half its former magnitude in the case of acetone; it is not certain whether or not the latter is outside the limits of experimental error.

This suggests that HF_2^- may in general have an acid catalytic power considerably inferior to that of HF. This would be consistent with the expected greater difficulty of removing a proton from between two electronegative fluorine atoms in HF_2^- than from just one such atom in HF. It also agrees with the fact that, although basic catalysis by F^- is common,[2,9] no base-catalyzed term in $[F^-]^2$ has ever been detected;[2,9] the latter would correspond to basic catalysis by the conjugate base of HF_2^-, and, if general acid catalysis by HF_2^- were to operate in A2 reactions such as the iodination of acetone and acetylacetone, then the conjugate base of this acid would have to serve as the general base in the second steps of these processes.

(9) R. P. Bell, J. A. Fendley, and J. R. Hulett, *Proc. Roy. Soc.* (London), **A235**, 453 (1956); J. R. Hulett, *ibid.*, **A251**, 274 (1959); *J. Chem. Soc.*, 468 (1960).

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An Estimate of the Relative Rates of Conrotatory *vs.* Disrotatory Electrocyclic Ring Opening

Sir:

A quantitative estimate for the difference in energy between the symmetry-allowed and -forbidden pathways for a thermal electrocyclic cyclobutene reaction has recently been reported by Braumann and Golden.[1] Their value of ~15 kcal, in favor of the Woodward–Hoffmann-predicted[2] conrotatory mode, was based on an estimate of ground- and transition-state strain energies, and they correctly pointed out that, for compounds with no added strain for either pathway, only the allowed product can be detected by conventional techniques. In principle, however, it should be possible to obtain a quantitative evaluation for unstrained (or equally strained) compounds by product determination in a cyclobutene–butadiene isomerization in whichrever sibility has been established at some temperature at which the rate constants are known. We now report the results of such an experiment.

cis-3,4-Dimethyltetraphenylcyclobutene (*cis*-I, nmr: 20 phenyl protons at δ 6.7–7.7, 6 methyl protons at δ 1.91) was obtained in 82% yield from the reaction of 3,4-dibromotetraphenylcyclobutene[3] with excess CH_3MgBr in ether. The three geometrical isomers of 1,4-dimethyl-1,2,3,4-tetraphenylbutadiene were prepared by methylation of the appropriate anion generated by the action of BuLi on *cis,cis*-1,4-dibromo-1,2,3,4-tetraphenylbutadiene[4] under varying conditions.[5] Their properties are summarized in Table I.

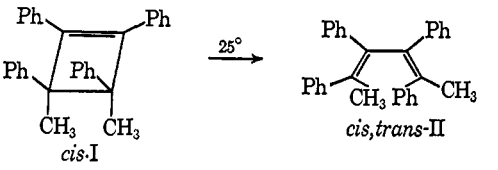
(1) J. I. Braumann and D. M. Golden, *J. Amer. Chem. Soc.*, **90**, 1920 (1968).
(2) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).
(3) H. H. Freedman and G. A. Doorakian, *Tetrahedron*, **20**, 2181 (1964).
(4) H. H. Freedman, *J. Org. Chem.*, **27**, 2298 (1962).
(5) Details of these and similar reactions will be given in a paper describing the preparation and rearrangements of the 1,2,3,4-tetraphenylbutadienyl mono- and dianions.

Table I. Properties of the 1,4-Dimethyl-1,2,3,4-tetraphenylbutadienes (II)[a]

Isomer	Mp, °C	Nmr, δ_{CH_3}[b]	% at equilibrium[c]
cis,cis	207–208.5	2.40[d]	61.0 ± 1
cis,trans	156–157	1.98,[e] 2.18[e]	36.8 ± 1
trans,trans	168–170	1.89[d]	2.2 ± 1

[a] All new compounds gave satisfactory analyses. [b] In $CDCl_3$; measured in parts per million. [c] Accomplished by reversible protonation of the anions generated from either *cis,trans*- or *cis,cis*-II by potassium *t*-butoxide in DMSO–THF at 25°. [d] Six-proton singlet. [e] Three-proton singlet.

