

squares. Correlation coefficients were always 0.998 or greater and usually 0.999.

B. UV Procedure. This method was used with the less reactive substrates because the lower concentrations needed to minimize interference from reaction 4 rendered the NMR method too insensitive. The strong absorption of the dinitrobenzoate moiety, ca. 2.3×10^4 in the 200–260-nm region, was exploited. Absorbances were usually measured at 240 nm at which interference due to the arylcyclopropane was absent. Samples ca. 2×10^{-3} M in substrate were dissolved in the solvent; 2-mL aliquots were sealed in ampules under reduced pressure and immersed in the constant temperature bath. Samples were removed at suitable intervals and transferred, with rinsing of the ampule with hexane, into a separatory funnel so that its total volume was about 40 mL. This was washed twice with 5% aqueous sodium chloride to remove trimethylstannyl 3,5-dinitrobenzoate and made up to volume in a 50-mL volumetric flask. The absorbance was read and the data from six to ten samples were used to compute the rate constant. When applied to the same substrate the UV and NMR methods gave the same results within experimental error.

C. Rapid Reaction Procedure. 1-*p*-Anisyl-3-trimethylstannylpropyl 3,5-dinitrobenzoate was shown initially to have a half-life of solvolysis of about 3 min at 40 °C. In order to obtain rapid sampling the apparatus shown in Figure 3 was used. Enough substrate to make a solution 0.004 M was placed in the addition tube, which was attached in position A. The assembly with solvent in the flask was placed in the constant temperature bath. After temperature equilibration the substrate was added by turning the addition tube to position B. The solvent was stirred until the substrate was completely dissolved before sampling was begun. The stopcock was turned into the position which allowed about 2 mL of solution to be drawn into the syringe. It was then turned into the position shown in the figure and the sample forced through the 2-mm i.d. outlet tube into a vial to which had been added 9 mL of hexane and 2 mL of 5% aqueous sodium chloride, and was then weighed. The resulting solvent mixture was shaken vigorously for 0.5 min and stored in an ice-water bath, if necessary, until it could be weighed again to determine the aliquot size. The layers were separated, the hexane layer was washed again with the saline solution and made up to volume, and the absorbance was read at 247.5 nm.

D. Titrimetric Procedure. A simple titrimetric procedure using a pH meter was initially used for the model compounds. Good first-order rate plots ($r \leq 0.98$) were obtained over 2 half-lives with the following results: 1-phenylpentyl 3,5-dinitrobenzoate, $k = 2.18 \times 10^{-5} \text{ s}^{-1}$ at 100 °C; 4,4-dimethyl-1-phenylpentyl 3,5-dinitrobenzoate, $k = 2.42 \times 10^{-5} \text{ s}^{-1}$ at 100 °C and $8.8 \times 10^{-7} \text{ s}^{-1}$ at 65 °C; $\Delta H^\ddagger = 23 \text{ kcal/mol}$, $\Delta S^\ddagger = -19 \text{ eu}$. Infinity titers were only about 90% of the expected values, presumably owing to reversibility of the solvolysis.

E. Modifications for Model Compounds. Because of the difficulty mentioned above further solvolyses were conducted in the presence

of 2,6-lutidine to drive the reaction to completion, which was indeed observed. The NMR method used with the organostannyl derivatives was adopted with two modifications. A solution of 5% aqueous sodium carbonate was used for the water extraction to remove the 3,5-dinitrobenzoic acid. The peak heights due to the protons of the *tert*-butyl groups in the substrate and of the products, which were trifluoroethyl ether and the olefin formed by elimination, were monitored. These could be separated on the HA-100 instrument because their chemical shifts were 0.90, 0.84, and 0.93 ppm, respectively. For the more reactive *p*-methoxy derivative the special apparatus was used, and aqueous sodium carbonate again used in the extraction process. Proportions of olefin and ester shown in Table III were estimated from the respective *tert*-butyl proton peak heights.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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π, π -Biradicaloid Hydrocarbons. The Pleiadene Family. 3.¹ A Facile Symmetry-Forbidden Thermal Conversion of a Polycyclic Butadiene Moiety to a Cyclobutene

