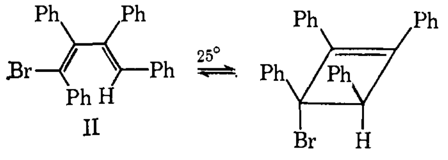
The Influence of Ground-State Conformation on the Rates of Electrocyclic Ring Closure of Sterically Hindered Dienes

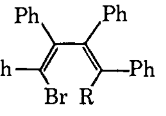
Sir:

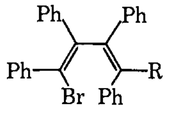
We have previously noted[1] that steric constraints in the hindered diene, *trans*-1-bromo-*cis*-1,2,3,4-tetraphenylbutadiene (II), may play a key role in its remarkably facile ring closure to the cyclobutene valence tautomer I. We now present a combination of kinetic and X-ray structural data on a series of related, nonplanar dienes (II–V) which demonstrates clearly the interdependence of rate of ring closure and diene conformation.

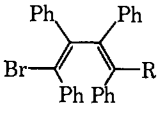


II

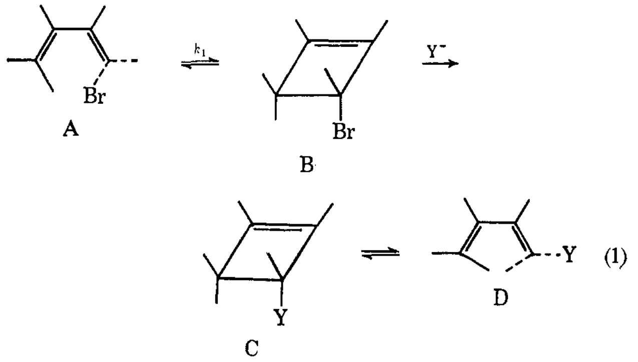
I


IIIa, R = H
b, R = Br


IVa, R = H
b, R = Br


Va, R = H
b, R = Br

To determine rates of ring closure of the dienes we have taken advantage of the fact that the vinylic bromines of II–V are inert toward nucleophilic exchange, whereas cyclization leads to a 3-bromocyclobutene (*cf.* I) in which spontaneous ionization to a delocalized cyclobutenyl cation[1] provides a ready pathway for exchange of Br with any nucleophile present in excess. This is schematically outlined in eq 1 for the generalized case where the rate-determining step, k_1, the ring closure of A to B, has been followed by measuring the incorporation of Y in C and/or D. For temperatures below 150°



(1)

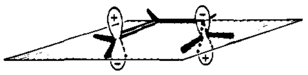
the nucleophile of choice (Y^-) is CH_3MgBr, and for those dienes which require higher temperatures for cyclization, exchange with chloride was used. The latter method ($Y = Cl$) affords less accurate estimates of $\Delta G^{\ddagger}$ but for those cases where both nucleophiles were employed at comparable temperatures, the results were in excellent agreement. The kinetic constants thus obtained are listed in Table I. The data for all but IIIb and IVa were obtained from Grignard exchange by monitoring the appearance of the CH_3 resonances and the error in $\Delta G^{\ddagger}$ is estimated to be 1 kcal or less.[2] Data for $\Delta G^{\ddagger}$ for IIIb and IVa were obtained by Cl^- exchange, accomplished by product isolation and analysis for halogen. Inasmuch as no exchange occurred with IVa after 3 days at 200°, the $\Delta G^{\ddagger}$ is a minimum value, estimated from the limits of detection of the analytical method.[3]

Table I. Kinetic Data for Diene Ring Closure

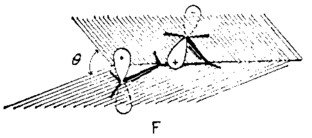
Compd	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]	$\Delta G^{\ddagger}$ [c]
II	19.0 ± 0.6	−15.6 ± 1.7	23.6 ± 0.5
IVb	27.9	−5.1	29.4
IVa			>45[d]
IIIa	26.1	−8.8	28.7
IIIb			37 ± 2[e]
Va	29.5	−4.7	30.9
Vb	20.9 ± 0.4	−8.5 ± 1.4	23.4 ± 0.5

[a] Kilocalories per mole at 25°. [b] Eu at 25°. [c] At 25° unless otherwise specified. [d] At 200° (see text). [e] At 175°.

