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
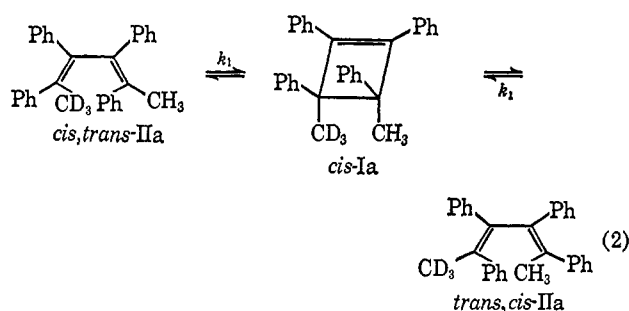
must be equal to 1.00 at all temperatures. This is confirmed by noting that the simultaneous decrease in the intensity of the δ 2.18 resonance is paralleled by the appearance and growth of the δ 1.98 resonance until, within our limits of detection, their intensities are equal. As before, the intermediacy 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) $\Delta G° = 7.9$ 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

(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).

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 × 10⁶. Inasmuch as <1% of disrotatory product was formed, we conclude that there is less than one symmetry-forbidden ring opening for 2.6 × 10⁸ 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.

(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[3.3.1.0³,⁷]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.-1.0³,⁷]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.
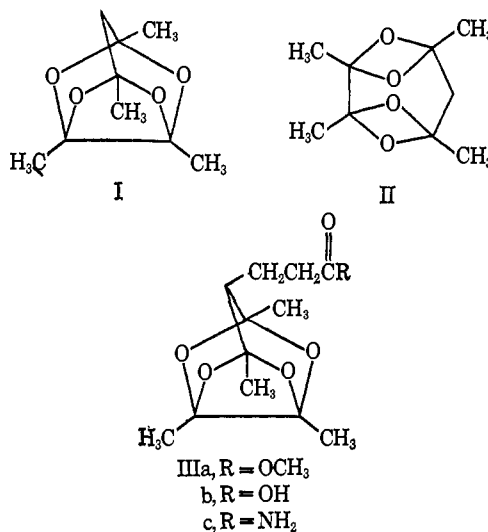

I

II

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

Table I. Heterotricyclononanes

$$R_3\overset{OO}{\overset{||\,||}{C\,C}}R_7 \;+\; R_1\overset{O}{\overset{||}{C}}CHR_9\overset{O}{\overset{||}{C}}CH_3 \longrightarrow$$

R₁	R₃	R₇	R₉	Yield, %	Mp, °C
CH₃	H	H	H	3	142–143
CH₃	H	CH₃	H	40	53–54
CH₃	CH₃	CH₃	H	80	135–136
CH₃	CH₃	CH₃	CH₃	70	94–95
CH₃	CH₂Cl	CH₃	H	75	183–184
CH₃	CH₂Br	CH₂Br	H	50	200–201
CH₃	CH₃	CH₃	CH₂CH=CH₂	23	49–50
CH₃	CH₃	CH₃	CH₂C≡CH	31	116–117
i-C₄H₉	CH₂Br	CH₃	H	12	76–77
CH₃	CH₃	CH₃	CH₂CO₂CH₃	10	80–81
CH₃	CH₃	CH₃	CH₂CH₂CO₂CH₃	60	84–85
R₃ = R₇ = CH₃; R₁–R₉ = (CH₂)₄				40	128–130
R₁ = R₉ = CH₃; R₃–R₇ = (CH₂)₄				12	162–163

The structure of I is based on elemental analyses and molecular weight ($C_9H_{14}O_4$); strong C–O–C absorbtion bands in the infrared at 8–12 μ and no OH, C=O, or C=C absorbtions; a transparent ultraviolet spectrum from $\sim$200 mμ; and a well-defined proton magnetic resonance spectrum with signals at 1.40 (6 H), 1.49 (6 H), and 1.75 (2 H) ppm. Structure II is considered

Table II. Chlorination of
1,3,5,7-Tetramethyl-2,4,6,8-tetraoxatricyclo[3.3.1.0³,⁷]nonane

R₃	R₇	R₉	R₉	Mp, °C
CH₂Cl	CH₃	H	H	181–183
CHCl₂	CH₃	H	H	146–148
CH₃	CH₃	Cl	H	98–99
CH₃	CH₃	Cl	Cl	79–80
CHCl₂	CHCl₂	Cl	Cl	175–176

unlikely based on the pmr spectra of the 9-methyl derivative of I which indicates different chemical shifts for the 3- and 7-methyl groups, and of the 3-dichloromethyl-1,5,7-trimethyl derivative which demonstrates nonequivalence for the methylene bridge hydrogens. Additionally, X-ray diffraction studies on the 3-chloromethyl-1,5,7-trimethyl derivative illustrate conclusively that the ring system of I is the correct one.

Although I upon treatment with acid at elevated temperatures reverts to its original constituents, it is possible with properly chosen reaction conditions to perform other transformations with little or no ring

degradation. For example, methyl 1,3,5,7-tetramethyl-2,4,6,8-tetraoxatricyclo[3.3.1.0³,⁷]nonane - 9 - propionate (IIIa) may be hydrolyzed with aqueous sodium hydroxide to the acid IIIb, mp 156–157° (*Anal.* Found: C, 55.96; H, 6.94), which in turn, upon treatment with thionyl chloride followed by ammonia, may be converted to the amide IIIc, mp 191–192° (*Anal.* Found: C, 55.92; H, 7.41; N, 5.37).

The liquid-phase chlorination of I with chlorine in carbon tetrachloride solution proceeds smoothly. A variety of chlorinated products were isolated in a pure state and characterized through pmr techniques (Table II). Prolonged chlorination leads to complex, highly viscous liquid mixtures approximating $C_9H_{8-5}Cl_{6-9}O_4$ compositions, bp 150–180° (1.0 mm).

The reaction to produce structures with the ring system of I is not necessarily limited to the interaction of 1,2- and 1,3-diketones, as 2,3-butanedione and 2,5-hexanedione yield 1,3,5,7-tetramethyl-2,4,6,8-tetraoxatricyclo[3.3.2.0³,⁷]decane, mp 102–103°. *Anal.* Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.98; H, 7.86. The pmr spectrum exhibited signals at 1.42 (6 H), 1.51 (6 H), and 2.04 (4 H) ppm analogous to those observed for the nonane derivative I. Attempts to dimerize 2,3-butanedione or 2,4-pentanedione under a variety of conditions related to those described in this communication were not successful. It may be possible, however, that with the proper choice of substituted diketones a stable dimer may be isolable.

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