

It is our conclusion that the process we observe with acetals derived from formaldehyde is not classical general acid catalysis, due to the instability of the derived oxocarbenium ion. We suggest that any reaction not subject to intermolecular general acid catalysis could not be subject to intramolecular general acid catalysis, since the major determinant for observation of this mechanism is a relatively stable oxocarbenium ion.

Finally, it should be pointed out that the carboxylate-stabilized *A-1* process favored in our system does provide substantial rate enhancements and could be a plausible mechanism for the enzymatic hydrolysis of glycosides, particularly if conducted in a hydrophobic environment.

Acknowledgment. This work was supported by a grant from the National Institutes of Health.

Dielectrocyclic Reactions

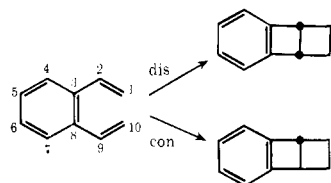
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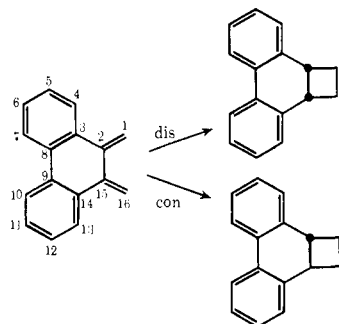
Abstract: Using the cyclizations of *o*-divinylbenzene and 2,2'-divinylbiphenyl to yield cyclobutane containing structures to illustrate the method, a "dielectrocyclic" classification of these reactions is carried out. The conclusions are compared to the Woodward-Hoffmann cycloaddition classification and the, *in principle*, advantages of the present approach are examined. The change in the predicted products due to heteroatom substitution is also investigated.

The orbital symmetry¹ method as developed by Woodward and Hoffmann^{2,3} has had considerable application in the treatment of cycloaddition and electrocyclic reactions. The concern of this paper is the treatment of a type of reaction of which the cyclizations indicated in Schemes I and II are illustrative. At

Scheme I. Dielectrocyclic Reaction I



Scheme II. Dielectrocyclic Reaction II



first glance it might appear that these reactions would be best treated as cycloaddition reactions (*i.e.*, 2 + 2 cis/cis or supra,supra³). However, the bonding of the ethylenic fragments to the ring rather restricts the orientation of each ethylenic π system and the reaction might better be considered as a type of electrocyclic

reaction. One might classify the reactions as "dielectrocyclic reactions," *i.e.*, reactions in which electrons in *two* π orbitals transform by a rotation of part of the orbitals into electrons in *two* σ bonds. Such a treatment would of course preclude consideration of say the *antara,antara*³ (*trans/trans*) and the *antara,supra*³ (*trans/cis*) modes normally included in cycloaddition reactions. However, in view of what is clearly a very restricted motion,⁴ particularly in reaction I, and in view of the experimental results for reaction II⁵ (see also section I-2 to follow) the contribution of these modes is unlikely.

An advantage of the dielectrocyclic classification is that, in contrast to the cycloaddition approach, one would be able to separately consider the possibility of the *trans*- and *cis*-fused products of the *supra,supra* mode since under the electrocyclic classification these products correspond to, respectively, the *conrotatory* and *disrotatory* modes. Further, the consideration of these reactions as proceeding from rotation of π orbitals about a semirigid σ skeleton allows one to comment on the degree of overlap and hence the relative stability of the cyclized products. A final and most important advantage over a simple 2 + 2 cycloaddition classification is that one can readily include the perturbation of the ring system on the course of the reaction.

In proceeding with a dielectrocyclic classification it should be recognized that since four electrons are involved (in contrast to the two electrons in a simple electrocyclic reaction), the symmetry restrictions will be determined by the *product* of two or more spatially different orbitals and consequently the use of state cor-

