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# Electrical Discharge Mechanisms. Stereochemistry of Electrocyclic Reactions of *cis*- and *trans*-1,2,3,4-Tetramethylcyclobutene and *cis,cis,cis*-, *cis,cis,trans*-, and *trans,cis,trans*-2,4,6-Octatriene. Hot Ground States as Probable Reactive Species[1]

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**Abstract:** The electrical discharge reactions of *cis*- and *trans*-1,2,3,4-tetramethylcyclobutene, *cis,cis,cis*-, *trans,cis,trans*-, and *cis,cis,trans*-2,4,6-octatriene, and *trans*-5,6-dimethylcyclohexadiene were studied, the products being isolated and identified for comparison with products formed in thermal and photochemical electrocyclic reactions. The major liquid products from the cyclobutenes were *cis,trans*-3,4-dimethyl-2,4-hexadiene (27%) and *trans,trans*-3,4-dimethyl-2,4-hexadiene (53%), respectively. The electrocyclic product from 99% isomerically pure *cis,cis,trans*-2,4,6-octatriene was *trans*-5,6-dimethyl-1,3-cyclohexadiene (5.4%), and studies of isomeric mixtures established that the other isomers give *cis*-5,6-dimethyl-1,3-cyclohexadiene. The products are the same as the products of thermal electrocyclic ring opening, and the reactions occur with essentially complete stereospecificity. Orbital-symmetry correlations and experimental analogies appear to rule out electronically excited molecules, as well as ground-state and excited-state molecular cations and anions, and to suggest that electrocyclic reactions in the electrical discharge proceed from vibrationally excited, but thermally nonequilibrated, ground states of the neutral molecules.

Although the reaction of an organic molecule in an electrical discharge typically leads to a complex mixture of products,[2] including a considerable quantity of one, two, and three carbon fragments, various rather specific reactions can occur. Under high-energy conditions, whether thermal, photochemical, or electron impact (mass spectrum or electrical discharge), entropy control—favoring smaller molecules through the resulting increase in translational degrees of freedom—drains off reactant molecules in fragmentations. However, the mechanistic pathways for the specific electrical discharge reactions are conceptually very interesting, because they are caused by electron impact, an energy source different from the more widely studied and understood sources, heat and light.

Since the stereochemistry of many reactions is controlled by orbital-symmetry effects,[3] it appeared that a search for stereochemical specificity in electrocyclic reactions, which have been studied under thermal and photochemical reaction conditions, would, if successful, be a valuable tool. Applying symmetry considerations, we could predict the stereochemistry of our reactions for the set of mechanistic possibilities (electronically excited and vibrationally excited neutral molecules, and molecular cations and anions) and then rule out those which disagreed with the observed stereochemistry. While such evidence would apply only to the electrocyclic component of the reaction(s) investigated, it might begin to provide a key to the elusive mechanistic features of electrical discharge and related electron-impact reactions.[4-11]

In addition to its present application to the production of ozone, direct industrial use of electrical energy for chemical transformations is being explored, both for possible commercial value and for possible conservation of fossil fuels as environmentally acceptable alternative sources of electricity are developed.[12] Studies of reaction pathways and intermediates may provide useful guidelines for such developments as well.

In view of the extensive recent investigations on thermolysis[13] and photolysis[14] of derivatives of cyclobutene, conjugated acyclic dienes, cyclohexadiene, and conjugated acyclic trienes, we examined the products of the electrocyclic reactions of *cis*- and *trans*-1,2,3,4-tetramethylcyclobutene, *cis*- and *trans*-5,6-dimethyl-1,3-cyclohexadiene, and *cis,cis,cis*-, *cis,cis,trans*-, and *trans,cis,trans*-2,4,6-octatriene in an ac electrical discharge, using platinum electrodes in a flow system, and quenching the products on a liquid nitrogen-filled cold finger placed 9 cm from the second electrode. We found substantial yields of electrocyclic ring-opening products in the case of the cyclobutenes, and they were formed with complete stereospecificity in the conrotatory mode. The cyclohexadienes did not undergo electrocyclic ring opening, but the octatrienes gave substantial amounts of ring-closure products (cyclohexadienes), and these were formed with complete stereospecificity in the disrotatory mode.

These results agree with experiment for thermal rearrangements, do not agree with experiment for photochemical rearrangements, and thus rule out a photochemical analogy for electrical discharge in this case. Thermocouple measurements lead us to believe that the electrical discharge is not hot enough (translationally) to account for the results by a simple pyrolysis mechanism. We present arguments which make reaction through molecular cations or anions appear unlikely and conclude that the most reasonable interpretation involves reaction through vibrationally excited electronic ground states.

Table I. Observed Yields from Electrical Discharge Reactions of *cis-* and *trans*-1,2,3,4-Tetramethylcyclobutene[a]

