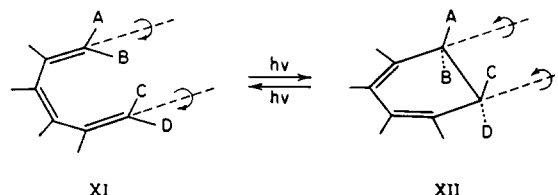


By contrast, the thermal cyclization of hexatrienes is uniquely *disrotatory* ( $\text{IX} \rightarrow \text{X}$ )<sup>2</sup>; this case is the more

(1) *cis*-3,4-Dicarbomethoxycyclobut-1-ene: E. Vogel, *Ann.*, **615**, 14 (1958). *cis*- and *trans*-1,2,3,4-tetramethylcyclobut-1-ene: 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.

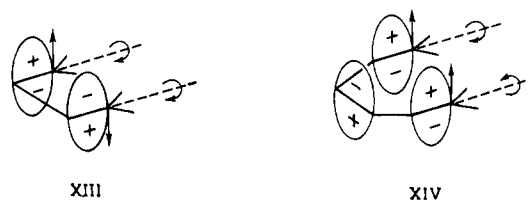


striking in view of the fact that factors of steric demand and angle strain clearly suggest that a conrotatory process should be followed.<sup>3</sup> Finally, the stereospecific *conrotatory* process ( $\text{XI} \rightarrow \text{XII}$ ) is observed when



hexatrienes are subjected to photochemical cyclization to cyclohexadienes, and *vice versa*.<sup>4</sup>

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.<sup>5</sup> Thus, in an open-chain system containing  $4n$   $\pi$ -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  $4n + 2$   $\pi$ -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.

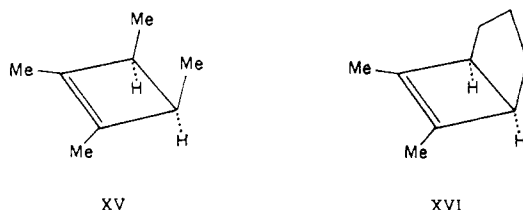
(3) Cf. K. E. Lewis and H. Steiner [*J. Chem. Soc.*, 3080 (1964)], who do not even consider the disrotatory course which is in fact very probably followed in the thermal cyclization of hexa-1-*cis*-3,5-triene itself.

(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.

electrocyclic transformation in the ground state should follow a conrotatory course when photochemically excited, and *vice versa*.<sup>6</sup>

It should be emphasized that our hypothesis specifies in any case which of two types of geometrical displacements will represent a favored process, but does not exclude the operation of the other under very energetic conditions. Thus, *cis*-1,2,3,4-tetramethylcyclobut-1-ene (XV) is smoothly transformed to



*cis*,*trans*-tetramethylbutadiene in a conrotatory process at 200°. In the dimethylbicyclo[0.2.3]heptene derivative (XVI), the presence of the five-membered ring makes a conrotatory process impossible, and the disrotatory opening is observed, but only slowly at 400°.<sup>7</sup>

Our hypothesis accommodates the known dramatic stereospecificities in electrocyclic reactions. It further permits clear predictions of the outcome in numerous interesting cases which have not yet been scrutinized. Some of these predictions are summarized in Table I; it may be noted specially that electrocyclic transformations within odd-electron systems should follow the same stereochemical course as the even-electron systems containing one further electron, and that charged systems should behave in the same manner as neutral systems containing the same number of electrons.

Table I

Predicted ground-state reactions	Type
Cyclopropyl cation $\rightarrow$ allyl cation	Disrotatory
Cyclopropyl radical $\rightarrow$ allyl radical	Conrotatory
Cyclopropyl anion $\rightarrow$ allyl anion	Conrotatory
Cyclopentenyl cation $\leftarrow$ pentadienyl cation	Conrotatory

The simple symmetry argument presented above is supported by our results in a study of several cases by the extended Hückel theory.<sup>8</sup> Although the energetic preferences revealed by these calculations cannot be associated entirely with single energy levels, the major directive factor for displacements within ground states arises from energy variations within the highest, doubly occupied molecular orbital, and in excited states within the two highest, partially occupied orbitals, of which the higher level is dominant.

In the study of the butadiene cyclization, the initial conformation was the planar, *s-cis* form VII, with  $d_{12} = d_{34} = 1.34$  Å.,  $d_{23} = 1.48$  Å.,  $d_{CH} = 1.10$  Å., and a range of values for the internal angles,  $\alpha$ . The

(6) The situation in photochemical reactions is of course subject to many complications which are absent in the thermal cases. The generalization suggested here will apply only to electrocyclic transformations which actually take place within an excited state, before energy degradation occurs, with transformation to a new geometry, or to a different state.

(7) R. Criegee and H. Furrer, *Chem. Ber.*, **97**, 2949 (1964).