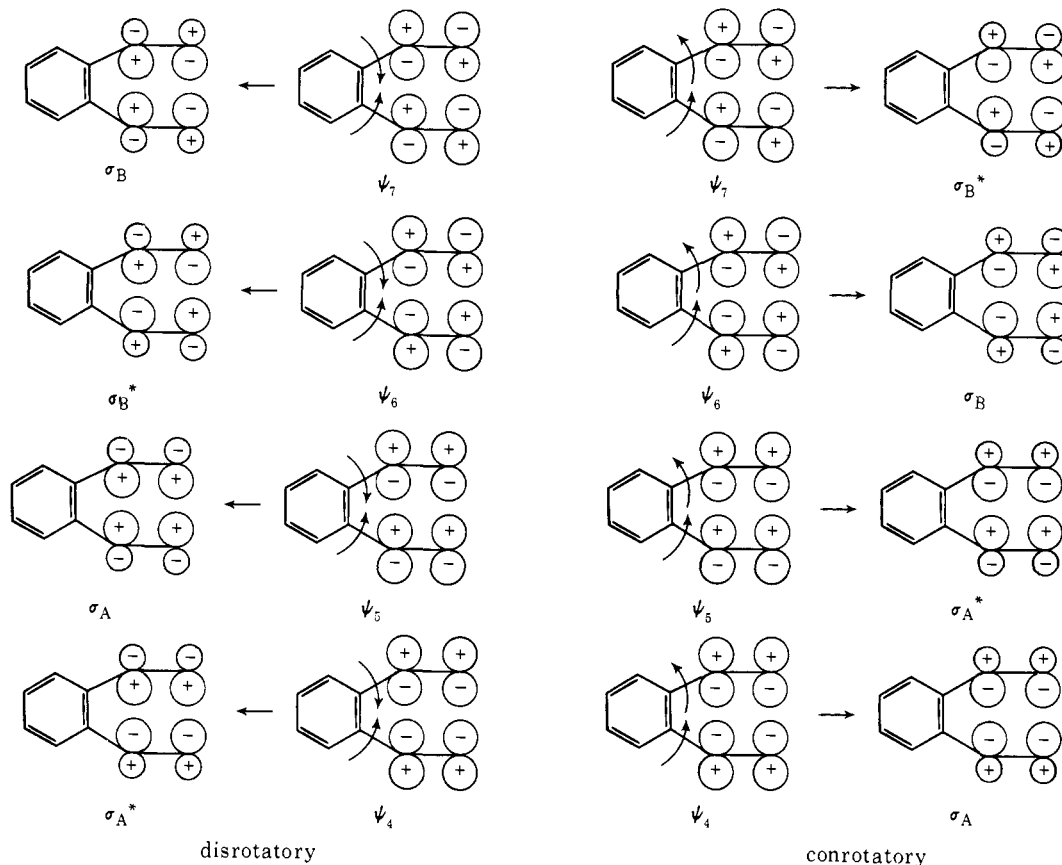
(1) L. J. Oosterhoff quoted by E. Havinga and J. L. M. A. Schlattmann, *Tetrahedron*, **16**, 151 (1961).

(2) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395, 2046 (1965); *Accounts Chem. Res.*, **1**, 17 (1968).

(3) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Springer-Verlag, West Berlin and Heidelberg, 1970.

(4) The orientations necessary for the *supra,antara*, etc., modes are illustrated in ref 3, pp 67-69. These modes could only be accommodated at the expense of considerable steric strain and/or a "free" rotation of the termini of the ethylenic fragments.

(5) D. F. Tavares and W. H. Ploder, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. P216.

Chart I. Correspondence of π and σ Orbitals^a

^a In the two center columns the π lobes are perpendicular to the plane of the diagram and in the outer columns the σ lobes illustrated are in the plane of the diagram.

relation diagrams (as compared to orbital correlation diagrams) will be essential. Further, it is clear that, in general, the orbitals considered should be those of the entire π system, and not just a fragment (for example, not just the hexatriene fragment contained in *o*-divinylbenzene), for certainly the remainder of the π system can, in general, alter the energy ordering and hence the symmetry of the highest orbitals can be altered.

Although unequivocal experimental verification⁶⁻⁷ of the efficacy of this approach (as compared say to an $m + n$ cycloaddition classification) is not available, the apparent advantages and the, *in principle*, uniqueness of the results prompted a full analysis of reactions typified by I and II, using the dielectrocyclic classification. In addition, the change in the predicted modes, due to heteroatom substitution in the ring, was investigated.