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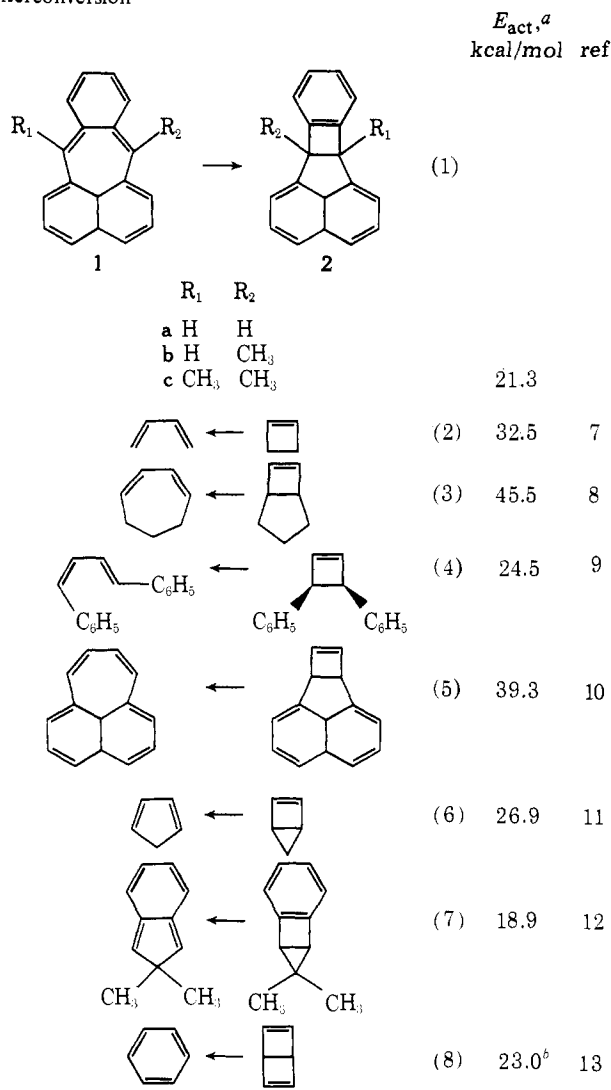
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Abstract: The orbital symmetry "forbidden" thermal electrocyclic ring closure of the "biradicaloid" hydrocarbon 7,12-dimethylpleiadene (**2c**) to 6b,10b-dimethyl-6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (**1c**) proceeds readily below room temperature, $E_{\text{act}} = 21.3 \pm 0.6 \text{ kcal/mol}$, $\log A = 15.6 \pm 0.5 \text{ (s}^{-1}\text{)}$.

Thermal interconversions of butadienes and cyclobutenes generally have a reputation for strict adherence to the orbital-symmetry rules.² We presently report an unusually facile

butadiene \rightarrow cyclobutene thermal ring closure, **1c** \rightarrow **2c**, proceeding along the "forbidden" disrotatory pathway and discuss the factors which make it unique.

Chart I. Selected Examples of Thermal Butadiene–Cyclobutene Interconversion



^a Arrhenius activation energy. ^b Activation enthalpy.

Results

The preparation of dilute (ca. 10^{-4} M) deoxygenated rigid solutions of pleiadenes in solvents such as 3-methylpentane (3-MP) by the low-temperature (-196 °C) two-photon photochemical process $2 \rightarrow 1$ ($2h\nu$) has been described.³ Upon solvent melting (~ -160 °C), the parent **1a** disappears in a few seconds and produces a dimer.³ In striking contrast, the solution of **1c** is stable almost up to room temperature, and its yellowish-green color persists for minutes at 0 °C. The disappearance of **1c** is a strictly first-order process and produces a quantitative yield of **2c** as determined by UV spectroscopy. The solution can then be cooled and reirradiated, and the process repeated many times. A least-squares analysis of the thermal decay in 3-MP solvent yields the reaction parameters $E_{act} = 21.3$ kcal/mol, $\log A = 15.6 \pm 0.5$ (s^{-1}). The cyclization cannot be reversed thermally to a perceptible degree at temperatures up to 200 °C in decalin.

An intermediate behavior is observed for **1b**. Upon warming, its yellowish-green color persists up to about -25 °C. Its decay produces a mixture of **2b** and a poorly soluble additional product or products, presumably dimeric in nature.