| | Cis reactant | | Trans reactant | |
|---|---|---|---|---|
| Product | % | SD | % | SD |
| Gaseous products | | | | |
| Ethane | 28.5 | 4.7 | 34.4 | 5.8 |
| Acetylene | 16.5 | 2.5 | 10.6 | 2.4 |
| Propane | 6.5 | 0.2 | 5.2 | 0.1 |
| Propene | 2.4 | 0.3 | 2.47 | 0.13 |
| Allene | 7.0 | 0.5 | 7.1 | 0.3 |
| Propyne | 2.47 | 0.05 | 2.28 | 0.25 |
| 1-Butene | 1.83 | 0.11 | 2.24 | 0.44 |
| Isobutene | | | 2.38 | 0.59 |
| 1,3-Butadiene | 4.43 | 0.24 | 5.29 | 0.89 |
| 1-Butyne | 2.42 | 0.17 | 3.11 | 0.22 |
| 1-Buten-3-yne | 3.40 | 0.15 | 4.10 | 0.32 |
| 2-Methyl-1-butene | 1.81 | 0.11 | 1.56 | 0.08 |
| 2-Butyne | 2.40 | 0.11 | 2.76 | 0.52 |
| 1-Pentyne | 5.55 | 0.35 | 6.41 | 0.57 |
| Miscellaneous[b] | 13.06 | 1.44 | 9.66 | 0.45 |
| Liquid products | | | | |
| *cis*-1,2,3,4-Tetramethylcyclobutene | 50.3 | 1.7 | | |
| *trans*-1,2,3,4-Tetramethylcyclobutene | | | 21.2 | 1.3 |
| *trans,trans*-3.4-Dimethyl-2,4-hexadiene | <0.2[c] | | 53.0 | 1.8 |
| *cis,trans*-3,4-Dimethyl-2,4-hexadiene | 26.8 | 0.2 | <0.2[c] | |
| *cis,cis*-3,4-Dimethyl-2,4-hexadiene | <0.2[c] | | <0.2[c] | |
| Benzene | 1.68 | 0.22 | 1.71 | 0.12 |
| 2,4-Dimethyl-1,3-pentadiene | 2.1 | 0.1 | 4.07 | 0.18 |
| Toluene | 1.57 | 0.09 | 1.03 | 0.06 |
| Miscellaneous[b] | 17.8 | 0.9 | 19.0 | 1.3 |

[a] >99% purity. Flow rates, $4.81 \times 10^{-4}$ and $5.1 \times 10^{-4}$ mol/min for cis and trans reactants, respectively. Pressure of discharge system, 0.4 mm. Temperature of electrodes, 170–200°. Potential drop across electrodes, 615 V; current, 30 mA. Product percentages are uncorrected gas-chromatogram peak areas; standard deviations (SD) are also given. [b] Sum of all unidentified products. [c] Estimated upper limits of these undetected products.

## Results

The products and yields of the electrical discharge reactions studied are given in Tables I and II. Results shown are mean yields and standard deviations for three discharge experiments for each reactant. It will be noted that the electrocyclic reactions proceed with essentially complete stereospecificity, the tetramethylcyclobutenes giving dimethylhexadienes by electrocyclic ring opening, and the octatrienes giving dimethylcyclohexadienes by electrocyclic ring closure.

The electrical discharge reaction of 99% pure *cis,cis,-trans*-2,4,6-octatriene gives only *trans*-5,6-dimethyl-1,3-cyclohexadiene; cis product could not be detected. A graph of mole fraction of *cis*-5,6-dimethyl-1,3-cyclohexadiene product vs. mole fraction of *cis,cis,cis-* plus *trans,cis,trans*-2,4,6-octatriene reactants is linear and passes very close to the origin. This line can be extrapolated to a mole fraction of 1.04 of *cis*-5,6-dimethyl-1,3-cyclohexadiene for a mixture consisting of only cis,cis,cis and trans,cis,trans reactants. Therefore, the electrocyclic ring closure of these latter reactants proceeds to give essentially stereospecific formation of cis product within experimental error.

Recovery of cis,cis,trans reactant is considerably lower than the sum of recovery of reactants in mixtures (Table II). This phenomenon may represent some type of energy transfer and preferential formation of benzene and toluene from this isomer. However, the ratios of recovered trienes are similar to the starting ratios, and the yields of electrocyclic ring-closure products are close to 6% for all four mixtures. These facts, together with the demonstration of stereospecificity for formation of both cis and trans products from different reactant isomers, show that the stereospecificities are real and are not perturbed by the presence of mixtures of reactants. It was not possible by reasonable procedures to enrich the octatriene mixture to better than 50.5% trans,cis,trans.

The stereospecificities are those found for thermal reactions of the reactants. The electrocyclic components of these reactions might therefore be proceeding by simple thermal processes, or they might be proceeding by some other mechanism more specifically associated with the electrical discharge. Thermolysis seemed relatively unlikely in this rapidly flowing, liquid nitrogen-quenched system, so two tests were carried out, ozonizer and thermolysis experiments.

**Ozonizer Experiments.** When *cis*-1,2,3,4-tetramethylcyclobutene was passed through an electrodeless (actually glass electrodes) discharge cell similar to an ozonizer under the same conditions employed for the platinum electrode discharge run, 1.86 ± 0.14% of *cis,trans*-3,4-dimethyl-2,4-hexadiene was detected on GLC, but no trans,trans isomer. Similar experiments with trans reactant gave 2.25 ± 0.18% of trans,trans product but no cis,trans isomer. At steady state during the discharge run, the temperature of the glass electrode was only 30°. Many other products were also detected on GLC but were not quantitated. These results show that the same stereospecific mode of reaction occurs in a cooler, highly diffuse discharge as in the platinum electrode system.

**Thermolysis Experiments.** At steady state, the temperature of the discharge gases was measured by use of a narrow thermocouple well formed in the discharge cell directly adjacent to the second electrode. The thermocouple was sealed in place with Apiezon Q wax, and the platinum electrode was attached to the thermocouple well with copper wire.

The temperatures thus measured, 170-200°, were much too low to account for electrocyclic product through simple thermal reaction, given the residence times of only a few hundreths of a second.

The electrical discharge cell was wrapped with electrical heating tape, and *trans*-1,2,3,4-tetramethylcyclobutene[15] was passed through under the same conditions as those of the electrical discharge experiments, except that no voltage was placed across the electrodes. The heating tape voltage was adjusted to produce various temperature readings on the thermocouple (in its well near the center of the tube). There was no detectable amount of thermal isomerization product on GLC at 250 and 320°, but 0.42% of *trans,trans*-3,4-dimethyl-2,4-hexadiene was detected at 350°, 4.7% at 400°.