I. The Dielectrocyclic Reaction

(1) *o*-Divinylbenzene. The molecular orbitals were obtained for the ten-center (see Scheme I) Hückel representation where all α and β were taken to be the same. (Setting all α and β the same is clearly an approximation, for certainly the matrix element $\beta' = \beta_{23} = \beta_{39}$ in *o*-divinylbenzene would not be expected to be the same as β for the ring. However, calculations show that such variations do not change the symmetry of the orbitals; see, for example, Table I.) Using the

(6) J. Meinwald, Abstracts, 21st National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 15-19, 1969, p 67.

(7) M. Pomerantz, *J. Amer. Chem. Soc.*, **89**, 694 (1967); J. Meinwald and P. H. Mazzocchi, *ibid.*, **89**, 696 (1967).

coefficients of the atomic orbitals at centers 1, 2, 9, and 10 as the basis allows the significant (for our purposes) portion of the π -molecular orbitals to be represented

Table I. Effect on MO Symmetry of Variation in β'

MO	Coefficients at the ethylenic centers					
	$\beta' = \beta$		$\beta' = 0.8\beta$		$\beta' = 0.8\beta$	
	<i>o</i> -Divinylbenzene					
ψ_4	0.27	0.33	-0.28	-0.34	-0.30	-0.35
	-0.27	-0.33	0.28	0.34	0.30	0.35
ψ_5	0.27	0.48	0.29	0.46	0.31	0.43
	0.27	0.48	0.29	0.46	0.31	0.43
ψ_6	0.27	-0.48	-0.29	0.46	0.31	-0.43
	-0.27	0.48	0.29	-0.46	-0.31	0.43
ψ_7	0.27	-0.33	-0.28	0.34	-0.30	0.35
	0.27	-0.33	-0.28	0.34	-0.30	0.35
	2,2'-Divinylbiphenyl					
ψ_7	0.28	0.39	0.29	0.39	0.31	0.38
	0.28	0.39	0.29	0.39	0.31	0.38
ψ_8	0.21	0.40	0.21	0.36	0.19	0.31
	-0.21	-0.40	-0.21	-0.36	-0.19	-0.31
ψ_9	0.21	-0.40	0.21	-0.36	-0.19	0.31
	0.21	-0.40	0.21	-0.36	-0.19	0.31
ψ_{10}	-0.28	0.39	-0.29	0.39	-0.31	0.38
	0.28	-0.39	0.29	-0.39	0.31	-0.38

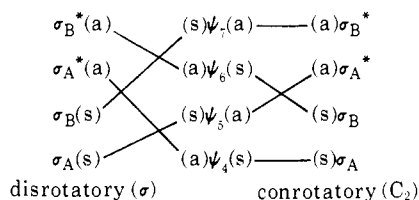
as in Chart I. The π -molecular orbitals ψ_4 , ψ_5 , ψ_6 , and ψ_7 are considered⁸ since there are four electrons

(8) The lower three π MO's, ψ_1 , ψ_2 , and ψ_3 , are taken to transform to the π MO's of the product and are not considered in the correlation diagrams.

involved in the transformation and they would presumably be in the highest occupied π MO's, (ψ_4 , ψ_5) for the thermal reaction or in some combination of the highest occupied and lowest unoccupied (ψ_6 , ψ_7) in the photoinduced reaction. The four-center σ -bond orbitals σ_A , σ_B , σ_A^* , and σ_B^* are used since these orbitals are in a 1:1 correspondence with the π MO's in either the con- or disrotatory transformations. (It might be pointed out that a linear combination of the four-center bonds generates the more usual two-center bonds, e.g., $\sigma_A + \sigma_B = \sigma_{2,9}$ and $\sigma_A - \sigma_B = \sigma_{1,10}$.)

The relative energy of the π MO's is $\psi_4 < \psi_5 < \psi_6 < \psi_7$ and, if we assume (see ref 9) that the relative energy of the σ bonds is $\sigma_A < \sigma_B < \sigma_A^* < \sigma_B^*$, then we can generate the orbital correlation diagram of Chart II. It might be pointed out that the orbital sym-

