and differential scanning calorimetry show this sample to be essentially all in the low-melting form. When heated at 105–140° the solid → solid transformation of the low- to high-melting forms of binaphthyl occurs and an optimum distribution of + seed crystals promotes the solid state resolution. At 105° a final rotation of $[\alpha]_D$ +220° (benzene) is attained in 12 days.

The last two experiments described are made possible by the polymorphic phase properties of binaphthyl. These are: (1) a racemic *R,S* compound, mp 145° (*i.e.*, the "low-melting form") which is easily obtainable at room temperature by crystallization from pentane but is metastable above *ca.* 90°; and (2) a eutectic type mixture of separate crystals of *R* and *S* enantiomers, mp 159°[9] (*i.e.*, "high-melting form") which is the stable phase above *ca.* 90° and which is produced readily either by solidification of the metastable melt or by maintaining the low-melting form at 105–145°. The results show that resolutions are possible during the following phase changes: transformation of the supercooled melt to high-melting form; transformation of the low-melting form to melt and then to the high-melting form; and the direct solid state transformation of the metastable low-melting form to the stable high-melting form.

These resolutions also depend on the interconversion of enantiomers which occurs rapidly in the melt and apparently also at the interface of the solid → solid phase transformation. Autocatalytic growth of predominantly one enantiomeric solid is prompted by seed crystals which have been added (or otherwise happen to develop first). Even though the two enantiomers have equivalent free energy, the growth of one may be kinetically induced by the presence of only one enantiomeric surface. The kinetic details of this type of resolution are complex (*e.g.*, see Figure 1). However, it is clear that the highly stereospecific character of the solid state promotes the development of optically active binaphthyl even at temperatures near 150° where the half-life for racemization in the melt is about 0.5 sec.

This solid state resolution illustrates some possibilities of specific melt → solid and solid → solid reactions. The solid → solid resolution definitely depends on the special properties of the binaphthyl phase system (*i.e.*, on the existence of a metastable racemate which transforms into a eutectic-type form). However, the growth of one of two rapidly interconverting enantiomers by spontaneous crystallization from a melt or solution[10] may be more general than commonly supposed and the method may be especially useful with compounds difficult to resolve by other means. It is also of interest that this example of binaphthyl resolution is an illustration of a hypothetical scheme for the selection of one enantiomorph in the genesis of optically active molecules.[11]

Acknowledgments. Financial aid from the National Research Council of Canada and the Air Force Office of Scientific Research (U.S.) is gratefully acknowledged. We thank the Alfred P. Sloan Foundation for a fellowship (to R. E. P.) and the National Research Council and the H. R. MacMillan Family Fund (University of B. C.) for fellowships (to K. R. W.).

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(9) In this eutectic system of (*R*)- and (*S*)-binaphthyl, the melting points of samples with any per cent composition are experimentally the same (*ca.* 159°). This is because a very rapid development of racemic melt depresses the melting point of resolved or partially resolved binaphthyl to that of the 50% *R*-50% *S* optically inactive mixture (mp 159°). The equilibrium melting point of pure *R* (or *S*) compound is unobtainable.

(10) For spontaneous resolution from solution, Havinga has described the necessary conditions and presented the example of spontaneous deposition of optically active methylethylallylanilinium iodide; see E. Havinga, *Biochim. Biophys. Acta*, **13**, 171 (1954). Partial resolutions of rapidly interconverting enantiometers have also been achieved by mechanical separations of single crystals: A. C. D. Newman and H. M. Powell, *J. Chem. Soc.*, 3747 (1952). Resolution of optical isomers by crystallization procedures is reviewed by R. M. Secor, *Chem. Rev.*, **63**, 297 (1963).