Calculated amounts of thermolysis at various temperatures for each reactant are given in Table III. The extent of reaction calculated in this way is considerably larger than observed with the heating-tape wrapped discharge cell, presumably because full temperature equilibration was not attained in the vapor passing through the hot cell.

The essential point appears to be demonstrated, however; both the thermolysis and ozonizer experiments indicate that ordinary thermolysis accounts for a negligible amount of the observed electrocyclic reaction products.

Thermolysis of *trans*-5,6-dimethyl-1,3-cyclohexadiene (with a trace of hydroquinone) in a sealed Pyrex glass tube was carried out in an oil bath at 200° for 90 hr, but no 2,4,6-octatriene isomers were detected on GLC, the substance having isomerized to 1,6-dimethyl-1,3-cyclohexadiene, as reported by Marvell, Caple, and Schatz.[131] It will be noted that none of this thermolysis product could be detected in the electrical discharge experiments (Table II).

Table II. Observed Yields of Liquid Products from Electrical Discharge Reactions of Mixtures of *cis,cis,cis-*, *cis,cis,trans-*, and *trans,cis,trans-*2,4,6-Octatriene and of *trans-*5,6-Dimethyl-1,3-cyclohexadiene[a]

| Liquid product | mixture 3.6:54.7:41.7 % | SD | mixture 2.6:68.8:28.6 % | SD | mixture 3.0:46.5:50.5 % | SD | mixture <0.05:98.75:1.25 % | SD | Dimethylcyclohexadiene % | SD |
|---|---|---|---|---|---|---|---|---|---|---|
| Benzene | 22.3 | 1.3 | 22.5 | 0.9 | 22.4 | 1.0 | 33.3 | 0.7 | 12.8 | 0.5 |
| *trans-*5,6-Dimethyl-1,3-cyclohexadiene | 3.14 | 0.04 | 3.62 | 0.19 | 2.73 | 0.10 | 5.45 | 0.10 | 33.2 | 1.2 |
| *cis-*5,6-Dimethyl-1,3-cyclohexadiene | 2.89 | 0.14 | 1.99 | 0.10 | 3.68 | 0.27 | <0.2[b] | | <0.2[b] | |
| Toluene | 20.3 | 0.5 | 18.1 | 0.8 | 19.1 | 0.6 | 23.4 | 0.5 | 25.9 | 0.6 |
| *cis,cis,cis-*2,4,6-Octatriene | 0.81 | 0.02 | 0.81 | 0.02 | 0.71 | 0.02 | <0.2[b] | | <0.2[b] | |
| *cis,cis,trans-*2,4,6-Octatriene | 13.7 | 0.3 | 17.0 | 0.8 | 10.6 | 0.1 | 8.65 | 0.64 | <0.2[b] | |
| *trans,cis,trans-*2,4,6-Octatriene | 9.8 | 0.4 | 8.2 | 0.1 | 11.2 | 0.2 | <0.2[b] | | <0.2[b] | |
| 1,6-Dimethyl-1,3-cyclohexadiene | <0.2[b] | | <0.2[b] | | <0.2[b] | | <0.2[b] | | <0.2[b] | |
| Miscellaneous[c] | 26.9 | 0.5 | 27.9 | 0.5 | 29.6 | 1.1 | 29.2 | 0.9 | 27.9 | 1.8 |
| Flow rate for given reactant, mol/min | $4.7 \times 10^{-4}$ | | $4.6 \times 10^{-4}$ | | $4.7 \times 10^{-4}$ | | $4.7 \times 10^{-4}$ | | $4.8 \times 10^{-4}$ | |

[a] Pressure of discharge system, 0.4 mm. Temperature of electrodes, 170–200°. Potential drop across electrodes, 615 V; current, 30 mA. Gaseous products were not identified. Product percentages are uncorrected gas-chromatogram peak areas; standard deviations (SD) are also given. Mixture headings give percent compositions of reactant in the order cis,cis,cis: cis,cis,trans: trans,cis,trans. [b] Estimated upper limit of this product. [c] Sum of all unidentified products.

Table III. Calculated Amounts of Thermolysis for Reactants Studied in Electrical Discharge

| Reactant | Temp, °C | $k$, sec$^{-1}$ | | Time,[a] sec | Calculated amount,[b] % |
|---|---|---|---|---|---|
| *cis-*1,2,3,4-Tetramethylcyclobutene | 250 | $2.1 \times 10^{-2}$ | $(2.47 \times 10^{-2})$[c] | $2.26 \times 10^{-2}$ | None |
| | 300 | $7.9 \times 10^{-1}$ | $(5.28 \times 10^{-1})$[c] | $2.05 \times 10^{-2}$ | 1.57 |
| | 350 | 4.8 | (4.6)[c] | $1.89 \times 10^{-2}$ | 8.7 |
| *trans-*1,2,3,4-Tetramethylcyclobutene | 200 | | $(3.85 \times 10^{-2})$[c] | $2.34 \times 10^{-2}$ | None |
| | 250 | | $(6.9 \times 10^{-1})$[c] | $2.11 \times 10^{-2}$ | 1.4 |
| | 300 | | (3.45)[c] | $1.92 \times 10^{-2}$ | 6.4 |
| *cis,cis,trans-*2,4,6-Octatriene | 250 | | $(2.5 \times 10^{-3})$[d] | $2.34 \times 10^{-2}$ | None |
| | 300 | | $(3.6 \times 10^{-2})$[d] | $2.14 \times 10^{-2}$ | None |
| | 350 | | $(3.5 \times 10^{-1})$[d] | $1.97 \times 10^{-2}$ | 0.6 |
| *trans,cis,trans-*2,4,6-Octatriene | 200 | $1.74 \times 10^{-3}$ | $(7.84 \times 10^{-3})$[d] | $2.54 \times 10^{-2}$ | None |
| | 300 | $2.83 \times 10^{-1}$ | (1.38)[d] | $2.09 \times 10^{-2}$ | 0.6 |
| | 350 | 1.0 | (6.07)[d] | $1.93 \times 10^{-2}$ | 1.9 |