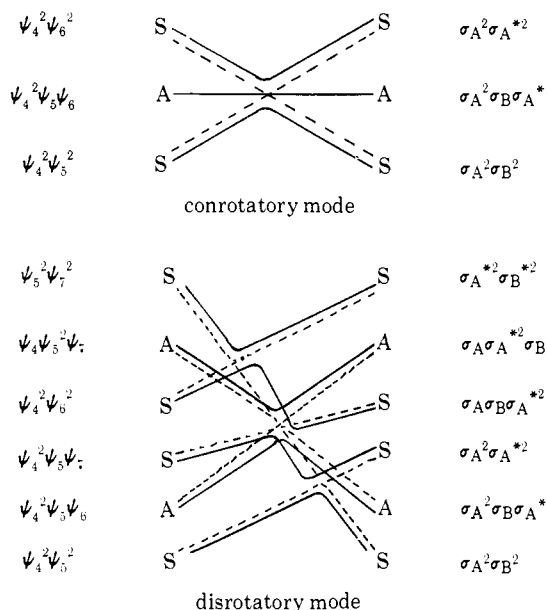
Chart II. Orbital Correlation Diagram for Reaction I^a



^a In Chart II (s) and (a) denote the orbital symmetry according to the C_2 axis for the conrotatory mode and according to the σ plane for the disrotatory mode.

metries given in Chart II for the ten-center π MO's are the same as those obtained for hexatriene π MO's. However, the use of orbitals from a fragment such as hexatriene is in general questionable since centers of the remaining part of the molecule can alter the MO's (see section I-3 especially Chart VIII). The orbital correlation diagram of Chart II allows the *state* correlation diagrams to be generated as in Chart III. The noncrossing rule prevents states of the same

Chart III. State Correlation Diagram for Reaction I^a



^a In this figure (S) and (A) refer to the symmetry of the state function under C_2 and σ .

(9) M. Orchin and H. H. Jaffé, "The Importance of Antibonding Orbitals," Houghton Mifflin, Boston, Mass., 1967, pp 89-92.

symmetry from crossing and hence leads to the curved line "correlations."¹⁰ It might be pointed out that we have included a number of states intermediate in energy between the ground state and those states to which the ground state and the first excited state correlate, for example, $\psi_4^2 \psi_5 \psi_7$ lies between $\psi_4^2 \psi_5^2$, the ground-state π configuration, and $\psi_5^2 \psi_7^2$, the π configuration to which the ground-state $\sigma_A^2 \sigma_B^2$ transforms in the disrotatory mode. Although in this case it has no effect, the omission of such states can lead to incorrect use of the symmetry noncrossing rule (see, for example, section I-3 to follow, where omission of intermediate states can give different results). It might be noted that although the orbital correlation diagram allows at least one "straight line" orbital transformation in the ground state this transformation is lost in the state correlation diagram. This disparity arises from the fact that in the state correlation diagram the π MO's are, in some cases, precluded by the noncrossing symmetry rule from transforming into the σ orbitals indicated by the orbital correlation diagram—one *must* indeed use the state correlation diagrams.

If one follows the usual practice of interpreting the "hump" in the correlation diagram as a barrier to the reaction (see for example ref 11), then Chart III serves to indicate that the conrotatory mode could proceed from the first excited state. Even for this case the cyclic product $\sigma_A^2 \sigma_B \sigma_A^*$ would probably be relatively unstable since there would be a net of only one σ bond distributed¹² over the two σ -bonding regions—between centers 1 and 10 and between centers 2 and 9. (Although antibonding orbitals have been noted in electrocyclic reactions, for example, in the cyclic product $\sigma^2 \pi^{*2}$ obtained from hexatriene, the antibonding orbital is a π orbital and hence does not have a significant effect on the centers which are to cyclize.) In any given case the relative stability of the cyclized product will depend on the bonding and antibonding characteristics of the σ bonds and in *o*-divinylbenzene the rather wide separation of centers 1,10 and 2,9 and the cyclic strain would probably preclude strong bonding overlap characteristics and hence support the suggested instability of $\sigma_A^2 \sigma_B \sigma_A^*$. Indeed the inability to obtain a cyclobutane structure from *o*-divinylbenzene^{7,13} would seem to indicate that other reaction paths are more favorable.

The implication of Chart III that *only* the photoinduced conrotatory result is favored does of course go *further* than the results obtained from a 2 + 2 cycloaddition classification that the supra,supra reactions *both* conrotatory and disrotatory are allowed. Furthermore, the simple 2 + 2 cycloaddition classification precludes any consideration of the perturbations due to the ring—a questionable procedure in general (see section I-3).