In solution, at room temperature, *cis*-I undergoes the expected, solvent-independent, conrotatory ring opening with complete conversion to *cis,trans*-II, the absence

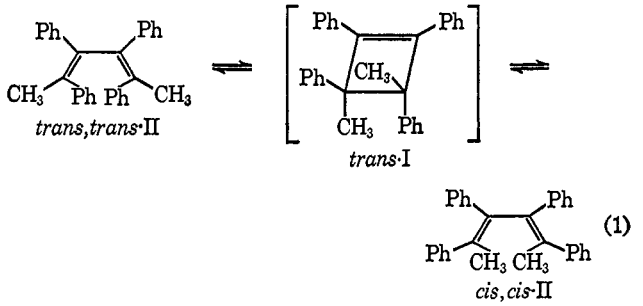


cis-I — *cis,trans*-II

of disrotatory isomers, *cis,cis*- and *trans,trans*-II, being evident from the nmr spectrum. The first-order rate constants and activation parameters for *cis*-I → *cis,trans*-II were determined in CCl_4–pyridine solution. Over the temperature range 26–55° the rate constants varied from $(1.89 \pm 0.1) \times 10^{-5}$ to $(7.43 \pm 0.1) \times 10^{-4}$ sec^{-1}, yielding $\Delta H^{\pm} = 24.1 \pm 0.5$ kcal/mol, $\Delta S^{\pm} = 0.5 \pm 1.5$ eu, and $\Delta G^{\pm} = 24.0 \pm 0.5$ kcal/mol.

Reversibility in a cyclobutene–butadiene electrocyclic reaction can be demonstrated by obtaining the same equilibrium distribution of diene and cyclobutene starting with either component.[6] Alternatively, in the typical case where the equilibrium concentration of cyclobutene is unobservable, reversibility can be inferred if thermal geometrical isomerization of the dienes occurs only between conrotatory isomers to give an equilibrium distribution which is demonstrably different from the normal thermodynamic distribution of isomeric dienes. Though this latter approach may have an element of ambiguity, it is a reasonable postulate, amply supported by the following data.

In pyridine solution at temperatures greater than 100°, both *trans,trans*- and *cis,cis*-II are equilibrated reversibly to the complete exclusion of other products. This is in decided contrast to the thermodynamic distribution of the diene isomers (Table I) and indicates (eq 1) that this thermal equilibration is occurring by both



trans,trans-II ⇌ *trans*-I ⇌ *cis,cis*-II (1)

(6) *Cf.* G. A. Doorakian and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 3582 (1968).

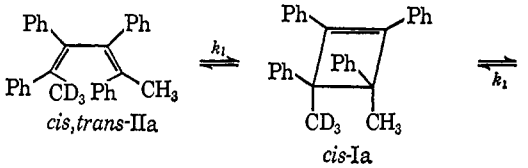
Table II. Kinetic and Thermodynamic Data for Equations 1 and 2 at 125 ± 1°

Reaction[a]	$k_1 \times 10^5$ [b]	K_{eq}	$\Delta H^{\ddagger}$ [c]	$\Delta S^{\ddagger}$ [d]	$\Delta G^{\ddagger}$ [c]
Eq 1	6.7 ± 0.1	~17	25.3 ± 0.2	−14.5 ± 0.4	31.0 ± 0.5
Eq 2	2.3 ± 0.1	1.00	29.2 ± 0.1	−6.5 ± 2.5	31.9 ± 0.5

[a] In 1:1 CCl_4–pyridine. [b] k_{obsd} in sec^{-1}. [c] kcal/mol. [d] Entropy units.

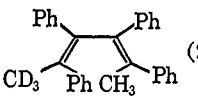
conrotatory ring-opening modes of the as yet unknown cyclobutene, *trans*-I. Table II lists representative rate and equilibrium constants and the derived activation data for eq 1 as obtained by nmr techniques.

The observation of a similar reversible electrocyclic process involving *cis*-I requires the labeling of *cis,trans*-II in order to distinguish between the two allowed, energetically degenerate, ring-opening modes. This was accomplished by the synthesis of *cis,trans*-IIa,[7] the *cis*-1-trideuteriomethyl analog of *cis,trans*-II. When heated in solution at temperatures above 110°, *cis,trans*-IIa equilibrates with *trans,cis*-IIa, most plausibly *via cis*-Ia, as shown in eq 2. In the absence of an observable steric isotope effect,[8] K_{eq} for the IIa isomers



cis,trans-IIa

cis-Ia



(2)

trans,cis-IIa

must be equal to 1.00 at all temperatures. This is confirmed by noting that the simultaneous decrease in the intensity of the δ 2.18 resonance is paralleled by the appearance and growth of the δ 1.98 resonance until, within our limits of detection, their intensities are equal. As before, the intermediacy of cyclobutene in eq 2 is strengthened by the complete absence of disrotatory products.