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Received November 5, 1970

Thermal Reorganization of *cis*-Bicyclo[6.2.0]deca-2,4,6-triene. Energetics of Allowed and Nonallowed Thermal $6\pi + 2\sigma \rightarrow 8\pi$ Electrocyclic Reactions

Sir:

Recently, a number of groups[1–7] have considered the important question of the energetic advantage of allowed relative to related nonallowed thermal electrocyclic reactions.[8] A major difficulty encountered in the problem concerns the fact that nonallowed processes are generally not observed and therefore only a minimum energy difference between alternate pathways can be obtained. We now report a slightly different approach to this problem which leads to a considerably larger estimate for the value for $6\pi + 2\sigma \rightarrow 8\pi$ electrocyclic reactions than previously reported.[5]

When *cis*-bicyclo[6.2.0]deca-2,4,6-triene (**1**)[9] was heated at 154° (1% (v/v) in octane) a single product, **3**, was initially observed. The structure of **3** was assigned on the basis of its uv (λ_{max}^{hexane} 259.5 nm (ϵ 3700)) and nmr (CCl_4, τ 3.91–4.48 (6 H, olefinic), 7.33 (d, 1 H, diallylic bridgehead, J = 18 Hz), 7.53–8.03 (3 H, allylic), 8.75–9.03 (2 H, methylene)) spectra and catalytic hydrogenation (3 mol equiv) to >94% *trans*-decalin.

The almost exclusive formation of a trans-fused product, **3**, from **1** is in marked contrast to the thermal behavior of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**5**) which affords *cis*-8,9-dihydroindene as the major product.[10] A reasonable mechanism for the former conversion, which is analogous to mechanisms suggested for the rearrangements of **6**[11] and of 9,9-dialkyl derivatives of

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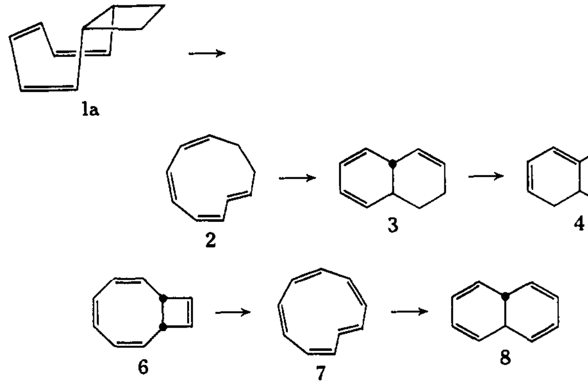
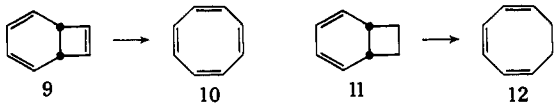
Scheme I

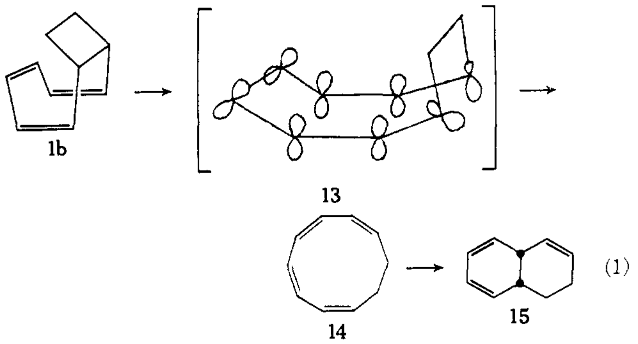


5,[12] is given in Scheme I. The *a priori* possibility that **3** is formed by an initial ${}_\pi4_s + {}_\sigma2_a + {}_\sigma2_s$ hydrogen migration from C-9 to C-5 in conformation **1b** to produce *cis,cis,trans,cis*-1,3,6,8-cyclodecatetraene, followed by a 1,5-hydrogen shift and ring closure,[13] is excluded by the observation that the *9,9,10,10-d*$_4$ derivative of **1**[14] is rearranged (within the limits of detection by nmr spectroscopy) solely to the *1,1,2,2-d*$_4$ derivative of **3**.[15] Upon further heating, **3** is converted (presumably *via* a 1,5-hydrogen shift) to **4**,[16] which is stable to further isomerization under the reaction conditions.[17]