Discussion

According to orbital symmetry rules, the “allowed” mode for the thermal electrocyclic butadiene \rightleftharpoons cyclobutene con-

version is conrotatory, and the “forbidden” mode is disrotatory.² The nonconcerted (biradical) analogue of these pericyclic processes is a “semirotatory”^{4,5} opening in which one methylene group, say, on carbon 1, rotates first, producing a geometry at which the cyclic overlap of the atomic orbitals on the four centers involved in the reaction is interrupted between carbons 1 and 4 (this path may well be followed in the triplet state⁵). In the presence of suitable steric constraints, only the disrotatory path remains energetically accessible.⁶ The least objectionable among thermal disrotatory paths may well involve a larger degree of rotation of one of the methylenes than the other in the transition state, but as long as some cyclic overlap of the four AOs is preserved throughout, the path classifies as pericyclic and its topology as disrotatory. Molecular models lead us to believe that the facile transformation **1c** \rightarrow **2c** has no alternative but to follow such a path.

In agreement with the symmetry rules, the reactions which are sterically constrained to the “forbidden” disrotatory path generally exhibit considerably increased activation energies (compare entries 2–5 in Chart I). Only very few cases of cyclobutene to butadiene conversions are known in which the “forbidden” disrotatory path is followed readily at temperatures near ambient, and unlike the process **1c** \rightarrow **2c**, which proceeds in the reverse sense, all of them clearly involve removal of a considerable amount of strain upon passage to the activated complex (cf. entries 6–8 in Chart I).

In the absence of special structural features, the butadiene \rightleftharpoons cyclobutene equilibrium lies far to the left. Instances of thermal butadiene \rightarrow cyclobutene ring closures are known for systems in which the butadiene moiety is relatively destabilized, e.g., by substitution,¹⁴ by conversion to a bisallene,¹⁵ by steric strain,¹⁶ or by incorporation into an *o*-xylylene¹⁷ unit which permits the gain of benzene resonance energy upon conversion to benzocyclobutene. All of these ring closures either have been shown to or are believed to proceed in the “allowed” conrotatory manner.

Our search of the literature failed to reveal any firmly documented case of the presently reported process **1c** \rightarrow **2c**, in which a butadiene moiety is thermally converted to a cyclobutene moiety in the “forbidden” disrotatory fashion at temperatures below 0 °C. The closest precedent apparently is a step which has been postulated as a part of a reaction sequence triggered by irradiation of a [4.4.3]propella-2,4-diene.¹⁸ Although the direction of our reaction, butadiene \rightarrow cyclobutene, is readily accounted for by the relative destabilization of the butadiene moiety upon incorporation into the *o*-xylylene unit similarly as in other cases,¹⁷ the remarkable facility of this “forbidden” reaction requires comment. While it does not necessarily represent a violation of the symmetry rules—we believe that the “allowed” process would be even easier if it were not prevented by steric constraints—it does represent an illustration of the general principle^{3,19} that the practical impact of the rules is limited if the reactant is a biradicaloid species. After all, a reaction is “forbidden” because two bonding electrons of the starting material will reside in nonbonding orbitals when the transition state is reached and will contribute nothing to the total amount of bonding in the molecule.²⁰ If they were almost nonbonding to start with, as would be the case in a biradicaloid species such as *o*-xylylene to a small degree and pleiadene to a larger degree (cf. the low-energy HOMO,HOMO \rightarrow LUMO,LUMO doubly excited state in the latter¹), there will be no great sacrifice involved in reaching the “forbidden” transition state. Stated differently, the butadiene moiety in pleiadene starts to look a little like a 1,4-but-2-enediyl biradical with limited coupling between the electrons at atoms 1 and 4 and those of the 2–3 π bond. In the limit of no coupling, the conrotatory and disrotatory paths are both just as allowed as the reaction of two methyl radicals to give ethane. This argument suggests that