Rate and activation data for the interconversion of the *cis,trans*-dienes are included in Table II. From the difference in $\Delta G^{\ddagger}$ for *cis*-I → *cis,trans*-II (24.0 kcal/mol at 125°) and $\Delta G^{\ddagger}$ for *cis,trans*-IIa → *trans,cis*-IIa (31.9 kcal/mol), we obtain (assuming no deuterium isotope effect) ΔG° = 7.9 kcal/mol for *cis-trans*-II ⇌ *cis*-I. We are not aware of any experimental technique which would allow direct detection of so minute a concentration of *cis*-I, yet the knowledge that, in fact, it is present permits us to evaluate the relative energetics of the alternate electrocyclic pathways in its thermal isomerization.

A sealed nmr tube containing a 30% (by weight) solution of *cis,trans*-II in CCl_4–pyridine was heated at 124° and its nmr spectrum monitored under instrumental conditions which would have revealed 1% of disrotatory product, *cis,cis*-II. After 51 days there was no detectable change in the spectrum and *cis,trans*-II was recovered quantitatively from the somewhat darkened solution. Since the rate constant for ring opening of *cis*-I can be calculated to be 0.6 sec^{-1} at 124°, the total number of ring openings for each molecule for this time interval is 2.6×10^6. Inasmuch as <1% of disrotatory product was formed, we conclude that there is less than one symmetry-forbidden ring opening for 2.6×10^8 allowed ring openings. Thus, despite the fact that steric interactions in the transition states in *cis*-I are reasonably similar for all possible pathways of ring opening, the predicted conrotatory mode[2] is favored by an absolute minimum of 15.3 kcal,[9] in agreement with ref 1.

(7) Prepared in 85% yield by the reaction of CD_3I with the anions generated from *cis*-1-bromo-*trans*-4-methyl-1,2,3,4-tetraphenylbutadiene by BuLi in ether at 0°. Its properties were identical with those of *cis,trans*-II except for the absence of the δ 1.98 resonance in its nmr spectrum.

(8) In agreement with J. L. Coke and M. C. Mourning, *J. Org. Chem.*, 32, 4063 (1967).

(9) It is pertinent that even if process 2 were allowed to proceed at 125° for a period of 1 year, and still yielded no disrotatory products, then the minimum for $\Delta G^{\ddagger}$ would be increased by less than 2 kcal. Variants of such an experiment are under consideration.

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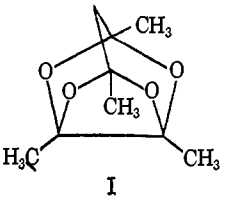
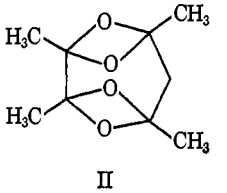
A Novel Heterotricyclic Ring System

Sir:

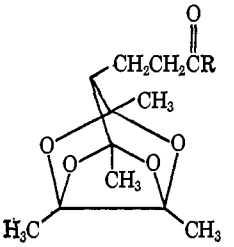
We have found that the acid-catalyzed interaction of 1,2- and 1,3-diketones leads to unique 2,4,6,8-tetraoxatricyclo[3.3.1.$0^{3,7}$]nonanes. Thus, the reaction of molar quantities of 2,3-butanedione and 2,4-pentanedione in the presence of 250 ml of 10% aqueous sulfuric acid for 1–3 days at 0–25° produced a 60–80% yield of 1,3,5,7-tetramethyl-2,4,6,8-tetraoxatricyclo[3.3.1.$0^{3,7}$]nonane (I), mp 135–136°, bp 183°. *Anal.* Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58; mol wt, 186. Found: C, 57.88; H, 7.45; mol wt, 187 ± 2. With reaction times varying from several hours to several months, many other combinations of diketones were shown to react similarly (Table I), thereby demonstrating the generality of this type of reaction.



I



II



IIIa, R = OCH_3
b, R = OH
c, R = NH_2