[a] Residence time = length of discharge zone times molecules per unit volume in discharge cell divided by molecules per unit area entering discharge cell per second = $l(PN_0/RT)/(V/A)$, where $l$ is the length of the discharge zone (2.5 cm), $V$ is the flow rate in molecules/sec, $A$ is the cross-sectional area of the discharge cell (6.2 cm$^2$), $P$ is the pressure of the discharge system (0.4 mm), $N_0$ is Avogadro's number, $R$ is the gas constant, and $T$ is the absolute temperature, with the assumption that perfect gas behavior is a sufficiently good approximation. [b] Calculated percentage of thermolysis product at $t$ = residence time. [c] Reference 15. [d] B. S. Schatz, Ph.D. Dissertation in Chemistry, Oregon State University, 1967.

## Discussion

**Stereochemistry of Electrocyclic Reactions in the Electrical Discharge.** It has been shown experimentally that thermolysis of the tetramethylcyclobutenes[13c] proceeds by conrotatory ring opening, while the reverse reaction, photochemically induced, proceeds by a disrotatory ring closure.[14f] Thermal cyclization of *trans,cis,trans-*and *cis,cis,-trans-*2,4,6-octatrienes proceeds by a disrotatory ring closure,[13l] while photocyclization of the trans,cis,trans isomer proceeds by a conrotatory motion.[14k]

The observed opposite rotatory senses for thermal and photochemical electrocyclic reactions of a given compound, and for four-electron vs. six-electron electrocyclic processes in each reaction type, are in complete agreement with orbital-symmetry predictions.[3]

We can therefore ascribe mechanistic and theoretical significance to the fact that the electrical discharge reactions proceed with complete stereospecificity according to the thermal (ground-state) mode, and not according to the photochemical (first excited electronic state) mode.

The electrical discharge reaction of *trans-*5,6-dimethyl-1,3-cyclohexadiene gives substantial amounts of benzene and toluene and no detectable electrocyclic ring-opening products. This result is similar to the observed formation of benzene in the radio frequency discharge reaction of 1,3-cyclohexadiene.[16]

Microwave discharge experiments on toluene and related hydrocarbons were shown *not* to proceed through photolysis or the excited state(s) important in photolysis since the microwave and photolysis products were shown to be different.[5a]

**Selection Rules for Electrocyclic Reactions of Molecular Cations and Anions.** Under electron-impact conditions, not only the electronic ground and excited states, but also molecular cations or anions could be the reactive species leading to electrocyclic reaction products, the products being subsequently neutralized by electron addition or subtraction and then collected. It is therefore of interest to see whether orbital-symmetry predictions, or other arguments, can rule such molecular ions in or out.

Electronic state correlations[3,17] for the cyclobutene ring opening and the hexatriene ring closure are given in Table IV, classified according to their stereochemical predictions. The familiar predictions for thermal and photochemical

Table IV. Electronic-State Correlations for Certain Electrocyclic Ring Openings of Cyclobutene and Electrocyclic Ring Closures of Hexatriene[a]