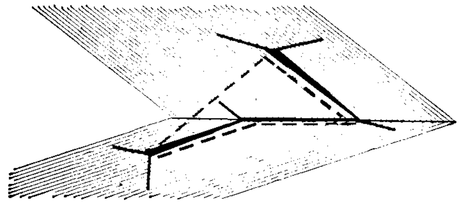
The extensive variation in the energy required for cyclization for the dienes in Table I clearly cannot be attributed to electronic factors,[4] but may well be related to their ground-state conformational requirements. Such a result would not be without precedent; conformational restraints have been demonstrated to have a profound effect on the rate of Diels–Alder cycloadditions where, other factors being equal, adduct formation parallels the accessibility of the required *s-cis* conformation.[5] Though a conformational preference must also be associated with electrocyclic diene closure, consideration of the geometrical requirements for conrotatory bond formation suggests that maximum orbital overlap occurs not in the *s-cis* rotamer E, but in the



E



F



G

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[1] G. A. Doorakian and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 3582 (1968).

[2] The general reliability of this technique can be assessed by a comparison of $\Delta G^{\ddagger}_{\mathrm{II}\rightarrow\mathrm{I}(25)^{\circ}}$ obtained by Grignard exchange (23.8 kcal) to that previously obtained by direct observation[1] (23.6 kcal). The kinetic parameters from ref 1 are used in Table I.

[3] Analyses were performed by Galbraith Lab., Inc., Knoxville Tenn., who estimate detection limits of ±0.1% for Cl in the presence of excess Br.

[4] However, electronic effects due to differing terminal substituents can be significant and will be discussed in detail in a full paper.

[5] B. Eisler and A. Wassermann, *J. Chem. Soc.*, 979 (1953); D. Craig, J. J. Shipman, and R. B. Fowler, *J. Amer. Chem. Soc.*, **83**, 2885 (1961); J. Sauer, *Angew. Chem.*, **79**, 76 (1967); J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

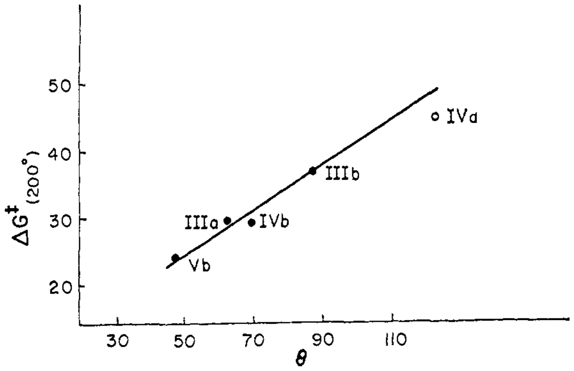

Figure 1. Plot of angle of skew (θ) *vs.* free energy of activation for ring closure ($\Delta G^{\ddagger}_{200°}$) of dienes. θ is defined as 0° for *s-cis* conformation. For comments on IVa, see footnote 10.

cisoid-skew rotamer F. This leads to a transition state for A $\rightleftharpoons$ B with the approximate geometry shown in G, and an estimated skew angle, θ, of ~45° from *s-cis*.[6] Accordingly, $\Delta G^{\ddagger}_{A \rightarrow B}$ for highly substituted dienes should reflect the attainability of G.[7]

To test this premise the ground-state molecular structure of dienes II–V have been investigated by single-crystal X-ray diffraction methods.[8] Table II lists unit-cell data and space-group constants for III–V. In all cases, an examination of the intra- and intermolecular contacts in the crystal structures leads to the conclusion that the particular configuration adopted by the butadiene backbone is a response to intramolecular interactions and is not noticeably affected by interactions with neighboring molecules in the crystal. Thus it is to be expected that the observed structures in the solid state closely resemble those found for the ground state of the molecule in solution. This assumption is strengthened by examination of the solution nmr spectra of the various isomers which may be categorized in a manner analogous to the crystallographic classification.

Table II. Unit Cell, Space Group, and Torsion Angles (θ) for the Substituted Tetraphenylbutadienes

Compd	*a*	*b*	*c*	β, deg	Space group	*Z*	θ, deg
Vb	14.34	11.68	14.08	106.0	C2/c	4	45[b]
IIIa	6.42	7.82	21.93	99.9	Pc	2	60[b]
IVb	12.14	9.47	19.61	98.0	$P2_1/c$	4	66 ± 3
IIIb	10.14	10.29	11.89	72.0[a]	P1	2	86 ± 4
IVa	11.03	20.24	9.74	98.9	$P2_1/c$	4	117 ± 4

[a] α = 96.7°, γ = 80.8°. [b] Error uncertain (probably ±7°) due to disorder.