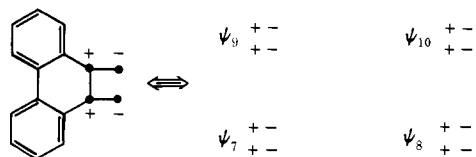
(2) **2,2'-Divinylbiphenyl.** Calculating the π MO's as before and using the two highest occupied (ψ_7 , ψ_8) and two lowest unoccupied (ψ_9 , ψ_{10}) π orbitals gives the sign of the coefficients at the four reacting centers in Chart IV. Following the appropriate disrotatory and

(10) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

(11) Reference 9, pp 87-89.

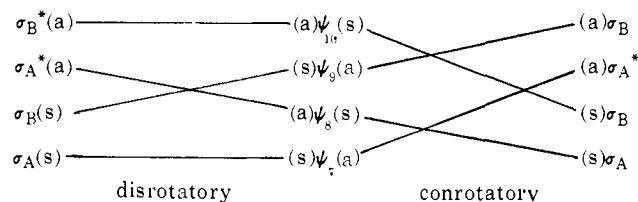
(12) These σ orbitals are four-center orbitals, hence the bonding-antibonding character is distributed over four centers.

(13) D. F. Tavares and W. H. Ploder, *Tetrahedron Lett.*, 1567 (1970).

Chart IV. Coefficients of π Orbitals in 2,2'-Divinylbiphenyl

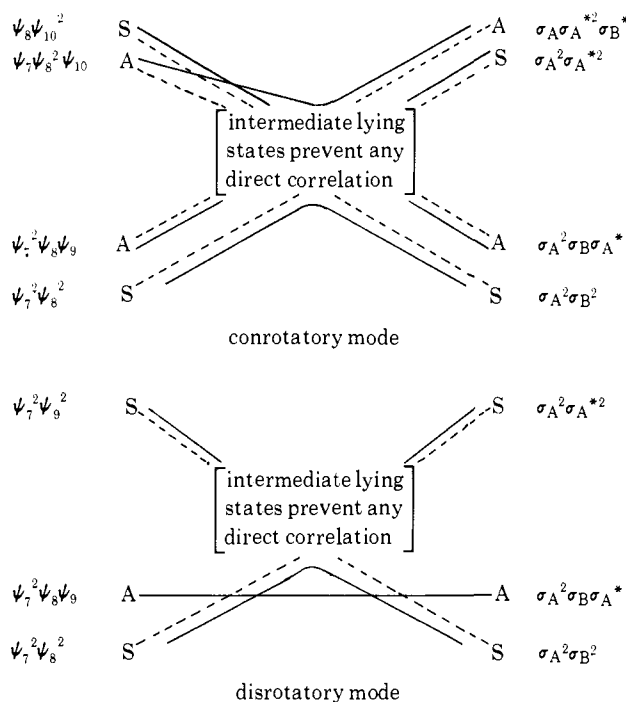
conrotatory operations one obtains the orbital correlation diagram of Chart V. Using the orbital correlation

Chart V. Orbital Correlation Diagram for Reaction II



tions allows the state correlation diagram of Chart VI

Chart VI. State Correlation Diagram for Reaction II



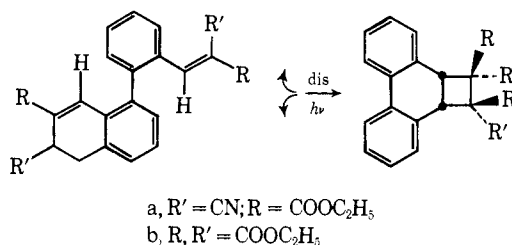
to be generated.

The results of the state correlation diagram (Chart VI) imply that only one reaction is allowed—a *disrotatory* photochemical reaction,¹⁴ a result which appears to be borne out by the *photochemical* work of Tavares and Ploder⁵ who studied the reactions¹⁵ indicated in Scheme III. Such results are of course similar to those obtainable for a simple $2 + 2 = 4q$ cycloaddition classification although once again the dielectrocyclic classification allows one to go *further* and distinguish between the conrotatory and disrotatory modes of the supra-supra reaction.