| Cyclobutene → butadiene | | Hexatriene → cyclohexadiene |
|---|---|---|
| | Stereochemistry Consistent with Electrical Discharge | |
| $(\sigma^2\pi^2)_0 \xrightarrow{\text{con}} (\psi_1{}^2\psi_2{}^2)_0$ | (1) | $(\phi_1{}^2\phi_2{}^2\phi_3{}^2)_0 \xrightarrow{\text{dis}} (\sigma^2\psi_1{}^2\psi_2{}^2)_0$ |
| $(\sigma^2\pi)_0{}^{\cdot+} \xrightarrow{\text{con}} (\psi_1\psi_2{}^2)_*{}^{\cdot+}$ | (3a) | $(\phi_1{}^2\phi_2{}^2\phi_3)_0{}^{\cdot+} \xrightarrow{\text{dis}} (\sigma^2\psi_1\psi_2{}^2)_*{}^{\cdot+}$ |
| $(\sigma\pi^2)_*{}^{\cdot+} \xrightarrow{\text{con}} (\psi_1{}^2\psi_2)_0{}^{\cdot+}$ | (4a) | $(\phi_1{}^2\phi_2\phi_3{}^2)_*{}^{\cdot+} \xrightarrow{\text{dis}} (\sigma^2\psi_1{}^2\psi_2)_0{}^{\cdot+}$ |
| $(\sigma^2\pi^2\pi^*)_0{}^{\cdot-} \xrightarrow{\text{con}} (\psi_1{}^2\psi_2{}^2\psi_4)_*{}^{\cdot-}$ | (5a) | $(\phi_1{}^2\phi_2{}^2\phi_3{}^2\phi_4)_0{}^{\cdot-} \xrightarrow{\text{dis}} (\sigma^2\psi_1{}^2\psi_2{}^2\psi_4)_*{}^{\cdot-}$ |
| $(\sigma^2\pi^2\sigma^*)_*{}^{\cdot-} \xrightarrow{\text{con}} (\psi_1{}^2\psi_2{}^2\psi_3)_0{}^{\cdot-}$ | (6a) | $(\phi_1{}^2\phi_2{}^2\phi_3{}^2\phi_5)_*{}^{\cdot-} \xrightarrow{\text{dis}} (\sigma^2\psi_1{}^2\psi_2{}^2\psi_3)_0{}^{\cdot-}$ |
| | Stereochemistry Consistent with Mass Spectral Analogy | |
| $(\sigma^2\pi)_0{}^{\cdot+} \xrightarrow{\text{dis}} (\psi_1{}^2\psi_3)_*{}^{\cdot+}$ | (3b) | $(\phi_1{}^2\phi_2{}^2\phi_3)_0{}^{\cdot+} \xrightarrow{\text{con}} (\sigma^2\psi_1{}^2\psi_3)_*{}^{\cdot+}$ |
| $(\sigma^2\pi^*)_*{}^{\cdot+} \xrightarrow{\text{dis}} (\psi_1{}^2\psi_2)_0{}^{\cdot+}$ | (4b) | $(\phi_1{}^2\phi_2{}^2\phi_4)_*{}^{\cdot+} \xrightarrow{\text{con}} (\sigma^2\psi_1{}^2\psi_2)_0{}^{\cdot+}$ |
| | Other | |
| $(\sigma^2\pi\pi^*)_* \xrightarrow{\text{dis}} (\psi_1{}^2\psi_2\psi_3)_*$ | (2) | $(\phi_1{}^2\phi_2{}^2\phi_3\phi_4)_* \xrightarrow{\text{con}} (\sigma^2\psi_1{}^2\psi_2\psi_3)_*$ |
| $(\sigma^2\pi^2\pi^*)_0{}^{\cdot-} \xrightarrow{\text{dis}} (\psi_1{}^2\psi_2\psi_3{}^2)_*{}^{\cdot-}$ | (5b) | $(\phi_1{}^2\phi_2{}^2\phi_3{}^2\phi_4)_0{}^{\cdot-} \xrightarrow{\text{con}} (\sigma^2\psi_1{}^2\psi_2\psi_3{}^2)_*{}^{\cdot-}$ |
| $(\sigma^2\pi\pi^{*2})_*{}^{\cdot-} \xrightarrow{\text{dis}} (\psi_1{}^2\psi_2{}^2\psi_3)_0{}^{\cdot-}$ | (6b) | $(\phi_1{}^2\phi_2{}^2\phi_3\phi_4{}^2)_*{}^{\cdot-} \xrightarrow{\text{con}} (\sigma^2\psi_1{}^2\psi_2{}^2\psi_3)_0{}^{\cdot-}$ |

[a] Electronic ground states are identified with $_0$. Electronically excited states are identified with $_*$. In all the correlations, it is assumed that the electronically excited state shown is the *lowest* electronically excited state; different possible assumptions as to which state is lowest are identified with the same number, followed by a or b. State designations include only those orbitals which are relevant to the stereochemical distinction between conrotatory (con) and disrotatory (dis) ring opening or ring closure.

reactions are given as (1) and (2). Four different correlations are given for molecular cations (3a,b; 4a,b) and for molecular anions (5a,b; 6a,b), there being two reasons why one cannot make a unique prediction with confidence in these cases.

First, it is found that for both molecular cation and molecular anion (odd-electron species), the ground electronic states of reactant and product are of opposite symmetry for both conrotatory (twofold axis) and disrotatory (mirror-plane) symmetry conservation. Therefore, in this approximation, the ground-state molecular cation or anion would be required to produce excited-state product, and electrocyclic reactions of the electronic ground states of these ions would appear to be highly forbidden. Since either reactant or product must be electronically excited, it is necessary to consider both cases, ground-state reactant (3, 5) and excited-state reactant (4, 6). However, considering the reactions in the directions in which they were observed to proceed in the electrical discharge, it is probable that (3) and (5) are ruled out as orbital-symmetry forbidden.

The second ambiguity in prediction arises from uncertainty as to which would be the orbital occupation of the lowest electronically excited state of such odd-electron species. Unfortunately, different possible choices of excited state lead to opposite stereochemistries, as denoted in each case by the suffixes a and b. The most natural choices would appear to be those represented in (4b) and (6b), in which case, reaction of either molecular cations (4b) or anions (6b) would give stereochemistry opposite to that observed in the electrical discharge and could thus be ruled out as the electrocyclic-reaction mechanism in the electrical discharge. This conclusion cannot be regarded as absolutely compelling, however, as it is difficult on purely theoretical grounds to rule out conclusively (3a) and (4a) as well as (5a) and (6a).

For reactions of ground electronic states of molecular ions, if it is assumed that the lowest excited-state product is formed and is the one in which a bonding electron from the next highest energy occupied orbital is promoted to the highest energy occupied orbital [cf. (3a, 5b)], the stereochemistry is predicted to be the same as is predicted by an aromaticity criterion. The aromaticity of an odd-electron system should be less than, but obey the same rules as, the corresponding conjugated system with one *more* electron since the odd-electron system can be pictured as being formed by removal of one electron from the highest energy occupied molecular orbital of the system with one more electron.[18,19]

The prediction for the molecular cation is that it would, if it underwent electrocyclic reaction, behave like the molecular ground state, as in thermal reactions.[18] However, there is evidence that electrocyclic processes in mass spectrometry, involving molecular cations, proceed with stereochemistry opposite to thermal, and like photochemical, electrocyclic processes of the neutral molecule.[20,21] These mass spectral results seem to implicate electronically excited molecular ions. The correlations of Table IV nicely explain these observations since they predict that the electrocyclic reactions of ground-state molecular ions should be forbidden, but reaction of excited states should be allowed. Therefore, the mass-spectral experiments provide some experimental support for our interpretation of the orbital correlations of Table IV, at least for molecular cations, in that reaction 4b is selected over (4a), and, since (3a) is probably favored[18] over (3b), reaction 3 is disfavored entirely.

