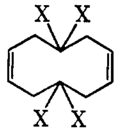
coincide with the long axis of the molecule, which, again, must be parallel with *c*, in either space group. The unit cell dimensions are such that this arrangement *is* possible in both space groups. The conformation is accordingly chair form Ib. Space group Abam appears more probable, with a molecular symmetry of C_{2h}-2/m. This work belongs in a rather rarely encountered group of X-ray crystallographic studies in which useful information is obtained merely on the basis of the determination of the space group and unit cell. We do, nevertheless, intend to carry out a complete structure refinement in order to obtain the details of the distribution of the strain in the molecule.

I
chair

II
boat



III
a, X = $CO_2C_2H_5$
b, X,X = =O

The results of this study are in accord with the previously predicted preference of *cis,cis*-1,6-cyclodecadienes for the chair conformation. Moreover, a study of other derivatives of the ring system in solution by nuclear magnetic resonance spectroscopy independently points toward a consistent predilection for this form.[6]

Acknowledgment. We wish to thank the National Science Foundation and the Advanced Research Projects Agency for support of this research.

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[7] National Science Foundation Cooperative Fellow, 1965–1967; Stauffer Fellow, 1967–1968.

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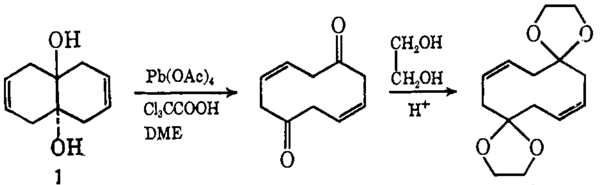
Conformational Mobility in *cis,cis*-1,6-Cyclodecadienes

Sir:

In the past decade nuclear magnetic resonance spectroscopy has proved to be an invaluable tool in gleaning otherwise difficultly accessible information on the structural and chemical dynamic properties of cycloalkanes. The majority of such studies has been confined to the C_6 to C_8 ring systems which, as a consequence, are now relatively well understood.[1] With the exception of the elegant work by Binsch and Roberts on *trans*-cyclodecene,[2] the C_{10} ring system has been largely neglected. In the present investigation we have studied the conformational characteristics of *cis,cis*-1,6-cyclodecadienes, all bearing substituents at positions four and nine.

In a modification of the procedure of Grob and Schiess[3a] *trans*-diol **1** was cleaved with lead tetraacetate in 1,2-dimethoxyethane (DME) to diketone **2**[3] in 60% yield. The latter was in turn converted by acid-catalyzed ketalization with ethylene glycol to diketal **3**[4] in 91% yield. The 100-Mc nmr spectrum of the diketone in $CHCl_3$–$CDCl_3$ at ambient temperature (Figure 1) consists of two symmetrical multiplets centered at 5.65 and 3.21 ppm, respectively (relative areas 1.0:2.0). The spectrum is best described as resulting from an $X_2AA'X_2'$ system[5] and has been analyzed as such to give the following coupling constants:[6] $J_{XX} = J_{X'X'} = -12.0$ cps, $J_{AX} = J_{A'X'} = 8.4$ cps, $J_{A'X} = J_{AX'} = -1.3$ cps, $J_{AA'} = 10.5$ cps, and $J_{XX'} = 0$. Either multiplet when spin decoupled from the other collapses to a sharp singlet. Interpretation of the spectrum as an $X_2AA'X_2'$ system and the results of the spin decoupling of the allylic multiplet imply the equivalence of the allylic protons at ambient temperature. As the temperature of the sample in $CHClF_2$ is progressively lowered, the undecoupled allylic resonance begins to broaden and separates into two distinct multiplets (apparent maximum chemical shift difference = 0.89 ppm) below −100°. The most reasonable explanation for these observations is an interconversion of conformers which, relative to the nmr time scale, is rapid at room temperature but slow at lower temperatures.