(14) It may be worthwhile emphasizing here that the π system converts to the cyclized product through the same type of σ state ($\sigma_A^2 \sigma_A^* \sigma_B$) as encountered in the *o*-divinylbenzene. However, in this case the bonding centers are much closer and the cyclic strain less, both of which should enhance the bonding characteristics.

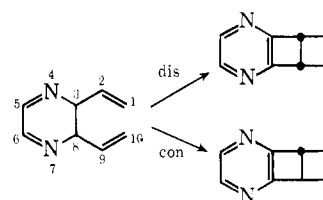
(15) In the case where CN is a substituent, calculations were carried out on the molecules including the substituents as part of the conjugated system. No substantial change was noted for reasonable values of $\beta_{C,CN}$ ($\beta \approx 0.8$) and the essential features of the correlation diagram of Chart VI were obtained.

Scheme III. Experimental Results for Dielectrocyclic Reaction II

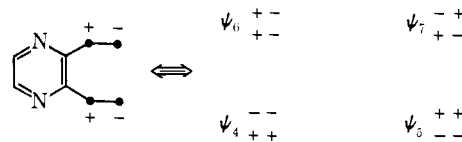


(3) **N-Substituted *o*-Divinylbenzenes.** Since the π -electron region which transforms to the two σ bonds is part of a much larger π -electron system, a substitution (perturbation) at one point might affect the course of the reaction occurring elsewhere in the π -electron system. To investigate this we carried out HMO calculations¹⁶ on the N-substituted homolog of *o*-divinylbenzene indicated in Scheme IV. The signs

Scheme IV. Nitrogen-Substituted Dielectrocyclic Reaction I'

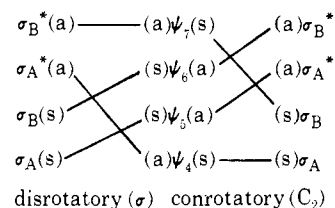


of the coefficients for the π MO's at centers 1, 2, 9, and 10 in 2,3-divinylpyrazine are given in Chart VII.

Chart VII. Coefficients in the π Orbitals of 2,3-Divinylpyrazine

It should be noted that the N substitution *has* indeed altered the relative signs (*cf.* Charts I and VII) and hence the symmetry of the relevant π -molecular orbitals (*cf.* Charts II and VIII). Such a result would of course

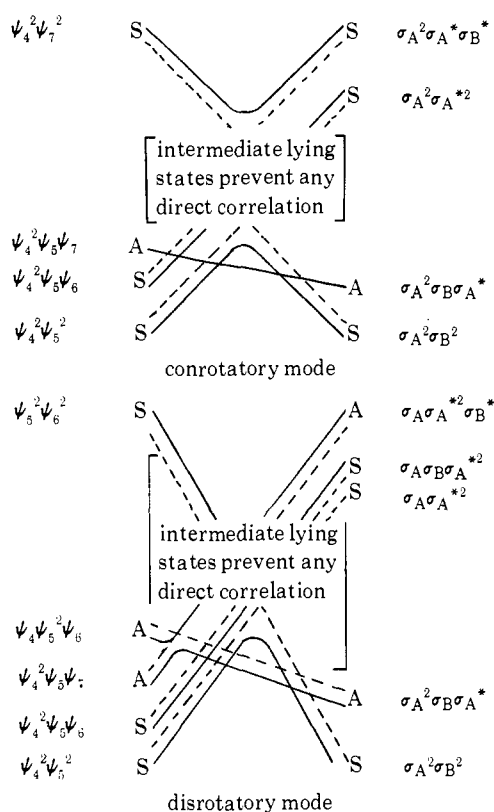
Chart VIII. Orbital Correlation Diagram for Reaction I'



have been missed had one treated this as a simple $2 + 2$ cycloaddition or if the hexatriene orbitals were used as the basis for the dielectrocyclic treatment. Taking the ordering of the σ orbitals to be the same as in the unsubstituted case allows the orbital correlation diagrams to be drawn as in Chart VIII and the state correlation diagrams to be drawn as in Chart IX. The state correlation diagrams of Chart IX indicate that only a conrotatory photochemical dielectrocyclic reaction is allowed, and it involves a second excited state. A similar disrotatory reaction would be permitted *if* the intermediate state, $\psi_4^2 \psi_5 \psi_7$, were omitted. In any case it is clear that the substitution (perturbation) in the aromatic

(16) $\alpha_N = \alpha_C + 1.5\beta_{CC}$; $\beta_{CN} = \beta_{CC}$.