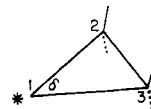
(8) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2480 (1964); identical parameters were used in this work.

terminal methylene groups were twisted in disrotatory and conrotatory modes through a range of angles, while retaining their trigonal conformation. This calculation indicated that in the ground state, for  $\alpha \geq 117^\circ$ , the disrotatory displacement was slightly favored.<sup>9</sup> However, in the disrotatory motion the 1,4 bond order becomes more negative as twisting increases, while in the conrotatory mode a positive bond order develops. As  $\alpha$  was decreased a sharply increasing preference for the conrotatory mode was found. In the first excited state these relationships are precisely reversed.

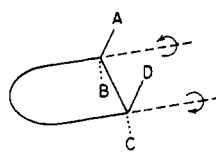
Approaching the transition state for a  $k = 4$  case from the cyclic form, a model cyclobutene geometry (VIII) with  $d_{23} = 1.34$  Å.,  $d_{12} = d_{34} = d_{14} = 1.54$  Å.,  $\beta = 93.7^\circ$ , was chosen. Hydrogen atoms at C-1 and C-4 were so placed that the C-H bonds formed tetrahedral angles with each other, and with C-1-C-2 or C-3-C-4. Disrotatory and conrotatory modes of twisting, retaining tetrahedral hydrogen dispositions, were studied as a function of  $\beta$ . There was a clear preference for conrotatory twisting in the ground state, disrotatory motion in the first excited state. In this case the preferred ground-state conrotatory process was associated with a much more rapidly decreasing 1,4 overlap population.

For the study of the hexatriene-cyclohexadiene transformations, it was decided to approach the transition states from the cyclic side, since the initial geometry of the hexatriene partner cannot be specified easily. A model geometry (X) was chosen, with  $d_{34} = 1.48$  Å.,  $d_{45} = d_{23} = 1.34$  Å.,  $d_{12} = d_{16} = d_{56} = 1.54$  Å. A slightly unrealistic simplification was made in assuming coplanarity of the six carbon atoms. Disrotatory and conrotatory processes were examined in the above geometry, as well as for one with  $\gamma = 150^\circ$  ( $d_{16} = 2.42$  Å.). In both cases it was found that the disrotatory mode was favored in the ground state, while the conrotatory process was preferred in the first excited state.

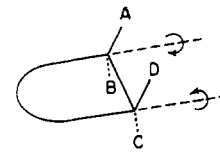
In the case of the cyclopropyl-allyl transformations, the contrasting twisting motions were considered in an intermediate geometry (XVII) with tetrahedral hydrogen



XVII



XVIII

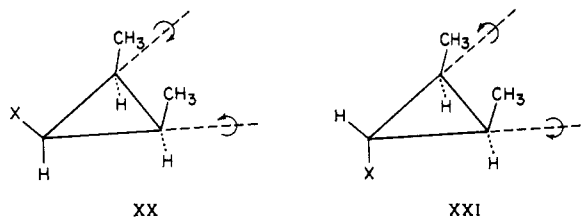


XIX

atoms, and  $d_{12} = d_{13} = 1.50$  Å.,  $\delta = 90^\circ$ . The disrotatory process was found to be favored in the ground state of the cation, the conrotatory mode in the radical or anion.

(9) For large values of  $\alpha$ , the 1,4-interaction is minimal, and the energetically decisive factor is the extent to which the  $\pi$ -system is uncoupled by a given rotation; the conrotatory motion uncouples the  $\pi$ -orbitals considerably more than the disrotatory mode.

Except in cases possessing special symmetry axes, two alternative conrotatory or disrotatory processes are possible and physically differentiable (*cf.* XVIII and XIX). Ordinarily, simple steric factors will be expected to direct the changes preferentially along one of the two paths, but in some cases, very interesting special stereoelectronic factors may be definitive. Thus, when a cyclopropyl cation is produced by ionization of a group X, and suffers concerted electrocyclic transformation to an allyl cation, our calculations indicate that the favored processes are XX and XXI.



(10) Junior Fellow, Society of Fellows, Harvard University.

R. B. Woodward, Roald Hoffmann<sup>10</sup>

Department of Chemistry, Harvard University  
Cambridge, Massachusetts 02138

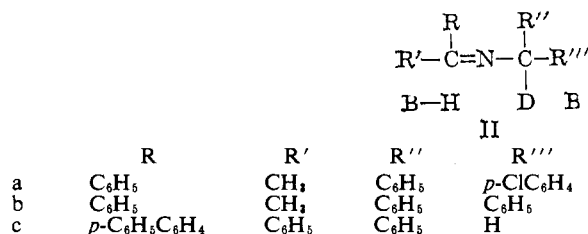
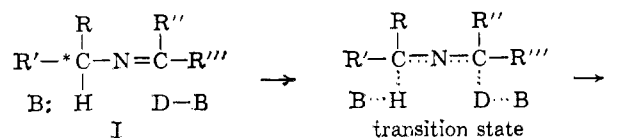
Received November 30, 1964

## On the Claim of a Bimolecular Mechanism of Prototropy

Sir:

The claim of a "bimolecular mechanism of prototropy" was based on an identity of values for the initial rate constants for  $k_i$  (isomerization),  $k_e$  (isotopic exchange), and  $k_a$  (loss of optical activity) for ethoxide ion catalyzed conversion of I to II in solvents such as 2:1 dioxane-ethanol-O-*d* or ethanol-O-*d*.<sup>1</sup>