The kinetics for the conversion of **1** to **3** (1% (v/v) in octane) were measured at 131.6, 154.0, and 170.3° and $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were calculated to be 32.2 ± 0.2 kcal/mol and −3.4 eu, respectively. Interestingly, the value of $\Delta H^{\neq}{}_{6\rightarrow8}$[11] is 7 kcal/mol less than $\Delta H^{\neq}{}_{1\rightarrow3}$, the same amount by which $\Delta H^{\neq}{}_{9\rightarrow10}$[18] is less than $\Delta H^{\neq}{}_{11\rightarrow12}$.[19] This is also equal to the increase in *angle strain* in going from cyclobutane to cyclobutene[20] and suggests that the isomerization of **6** is faster than that of **1** not because of any incipient aromaticity in the transition state leading to a 10π intermediate, **7**, but (at least in part) because of release of angle strain.

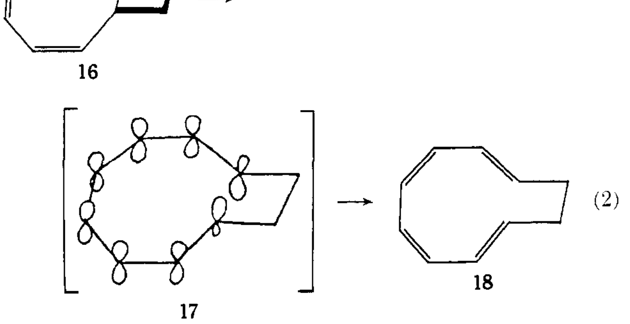


We also prepared the cis isomer of **3**, **15**,[21] by the photolysis of **1** or **3**[22] and showed it to be stable at 174°. A very small glpc peak with the retention time of **15** was detected (by digital integration) in the thermal reorganization of **1**; from the appropriate peak area ratios at 131.6, 154.0, and 170.3° one can calculate that $\Delta G^{\neq}{}_{154°}$ (and, less precisely, $\Delta H^{\neq}$) for the disrotatory opening[23] of **1** to **14** is at least 4 kcal/mol[24] greater than that for the reorganization of **1** to **3**.



Ideally, it would be of considerable interest to know the "intrinsic" energy differences between related allowed and nonallowed processes, *i.e.*, the differences in the unstrained binding energies (UBE$^{\neq}$) of the reacting bonds in the respective activated complexes.[2] Implicit in this comparison are the conditions that the overlap integrals for the reacting orbitals and the strain energies be nearly equivalent in the activated complexes of the two pathways. These two conditions are rarely met in practice but a reasonable estimate can nevertheless be made in the present case.

Thus, by comparing reaction 1 with the "allowed" interconversion of **16** and **18** (for which $\Delta H^{\neq} \approx 15$ kcal/mol),[9] it can be shown that $\text{UBE}^{\neq}{}_{17} - \text{UBE}^{\neq}{}_{13} > \Delta H^{\neq}{}_{(1)} - \Delta H^{\neq}{}_{(2)}$ if there is an increase in strain on going from **16** to **17** and a decrease in strain on going from **1** to **13**. The former condition is probably met but the latter is probably not since **13** is related to the less stable folded conformation, **1b**, of **1**. Nevertheless, it seems unlikely that the strain in **13** exceeds that in **1** (*i.e.*, **1a**) by more than a few kilocalories per mole. We, therefore, conclude that the "intrinsic" energy difference between allowed and nonallowed thermal



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(14) We thank Dr. L. J. Baccei for a sample of 1,2-dibromoethane-d_4 (96% d_4 and 4% d_3) used in this synthesis.

(15) The nmr spectrum of this compound (in CCl$_4$) showed, in addition to a complex multiplet for six olefinic protons, *only* a slightly broadened AB quartet at τ 7.30 and 7.87 (H-9 and H-10, J_{AB} = 18.4 Hz).

(16) Spectral data were: uv λ_{max}^{hexane} 301.5 nm (ε 12,600); nmr (CCl$_4$) multiplets for five olefinic (τ 3.78–4.51), five allylic (7.16–8.06), and two methylene (8.06–8.84) protons; catalytically hydrogenated to a 2:1 mixture of *cis*- and *trans*-decalin.