The 100-Mc nmr spectrum of diketal **3** in $CHCl_3$–$CDCl_3$ (Figure 2) at ambient temperature is strikingly different from that of diketone **2**. In addition to a sharp singlet at 3.98 ppm for the $-OCH_2CH_2O-$ protons (relative area 8.0) the spectrum consists of symmetrical multiplets at 5.60 and 2.62 ppm and a broad doublet at 1.96 ppm (relative areas 3.9:4.0:4.2) and can be characterized as arising from an ABXX'B'A' spin system. Upon irradiating the multiplet at 5.60 ppm the allylic resonances at 2.62 and 1.96 ppm simplify to an AB system centered at 2.22 ppm ($J_{AB} = -12.9$ cps, $\Delta\nu_{AB} = 0.67$ ppm). Increasing the sample temperature (tetrachloroethylene solvent) leads to a broadening of the resonances of the AB system at 70°, to coalescence at



1 **2** **3**

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[1] For some recent examples see: (a) F. A. L. Anet and M. Z. Haq, *J. Am. Chem. Soc.*, 87, 3147 (1965); (b) J. Jonas, A. Allerhand, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 3396 (1965); (c) J. D. Roberts, *Chem. Brit.*, 529 (1966); (d) M. St. Jacques, M. A. Brown, and F. A. L. Anet, *Tetrahedron Letters*, 5947 (1966).

[2] G. Binsch and J. D. Roberts, *J. Am. Chem. Soc.*, 87, 5157 (1965).

[3] (a) C. A. Grob and P. W. Schiess, *Helv. Chim. Acta*, **43**, 1546 (1960); (b) K. Grohmann and F. Sondheimer, *Tetrahedron Letters*, 3121 (1967).

[4] The spectroscopic properties and compositional analysis of this compound (mp 185.5–186.0°) were in agreement with the assigned structure.

[5] (a) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964); (b) R. K. Harris and C. M. Woodman, *Mol. Phys.*, **10**, 437 (1966).

[6] J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962) (J_{XX} assumed to be negative).

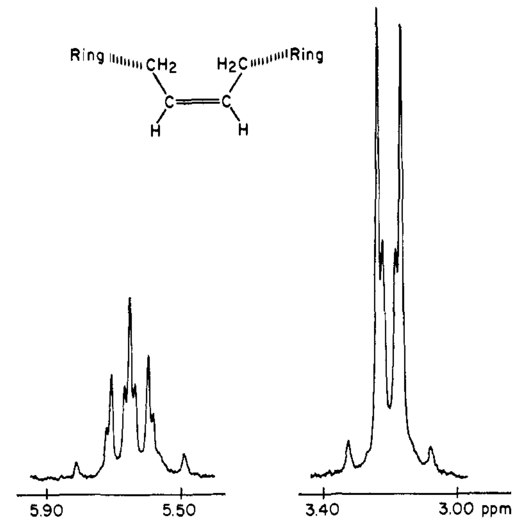


Figure 1. Nmr spectrum (100 Mc) of diketone **2** at ambient temperature.

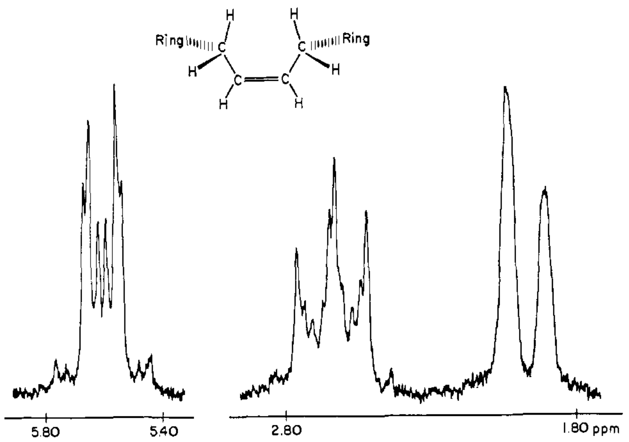


Figure 2. The vinyl and allyl regions of the 100-Mc nmr spectrum of diketal **3** at ambient temperature.

115°, and finally to a sharp singlet at 150°. At the latter temperature the undecoupled spectrum exhibits spin–spin splitting patterns essentially identical with those of the diketone at ambient temperature.