Chart IX. State Correlation Diagram for Reaction I'



ring has altered the products allowed for this reaction from those allowed for the unsubstituted case.

(4) **N-Substituted 2,2'-Divinylbiphenyl.** All the symmetrical tetranitrogen-substituted molecules follow the same pattern as the unsubstituted molecule in part 2 (molecules with adjacent nitrogens were not considered). This pattern also holds for three of the four symmetrical dinitrogen-substituted molecules (4,13-N was not done).

II. Conclusions

Perhaps the most significant point is that the *di-electrocyclic* classification of reactions of the type illustrated in Schemes I and II can, *in principle*, yield more unique information than a simple cycloaddition classification. It is apparent that the use of state correlation diagrams is essential in this treatment and that care must be exercised to ensure that the omission of intermediate states does not materially alter the conclusions. It is also apparent that in some cases the cyclized product states "favored" by the correlation diagram may be relatively unstable if they contain antibonding σ orbitals. Finally, it appears that perturbations in the ring can affect significantly the cyclization and hence a simple 2 + 2 cycloaddition classification is questionable. Hence, it appears possible to change the course and consequently the stereospecificity of reaction by heteroatom substitution at a site well removed from the reaction region.

Acknowledgments. The award of a National Research Council Scholarship to one of us (ECWS) is gratefully acknowledged. Several interesting discussions of this problem with Dr. D. F. Tavares and Dr. R. P. Haseltine are also acknowledged.

Synthesis and Interconversions of $(CH)_{12}$ Hydrocarbons

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Abstract: The cycloaddition of cyclobutadiene to a *cis,trans* mixture of 7,8-dichlorobicyclo[4.2.0]octa-2,4-diene gives a separable mixture of *cis*- and *trans-exo,exo*-3,4-dichlorotetracyclo[4.4.2.0^{2.5}.0^{7.10}]dodeca-8,11-dienes. Treatment of these dichlorides with sodium phenanthrene gives *exo,exo*-tetracyclo[4.4.2.0^{2.5}.0^{7.10}]dodecatetraene, which on pyrolysis at 500° affords *exo*-tricyclo[4.4.2.0^{7.10}]dodecatetraene (**15**). This last hydrocarbon is shown to be identical with the product of thermal rearrangement of *cis,syn,cis*-tricyclo[8.2.0.0^{2.9}]dodeca-3,5,7,11-tetraene (**3**). In ether, irradiation of **15** provides an equimolar mixture of *exo,exo*- and *exo,endo*-tetracyclo[4.4.2.0^{2.5}.0^{7.10}]dodecatetraenes (**14** and **16**); under triplet conditions, however, **15** affords principally tetracyclo[5.3.2.0^{2.5}.0^{6.8}]dodeca-3,9,11-triene (**4**). Partial decomposition of **14** and **16** at 500° revealed that **14** rearranges somewhat more rapidly than **16**; the latter undergoes rearrangement exclusively to give **15**. The mechanistic aspects of these $(CH)_{12}$ interconversions, as well as the thermal behavior of the 3-methyl and 3-chloro derivatives of **14**, are discussed.

The isomeric $(CH)_{12}$ hydrocarbons represent an interesting family of compounds because of the theoretical significance of many of its members and the varied electrocyclic and sigmatropic processes expected of the numerous valence tautomers. Despite these attractive features, chemical investigation in this area has been limited because of the relative unavailability of synthetic

entries to these polyenes. For these reasons, we have been interested in the possibility of developing facile and stereochemically controlled syntheses of several $(CH)_{12}$ isomers.

Prior to this investigation, access to the few known $(CH)_{12}$ hydrocarbons has been gained solely by way of the cyclooctatetraene dimers **1** and **2**.²⁻⁶ Both dimers

(1) National Institutes of Health Postdoctoral Fellow, 1969-1970; The Ohio State University Postdoctoral Fellow, 1969.

(2) [12]Annulene, the monocyclic member of the $(CH)_{12}$ series has recently been synthesized: J. F. M. Oth, H. Rottele, and G. Schröder,