Table II also lists θ, the angle of skew about the diene central bond. In contrast to unhindered dienes in which θ is invariably 180° (*i.e.*, *s-trans*),[9] the skew angle in III–V ranges from 45 to 120° and allo wsa decisive test of the premise that rates of diene ring closure are closely related to ground-state diene conformation. Figure 1, in which $\Delta G^{\ddagger}_{(200°)}$ is plotted *vs.* θ, demonstrates that such a relationship not only exists, but is reasonably quantitative.[10] Our assumption that $\Delta G^{\ddagger}$ is minimal when θ = 45° implies that $\Delta G^{\ddagger}$ will increase as θ approaches 0°. Though substantiation of this must await the availability of such a compound, we suspect that such *cis*, acyclic dienes will, as a consequence of severe steric interactions, be subject to an unusual amount of ground-state destabilization. This is not the case with dienes II–V, for which equilibration data clearly demonstrate that θ is of major influence on the transition rather than ground state.

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[6] A theoretical calculation of 40° for the optimum torsion angle (θ) has been reported by W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969).

[7] We note that this conclusion is applicable only to those dienes with a substantial barrier to rotation about the central single bond; moderately substituted dienes which lack this barrier lack also the driving force necessary for conrotatory orbital overlap and will ineffectually pass through conformation F.

[8] Structural details and methodology will be reported independently by R. F. Bryan, Department of Chemistry, University of Virginia, Charlottesville.

[9] *Cf.* W. Haugen and M. Traetteberg, *Acta. Chem. Scand.*, **20**, 1726 (1966); A. Almenningen, O. Bastiansen, and M. Traetteberg, *ibid.*, **12**, 1221 (1958); R. A. Beaudet, *J. Amer. Chem. Soc.*, 87, 1390 (1965); R. M. Conrad and D. A. Dows, *Spectrochem. Acta*, **21**, 1039 (1965).

[10] Compound IVa was excluded from the least-squares analysis of Figure 1 inasmuch as it represents an estimated minimum value for $\Delta G^{\ddagger}$(200°). Correlation of this point with the line predicts that cyclization of IVa will require a $\Delta G^{\ddagger}$ of ~50 kcal and is probably not attainable relative to other thermal processes. X-Ray investigation of II, currently in progress by R. F. B., will further test the validity of the relationship between $\Delta G^{\ddagger}$ and θ; Figure 1 predicts a skew angle of ~50° for II, a value not obvious from a consideration of intramolecular contacts based on space-filling models.

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Mutual Ligand–Metal Ion Oxidation State Stabilization in a System Containing a Quadridentate Macrocycle Analogous to the Porphyrin Ring

Sir:

Metal complexes of certain quadridentate macrocyclic ligands, which may serve as models for similar naturally occurring systems,[1] are expected to exhibit unusual redox behavior. Notable interdependence between ligand and metal ion in the electrochemistry of such complexes may be of particular importance in providing the basic foundations that are necessary in order to understand the more complicated native systems. Earlier work shows promise in this regard. The studies of Endicott, *et al.*,[2] show that polarographic reduction of the $[\mathrm{Cu^{II}}(trans\text{-}[14]\mathrm{diene})]^{2+}$ ion yields the Cu(I) complex of essentially unchanged coordination geometry, despite the contrary stereochemical proclivity of the product ion. Olson and Vasilevskis[3] have reported Ni(I) and Ni(III) in similar studies.

We report here the presence of unusual oxidation states together with evidence for extensive ligand–metal ion interdependence in the polarographic studies of the Co, Ni, and Cu complexes of tetrabenzo[*b,f,j,n*,]-[1,5,9,13]tetraazacyclohexadecine, structure I, hereafter called TAAB.[4] The most dramatic characteristic of

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[1] D. H. Busch, "Fasciculus Extraordinarius Alfred Werner, 1866–1919," Verlag Helvetica Chimica Acta, Basel, 1967, p 174.

[2] J. M. Palmer, E. Papaconstantinou, and J. F. Endicott, *Inorg. Chem.*, **8**, 1516 (1969).

[3] D. C. Olson and J. Vasilevskis, *ibid.*, **8**, 1611 (1969).

[4] G. A. Melson and D. H. Busch, *J. Amer. Chem. Soc.*, **86**, 4834 (1964).