## Conclusions

In the case of the electrocyclic electrical-discharge reactions reported here, a number of conclusions can be drawn, with varying degrees of confidence.

(1) In view of the well-established stereochemistry of electrocyclic reactions of electronically excited molecules, opposite to the present results, an electrical-discharge mechanism involving the first electronically excited state of the neutral molecule is ruled out.

(2) Available information suggests that an electrocyclic electrical-discharge mechanism involving molecular cations is ruled out.

Experimentally, the mass-spectral analogy[20,21] indicates the opposite stereochemistry to that observed in the electrical discharge. This probably constitutes direct experimental evidence ruling out the molecular cation mechanism for electrocyclic reactions in the electrical discharge; however, the examples are not extensive, nor is stereochemistry directly observable in the mass spectrometer, nor can it be conclusively argued that molecular cations formed in the mass spectrometer, under conditions where they undergo no collisions before reaction, will behave in the same way as molecular cations formed in an electrical discharge.

The discussion of Table IV, above, provides arguments based on orbital-symmetry theory which tend to support the mass-spectral experimental conclusions. First, the theory argues strongly against ground-state molecular cations, because their electrocyclic ring opening should be forbidden. Of the two correlations in Table IV which are consistent with the observed electrical-discharge stereochemistry (3a and 4a), (3a) is expected[18] to be the favorable path [relative to (3b)] for reaction of ground-state molecular cations but should be forbidden. Second, (4b) might be expected to be favored over (4a) since the excited-state cations in (4a) involve promotion of strongly bonding electrons. Thus, the lowest excited states of the reactant cations are probably as in (4b), and the stereochemistry is opposite to that observed in the electrical discharge. If (4a) were preferentially accessed, but the excited states of the reactant cations were not the lowest ones, it might be expected that at least some relaxation to the lowest excited state would take place and thus probably preclude stereospecificity as strong as that observed.

(3) There is reason to believe that an electrocyclic electrical-discharge mechanism involving molecular anions is also ruled out.

The correlations in Table IV which are consistent with electrical-discharge stereochemistry are (5a) and (6a). We tentatively rule out (5a) since it is predicted to be forbidden. Mechanisms involving excited states of molecular anions (6a,b) are not forbidden; however, reaction of an excited-state anion is expected to be most unlikely to allow for the observed substantial yields of electrocyclic products, given the conditions of fairly high pressure, permitting (though not requiring) rapid collisional deactivation, and the propensity of molecular anions to emit electrons if they have the slightest excess energy content.[22] These arguments seem sufficient to rule out mecanisms involving molecular anions, but they do suffer from lack of experimental analogy. The argument that (5a) is forbidden depends on the actual energy of the excited product state relative to the reactant and on the availability of vibrational excitation to the reactant under electrical-discharge conditions. The argument that (6a) is ruled out by the short lifetime of excited molecular anion states depends on the assumption that electrocyclic ring opening of such states would be slower than electron emission or other processes responsible for their instability.

(4) The remaining sources of the electrocyclic electrical-discharge reactions are the ground electronic state or higher excited electronic states above the first. In terms of orbital-symmetry theory, there will be higher excited electronic states which could undergo electrocyclic reactions with the stereochemistry observed. It is known that certain molecules, for example, benzene and toluene, can be excited to such higher states, which undergo photochemical reaction with quantum yields near unity, and which undergo internal conversion to the first excited state with very low efficiency.[23a] It is difficult to see how only higher excited states of our reactants might be formed in the electrical discharge since there is a wide spectrum of electron energies present under such conditions,[2] but this possibility can probably not be ruled out. There is a case where polytheylene has been shown to undergo surface cross-linking in an electrical discharge by vacuum ultraviolet radiation emitted from the discharge.[24] However, this reaction is presumably proceeding from the first excited ($\sigma \rightarrow \sigma^*$) state of the polymer, not from higher states, and the reaction time required was on the order of several hours, whereas the residence times in our discharge experiments were a few hundredths of a second. Therefore, although the vacuum ultraviolet radiation would be capable of producing higher excited electronic states of our reactants, the polyethylene experiments do not provide evidence of the formation of such states *to the exclusion of the first excited state,* as required by our stereochemical results. The time scales are so different that, to the extent there is analogy between the systems, it would appear that vacuum ultraviolet radiation could be contributing in only a minor way to our reactions.

Reaction via vibrationally excited ground states has been implicated in photochemical reactions of molecules similar to those we have studied, especially in the gas phase,[23b] and such reactions give products like hydrogen, ethene, acetylene, and benzene, which are also found in the electrical discharge. Photochemical electrocyclic ring opening of 1,3-cyclohexadiene has been interpreted as proceeding from the first excited singlet state, while concomitant formation of benzene, hydrogen, acetylene, and ethene proceeds from vibrationally excited electronic ground states.[14b,j]