Bimolecular (one-stage) mechanism of prototropy

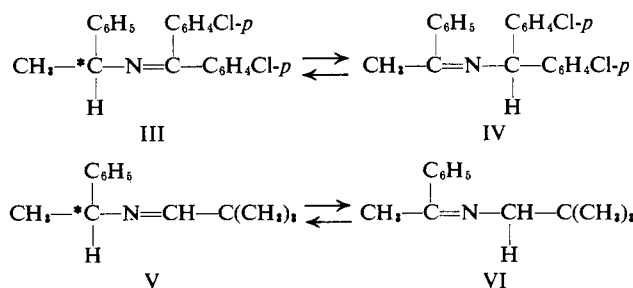


The discovery of an intramolecular component in the base-catalyzed rearrangement of 3-phenyl-1-butene to *cis*- and *trans*-3-phenyl-2-butene,<sup>2</sup> coupled with the fact that the rearrangement competes with simple isotopic exchange,<sup>2b</sup> led us to re-examine the evidence for a one-stage mechanism in the similar methylene-azomethine rearrangement.<sup>3</sup> Interconversions of III

(1) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 572; (b) C. K. Ingold and C. L. Wilson, *J. Chem. Soc.*, 1493 (1933); (c) C. K. Ingold and C. L. Wilson, *ibid.*, 93 (1934); (d) S. K. Hsu, C. K. Ingold, and C. L. Wilson, *ibid.*, 1774 (1935); (e) R. P. Ossorio and E. D. Hughes, *ibid.*, 426 (1952).

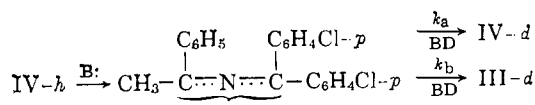
(2) (a) D. J. Cram and R. T. Uyeda, *J. Am. Chem. Soc.*, **84**, 4358 (1962); (b) D. J. Cram and R. T. Uyeda, *ibid.*, **86**, 5466 (1964).

and IV and of V and VI were investigated.<sup>4</sup> Values of 1.2 for  $k_{eq}(IV/III)$  and of 14.9 for  $K_{eq}(VI/V)$  were obtained at 100°.



Optically active III was allowed to undergo about 8% isomerization to IV as a 0.18 *M* solution in 1:1 dioxane-ethylene glycol-O-*d*, 0.22 *N* in potassium glycoxide at 100°. The amount of product present was determined by an n.m.r. technique with an added internal standard. The mixture was hydrolyzed, and the  $\alpha$ -phenylethylamine (isolated by v.p.c.) had undergone  $2.8 \pm 2\%$  racemization and no isotopic exchange (n.m.r. with an internal standard). These observations are compatible with  $k_i = k_a = k_e$  for III  $\rightarrow$  IV.

After a 0.17 *M* solution of IV in a 1:1 dioxane-ethylene glycol-O-*d* mixture (0.22 *M* in potassium glycoxide) at 100° was about 10% isomerized, the methyl and benzhydryl hydrogens of the starting material (n.m.r.) were >95% exchanged ( $k_e \gg k_i$ ). After a 0.26 *M* solution of IV in *t*-butyl alcohol-O-*d* (0.0782 *N* in potassium *t*-butoxide) at 75° was  $2.5 \pm 0.1\%$  isomerized (hydrolysis and v.p.c. with internal standard), the starting material was 38.2% exchanged at the benzhydryl (combustion and falling drop method), and  $68 \pm 4\%$  (of 3 protons) exchanged at the methyl position (n.m.r.). If  $k_e'$  is the rate constant for isotopic exchange of IV at the benzhydryl position, then  $k_e'/k_i \sim 19$ . This value approximates the ratio of rate constants for collapse of a carbanion intermediate in *t*-butyl alcohol to give IV and III, respectively ( $k_a/k_b$ ). The results of the run made in dioxane-ethylene glycol indicate that  $k_e'/k_i > 10$  in this solvent as well.



The high values of this collapse ratio indicate why the rate constants  $k_i$ ,  $k_a$ , and  $k_e$  were equal for III  $\rightarrow$  IV in spite of the fact that a carbanion intervened as an intermediate. Compound III structurally resembles Ia, and dioxane-ethylene glycol-glycoxide is similar to dioxane-ethanol-ethoxide. We conclude that carbanions intervened as intermediates in the conversions of I to II, and that the observed equalities of  $k_i$  and  $k_a$ , and of  $k_i$ ,  $k_a$ , and  $k_e$  of the previous work, reflect a carbanion collapse ratio that strongly favored product, as in the conversion of III  $\rightarrow$  IV.

A 0.305 *M* solution of optically active V in *t*-butyl alcohol-O-*d*, 0.441 *M* in potassium *t*-butoxide at 75°,

(3) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research Grant No. AF-AFOSR-124-63.

(4) Carbon and hydrogen analyses for all new compounds gave values within 0.3% of theory, and the physical properties of known compounds checked literature values.