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(23) Ring opening is assumed to be the slow step due to the relatively rapid rate of closure of *all-cis*-1,3,5,7-cyclononatetraene: (a) P. Radlick and G. Alford, *J. Amer. Chem. Soc.*, **91**, 6529 (1969); (b) G. Boche, H. Böhme, and D. Martens, *Angew. Chem., Int. Ed. Engl.*, **8**, 594 (1969); (c) S. Masamune, P. M. Baker, and K. Hojo, *Chem. Commun.*, 1203 (1969); (d) A. G. Anastassiou, V. Orfanos, and J. H. Gebrian, *Tetrahedron Lett.*, 4491 (1969).

(24) A correction for a statistical factor of 2 has been included in this calculation. It should be recognized that **15** (if actually formed) may arise by a nonconcerted mechanism; this is therefore a *minimum* activation enthalpy difference for the "nonallowed" concerted process.

$6\pi + 2\sigma \rightarrow 8\pi$ electrocyclic reactions probably amounts to at least 18–20 kcal/mol, a figure substantially larger than the previously suggested minimum value of 11–12 kcal/mol.[5,25]

Acknowledgment. We are pleased to acknowledge the support of this work by the National Science Foundation. Samples of cyclooctatetraene were kindly provided by Badische Anilin-und Soda-Fabrik AG.

(25) It is possible that the transformation to the "nonallowed" system (ref 5) actually occurs *via* allowed hydrogen shifts from *all-cis*-2,4,6,8-decatetraene. We acknowledge a stimulating discussion with Professor W. R. Roth concerning this point.

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Reaction between Azide Ion and $[\mathrm{Ru(bipy)_2(NO)Cl}]^{2+}$

Sir:

The preparation of a series of cis complexes $[\mathrm{Ru(AA)_2(NO)X}]^{3+}$ {AA = 2,2′-bipyridine and 1,10-phenanthroline; X = $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{NO_2^-}$, and pyridine} was reported recently.[1,2] In the complexes, coordinated nitrosyl behaves chemically as $\mathrm{NO^+}$ since reaction with hydroxide ion gives the corresponding nitro complexes.

$$[\mathrm{Ru(AA)_2(NO)X}]^{3+} + 2\mathrm{OH^-} \longrightarrow [\mathrm{Ru(AA)_2(NO_2)X}]^+ + \mathrm{H_2O} \quad (1)$$

We find that the reactivity of the nitrosyl as $\mathrm{NO^+}$ extends to a variety of nitrogen bases, including azide ion. In aqueous solution, a stoichiometric amount of $\mathrm{N_3^-}$ (3×10^{-3} *M*) reacts with $[\mathrm{Ru(bipy)_2(NO)Cl}]^{2+}$ (3×10^{-3} *M*) according to

$$\mathrm{H_2O} + \mathrm{Ru(bipy)_2(NO)Cl^{2+}} + \mathrm{N_3^-} \longrightarrow \mathrm{Ru(bipy)_2(OH_2)Cl^+} + \mathrm{N_2} + \mathrm{N_2O} \quad (2)$$

The aquo complex has been identified spectrophotometrically, and nitrogen and nitrous oxide have been identified by mass spectrometry. The reaction of $\mathrm{N_3^-}$ with $\mathrm{HNO_2}$ apparently involves the formation of a nitrosyl azide intermediate, $\mathrm{N_4O}$,[3] but no evidence for the existence of $[\mathrm{Ru(bipy)_2(N_4O)Cl}]^+$, $[\mathrm{Ru(bipy)_2(N_2O)Cl}]^+$, or $[\mathrm{Ru(bipy)_2(N_2)Cl}]^+$ has yet been obtained.