In view of these analogies, it is consistent and not unreasonable to suppose that the electrocyclic electrical-discharge reactions proceed from vibrationally excited electronic ground states, as the most likely origin of the observed stereochemistry. These species would not be thermally (translationally) equilibrated, however, since our experiments strongly suggest that the temperature (a measure of translational energy) is not high enough to account for the reaction. There is some question as to how such species could be formed since direct vibrational excitation by electron impact has a low probability.[2,25] An attractive, if speculative, mechanism involves formation of molecular cations by electron impact with relatively high-energy electrons and subsequent neutralization by a lower energy electron. Since we have concluded that ground-state molecular cations should have forbidden electrocyclic reactions, though they may well undergo other reactions, the electrocyclic products would arise only after electron capture to form the electronic ground state of the neutral molecule, and since electron capture is expected to be largely a Franck-Condon (vertical) process, these ground-state molecules would probably be vibrationally excited. Low-energy electrons, or else a three-body collision to dissipate the energy released upon impact, would be required, but low-energy electrons should be present in large numbers in such discharges, particularly the alternating (ac) ones we have used. Alternatively, molecular anions could be invoked since they, too, should not undergo electrocyclic reactions from their ground states. If they underwent charge transfer or electron emission, vibrationally excited ground-state molecules might result. Molecular anions, though not reactions of them via vibrationally excited ground states, have been suggested as microwave discharge reaction intermediates.[5a] It is known that in mass spectrometry there is a much lower probability of negative-ion formation than of positive-ion formation, however. In any case, all the states of Table IV no doubt contribute to a finite extent so that we are, as in any study of reaction mechanisms, only suggesting that those which are ruled out contribute only to a very minor extent, while vibrationally excited electronic ground states seem to be the best candidate for the major contributor to the formation of electrocyclic products.

Finally, it may be noted that the high *stereospecificity* characteristic of orbital-symmetry control is powerfully expressed, even under such high-energy conditions as the electrical discharge.

## Experimental Section[1c]

All reactants for electrical discharge were purified on a Perkin-Elmer F21 preparative gas chromatograph, using a 6.7 mm × 12 m column packed with 20% Carbowax 20M on 60–80 mesh Chromosorb P. The gaseous and liquid products were separated into their components by an Aerograph Model A-700 GLC instrument.

A vacuum line system was used for the reactions, evacuated by an oil-diffusion pump to $10^{-3}$ mm. During a run, the oil-diffusion pump was bypassed, and the system was pumped continuously by a mechanical vacuum pump to remove noncondensable gases such as hydrogen and methane. The pumps were protected by a cold trap. Pressures were measured by a McLeod gauge. Purified reactant in a flask attached to the system by a ground-glass joint was degassed thoroughly and passed through a precision 1.25-mm glass needle valve, used to control the flow rate. Vapors passed through an electrical discharge cell made from a 50/30 Vycor or Pyrex socket joint with an 18/9 joint attached for the inlet from the needle valve. A liquid-nitrogen cold finger with a matching 50/30 joint opening on its side was attached. Two electrodes made from coiled platinum wire were sealed into the discharge cell with a spacing of 2 cm using Pyrex graded seals and uranium glass seals; tungsten leads were welded to the electrodes. The cold finger surface was 9 cm from the second electrode. A thermocouple well was formed in the cell directly adjacent to the second electrode. The remainder of the discharge system was set up as a standard vacuum line for sample manipulation, with five U-shaped traps and stopcocks, and two auxiliary outlets.

The voltage to the electrodes was supplied by a Jefferson luminous tube transformer with a 15,000 V, 60 mA secondary. The primary voltage was set at 80 V with a variable transformer, and the glass needle valve was adjusted to give a flow rate such that the discharge glow extended through the discharge cell but not as far as the cold finger. Voltage measurements were made with a Simpson Model 260 multimeter placed in a parallel circuit with the discharge cell, and current measurements were made with a 250-mA full scale Weston ac ammeter in series with the discharge cell.

After the discharge run, the system was evacuated to $10^{-3}$ mm and isolated, and the cold finger was allowed to warm to room temperature so that the products would distill into two successive −78° traps (to collect "liquid" products) and then a third liquid nitrogen trap to collect gaseous products. The gaseous products were transferred to an Aerograph gas sampling valve cell which had been fitted so that it could be attached to the vacuum line, and the products were condensed into it with liquid nitrogen, injected directly into and collected from an Aerograph Model A-700 GLC instrument with a 6.35 mm × 8.88 m column packed with 20% dibutyl tetrachlorophthalate on 60-80 mesh Chromosorb W. The column temperature was programmed from −20 to 95°, while the injection and detector temperature were maintained at 115 and 110°, respectively. The collection cells (15-cm long) were made from triple coiled thick-walled (i.d. 8 mm) Pyrex glass tubing equipped with two Teflon vacuum stopcocks and a standard taper joint for vacuum-line manipulation and mass-spectral sampling.

The liquid products collected in the Dry Ice-acetone cooled traps were removed to a vacuum-tight thick-walled weighing vessel which had been previously evacuated and weighed. These products were again transferred to a collection cell which was constricted on the other end to form a capillary cone and drawn into a gas-tight syringe, injected into and collected from the GLC instrument which was used for gaseous products.

The discharge cell was cleaned after each experiment by baking overnight in a glass annealing oven (600°). This procedure removed polymer from the cell walls.

In order to identify both gaseous and liquid products, the mass spectra were taken at 76 and 15.5 eV ionizing potentials. After tentative identification by this technique, gas chromatographic retention times of the suspected compound were matched with those of authentic samples. Further proof of structure was obtained for both purified gaseous and liquid products by gas-phase infrared spectra and, where necessary, NMR spectra.

The ozonizer type discharge cell consisted of a glass cylinder covered with aluminum foil as one electrode, with a concentric, inner electrode made from a glass tube filled with a saturated copper sulfate solution with a copper wire extending through its length (made from an appropriately modified distillation condenser such that it could simply replace the electrode type discharge cell in the vacuum system).