it should be possible to find an essentially continuous range of increasingly facile "forbidden" electrocyclic reactions by making the reactant look more and more like an "ideal" singlet biradical (e.g., going to 2,3-naphthoquinodimethanes instead of *o*-benzoquinodimethanes; cf. ref 5). Alternatively, in the formulation of Dewar²¹ and Zimmerman,²² one notes that the disrotatory transition state for the process $1 \rightleftharpoons 2$ is isoconjugate with benzo[*j*]cyclobut[*a*]acenaphthylene and is therefore considerably less "antiaromatic" and unfavorable than a similar transition state for the interconversion of butadiene and cyclobutene, which is isoelectronic with cyclobutadiene (for an interesting analysis, see ref 23). This viewpoint appears to be inseparable from the one described above: a simple consideration of MO interaction diagrams shows that the same annelation which will produce increased biradicaloid character (small HOMO-LUMO gap) in the "butadiene" will also tend to increase the HOMO-LUMO gap in the corresponding cyclobutadiene which models the transition state.

Another interesting feature of the results is the striking effect of 7 and 12 methyl substitution on the ease of dimerization of **1a**. A 10^{-4} M solution of the parent **1a** produces a dimer completely in a few seconds at -160 °C and the electrocyclic ring closure apparently has no chance to compete. A similar solution of the 7,12-dimethyl derivative **1c** produces no dimer in minutes at 0 °C and the ring closure is the only reaction observed. The singly substituted 7-methyl derivative **1b** exhibits an intermediate behavior. Similar striking suppression of the extreme dimerization tendency of *o*-quinodimethanes by already relatively small amounts of steric hindrance has been found for simpler derivatives of *o*-xylylene.^{12,24}

Experiment Section

3-MP was purified by stirring over sulfuric acid, washing with water and base, and drying with $MgSO_4$, followed by distillation from CaH_2 through a 4-ft steel wool packed column. The distillate was then filtered through a silver nitrate impregnated alumina column.²⁵

Approximately 10^{-4} M solutions of **2c**²⁶ in 3-MP contained in Suprasil cells were degassed thoroughly on a 10^{-6} Torr vacuum line and immersed in liquid nitrogen in a loosely stoppered Dewar vessel with Suprasil windows. The rigid sample was photolyzed using a high-pressure mercury lamp equipped with a water filter and a Schott WG7 filter (cutoff 295 nm). After 15 min of irradiation no starting material was detectable in the UV spectrum of the irradiated region. The cell was then displaced vertically and the irradiation continued. This adjustment was made three times in order to assure that all the starting material was converted to **1c**. The total irradiation time was 60 min. The same technique was used for **2b**²⁶

After irradiation the liquid nitrogen was poured out of the Dewar, the stopper was replaced, a low-temperature thermometer with 0.1 °C divisions, calibrated in an ice-water mixture, was inserted, and the sample was allowed to warm slowly in the residual cool nitrogen vapor. When the temperature was 10 °C below that required for the kinetic run, precooled ethanol was added to the Dewar and a cooling coil, fitted to a special stopper for the Dewar, was immersed into the ethanol. The ethanol bath was kept at the required temperature by pumping cold ethanol through the coil by means of an FTS Systems Multi-Cool Refrigeration unit.

After the temperature stabilized the Dewar was placed into a modified sample chamber of a Cary 17 spectrophotometer and the absorption at 410 nm was measured periodically. At least five points were obtained at each of 18 different temperatures. A computer plot of $\log A/A_0$ vs. time was obtained to determine the rate constant and was linear over at least 3 half-lives (only runs with a correlation coefficient 0.99 or higher were used). The measured values of the rate constants were [standard deviation less than $\pm 4\%$, units of $10^{-2} s^{-1}$,

temperature (°C) in parentheses] 28.0 (3.6₃), 26.2 (3.4₀), 24.7 (2.1₈), 14.1 (-0.4₅), 12.4 (-0.9₆), 11.7 (-1.7₈), 7.2 (-4.9₈), 6.2 (-6.1₂), 6.1 (-6.4₈), 5.5 (-6.8₃), 4.6 (-7.4₇), 4.2 (-8.0₃), 3.4 (-9.5₀), 3.3 (-9.9₈), 2.8 (-11.9₀), 2.5 (-12.5₂), 1.4 (-16.5₉). The Arrhenius activation energy and frequency factors for the reaction were obtained by computer least-squares fitting: $E = 21.3 \pm 0.6$ kcal/mol, $\log A = 15.6 \pm 0.5$ (s^{-1}).

Acknowledgment. This work was supported by NSF Grant CHE 76-02446.

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