The rate law for the reaction in solutions containing either excess acid or excess azide ion is

$$\frac{-\mathrm{d}[\mathrm{Ru(bipy)_2(NO)Cl^{2+}}]}{\mathrm{d}t} = k[\mathrm{Ru(bipy)_2(NO)Cl^{2+}}][\mathrm{N_3^-}]$$

At 25.0° in 0.5 *M* lithium chloride, *k* is 32 ± 4 M^{-1} $\mathrm{sec^{-1}}$. $\mathrm{Ru(bipy)_2Cl_2}$ is *not* observed as a product of the reaction in 0.5 *M* LiCl.

Reaction 2 is analogous in the opposite sense to the nitrosation of azidopentaamminecobalt(III) studied by Haim and Taube[4] (reaction 3), since the nitrosating

$$\mathrm{H_2O} + \mathrm{Co(NH_3)_5N_3^{2+}} + \mathrm{NO^+}\ (\text{or } \mathrm{H_2NO_2^+}) \longrightarrow \mathrm{Co(NH_3)_5OH_2^{3+}} + \mathrm{N_2} + \mathrm{N_2O} \quad (3)$$

group is coordinated, and $\mathrm{N_3^-}$ free. When carried out in nonaqueous solvents using $\mathrm{NO^+ClO_4^-}$ as the nitrosating agent, reaction 3 has led to labile solvent complexes $\mathrm{Co(NH_3)_5S^{3+}}$ {S = triethyl phosphate, sulfolane, etc.} which have proven useful as synthetic intermediates.[4-7]

Reaction 2 can also be carried out in nonaqueous solvents, and it appears to be as synthetically useful for the ruthenium complexes as reaction 3 is for the cobalt complexes. A stoichiometric amount of sodium azide suspended in acetonitrile rapidly converts $[\mathrm{Ru(bipy)_2(NO)Cl}]^{2+}$ into the acetonitrile complex with gas evolution

$$\mathrm{CH_3CN} + \mathrm{Ru(bipy)_2(NO)Cl^{2+}} + \mathrm{N_3^-} \longrightarrow \mathrm{Ru(bipy)_2(NCCH_3)Cl^+} + \mathrm{N_2} + \mathrm{N_2O} \quad (4)$$

The complex has also been prepared by refluxing $\mathrm{Ru(bipy)_2Cl_2}$ in acetonitrile.[8] The same reaction in acetone apparently gives the acetone complex, $[\mathrm{Ru(bipy)_2(OC(CH_3)_2)Cl}]^+$ [$\lambda_{\max}$ 511 ($\epsilon \sim 7250$) and 359 nm ($\epsilon \sim 7850$)]. The coordinated acetone molecule is labile and addition of excess chloride ion, pyridine, or water gives $\mathrm{Ru(bipy)_2Cl_2}$, $[\mathrm{Ru(bipy)_2(py)Cl}]^+$, and $[\mathrm{Ru(bipy)_2(OH_2)Cl}]^+$, respectively, within a few minutes at room temperature.

Reactions analogous to (2) and (4) also occur for $[\mathrm{Ru(bipy)_2(NO)NO_2}]^{2+}$, and several complexes of the type $[\mathrm{Ru(bipy)_2(NO_2)X}]$ have been isolated. Initial experiments indicate that the entire series of complexes $[\mathrm{Ru(AA)_2(NO)X}]^{3+}$ behave chemically as a controlled source of nitrosonium ion.

Acknowledgments. Acknowledgments are made to the UNC Materials Research Center through Contract No. SD-100 with the Advanced Research Projects Agency, the University Research Council of the University of North Carolina, and the National Science Foundation through Grant No. GY-7311.

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[9] National Science Foundation Undergraduate Research Participant, Summer, 1970.

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A Novel Synthesis of 3-Substituted Pyridines from Pyridine

Sir:

While a wide variety of 3-substituted pyridines and their derivatives find many important applications, *e.g.*, in biological studies,[1] insecticide,[2] and anticorrosion formulations,[3] as intermediates in organic and pharmaceutical synthesis, and in mechanistic investigations,[4] the preparation of these compounds has been a problem. The direct alkylation, aralkylation, or arylation at the 3 or 5 position of the pyridine ring has been particularly difficult.[4,5] Thus, the alkylation

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