Rate constants were determined for thermolysis (Table III) in sealed thick-walled Pyrex ampules (trace of hydroquinone added as stabilizer), ampules being withdrawn from the constant-temperature bath and cooled, and the contents were examined by GLC to determine progress of reaction. The results are considered to be in reasonable agreememt with literature values (Table III) for the purposes of this work.

***cis*- and *trans*-1,2,3,4-tetramethylcyclobutene** were prepared according to Criegee and Noll.[13c]

***cis,trans*- and *trans,trans*-3,4-dimethyl-2,4-hexadiene** were also prepared according to Creigee and Noll.[13c]

***cis*- and *trans*-5,6-dimethyl-1,3-cyclohexadiene** were prepared according to Schatz.[26]

***cis,cis,cis*-, *trans,cis,trans*-, and *cis,cis,trans*-2,4,6-octatrienes (mixture)** were also made according to Schatz.[26] Purification for analytical purposes could be carried out on a small preparative scale with the Aerograph A-700 GLC instrument. Essentially pure cic,cis,trans isomer could be isolated on the scale needed for reactants with the Perkin-Elmer F21 GLC instrument; however, only mixtures enriched in the other isomers could be reasonably obtained on this scale (Table II).

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# Wallach Rearrangement Mechanisms for Hexamethylazoxybenzene. General Acid Catalysis in Strongly Acidic Solutions[1]

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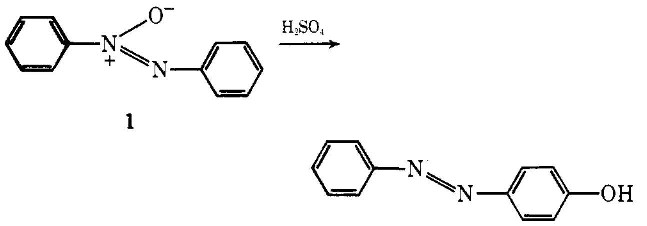
**Abstract:** The kinetics of the reaction of 2,2′,4,4′,6,6′-hexamethylazoxybenzene (**6**) to give 4-hydroxymethyl-2,2′,4′,6,6′-pentamethylazobenzene (**7**) in strong $H_2SO_4$ solutions have been investigated. The acidity dependence is complex, but the total reaction can be separated into two processes, one dominant below, and the other above ~80% $H_2SO_4$. Consideration of possible mechanisms leads to linear correlations of log $k_\psi$ − log $[C_{SH^+}/(C_S + C_{SH^+})]$ with 2 log $a_{HSO_4^-}$ and with log $a_{H_2SO_4}$, for these two processes, rather than with $-H_0$ or other acidity functions. These correlations lead to the following proposals of the reaction mechanism. The low-acidity process undergone by **6** involves rate-determining nucleophilic attack by $HSO_4^-$, subsequent to proton loss (para methyl) from the monoprotonated substrate to $HSO_4^-$ acting as a base. In the other mechanism, the monoprotonated substrate undergoes a rate-determining proton transfer to oxygen of $^+$NOH with loss of $H_2O$, giving an intermediate dication. The latter undergoes fast proton loss and nucleophilic attack, leading to the observed products. The dicationic mechanism thus represents general acid catalysis by $H_2SO_4$ species in the acid region 80% $H_2SO_4$ and above.



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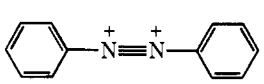
The Wallach rearrangement[2] of azoxybenzene (**1**) to give *p*-hydroxyazobenzene (**2**) in sulfuric acid has been investigated recently in several laboratories.[3-7] Apart from a requirement for the involvement of more than one proton and an intermediate which can react symmetrically, little agreement exists on the mechanism of this reaction.[8,9] As a reaction intermediate, this group[5] has favored the dication **3**,[10] but others prefer **4**, in unprotonated,[3] mono-,[4] or diprotonated form,[6] and another group believes that **5** is more likely.[7]



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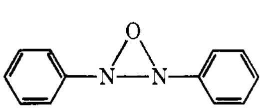

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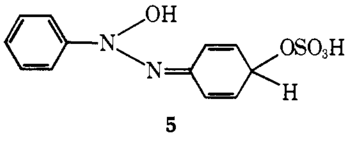

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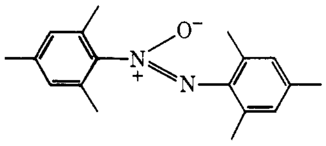
In an attempt to shed further light on this problem, a study of the Wallach rearrangement of hexamethylazoxybenzene (**6**) has been undertaken. The methyl groups



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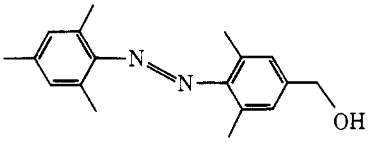

7

should stabilize structures like **3**, if formed, and help to prevent complications due to sulfonation previously found with **1** in the 95-100% $H_2SO_4$ region.[11] The formation of **7**, somewhat unexpectedly, as the product of the reaction of **6** in 85% $H_2SO_4$, has already been reported;[12] in this paper, the kinetics of this process are discussed. The results have yielded further information on the relevance of general acid catalysis in highly acidic solutions to the Wallach rearrangement pathways.[5,13]

## Experimental Section

The preparation of 2,2′,4,4′,6,6′-hexamethylazoxybenzene (**6**) and the isolation and identification of the reaction product 4-hydroxymethyl-2,2′,4′,6,6′-pentamethylazobenzene (**7**) have been previously described,[12] as well as the p$K_a$ determination, by standard methods.[14]

Kinetic runs were carried out in the thermostated cell compartment of a Unicam SP 800 uv-visible spectrophotometer, using the