Quantitative line-shape analyses of the allylic patterns after spin decoupling were used to obtain conformational lifetimes by visual comparison of experimental and computer-calculated spectra.[7] Some relevant spectra for diketal **3** are shown in Figure 3. An Arrhenius plot of the rate constants thus obtained gave upon least-squares treatment the activation parameters $E_a = 14.8 \pm 0.2$ kcal/mol and $A = 4.01 \pm 1.0 \times 10^{10}$ sec^{-1} for diketal **3** and $E_a = 4.67 \pm 0.18$ kcal/mol and $A = 2.98 \pm 1.4 \times 10^{8}$ sec^{-1} for diketone **2**.

The resonances for the ring protons in the 100-Mc nmr spectrum of tetramethylol derivative **4**[8a] in dimethyl-d_6 sulfoxide could also be analyzed as an ABXX'B'A' pattern similar to that for compound **3**. The methylol groups exhibit an ABX pattern which simplifies to an AB quartet for the methylene protons upon decoupling from the hydroxyl proton.

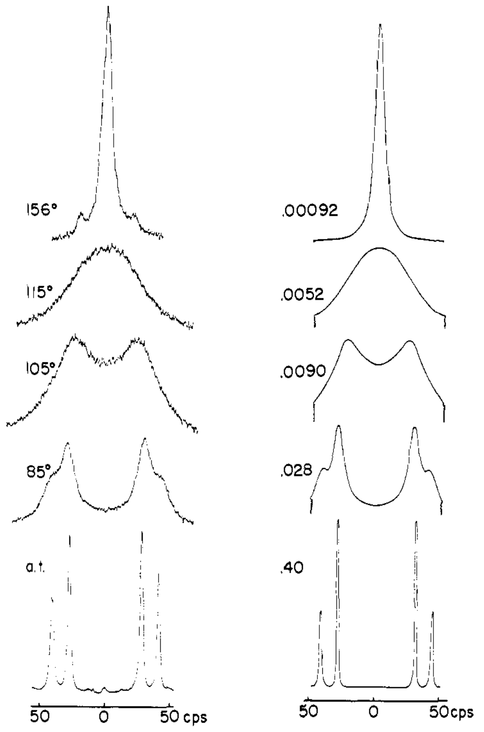
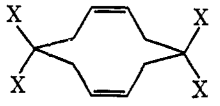
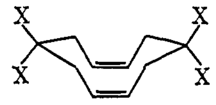


Figure 3. Experimental (left) and calculated (right) spectra of diketal **3** showing the spin-decoupled allyl region at various temperatures. Each of the calculated spectra is labeled with the appropriate mean lifetime in seconds.

Of the several conceivable conformations of the *cis,cis*-1,6-cyclodecadiene skeleton only the chair (**5**) and the boat (**6**) seem, judging from models, to be sufficiently favorable to merit detailed consideration. Arguments have been presented that the chair form should be preferred because of less transannular interaction.[3a,9] On the basis of a transannular addition



5



6

reaction,[8] it has been suggested that the boat form might be of lower energy.[8b]

Our results are most economically accounted for by the chair conformation being the most stable. The observation of the nonequivalence of the exocyclic methylene protons in compound **4** is not consistent with any conformation, such as **6**, having a plane of symmetry passing through positions four and nine. The chair conformation can also readily account for the observation of AB patterns for the allylic protons in compounds **2**, **3**, and **4** after spin decoupling. Furthermore, it has also been established that in diketone **2** the chair conformer is favored in the crystalline state.[10]

Although interpretation of our results in terms of a specific conformational inversion itinerary must remain speculative at present, we consider as a reasonable model a chair–boat–chair sequence involving simultaneous rotation about the C-1–C-10 and C-2–C-3 bonds (or equivalently C-5–C-6 and C-7–C-8 bonds). A study of the correlation of the activation energy for

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(9) C. A. Grob and P. W. Schiess, *Helv. Chim. Acta*, **47**, 558 (1964).

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ring inversion with the size of the substituents at positions four and nine and the hybridization of these carbons is now in progress.

Acknowledgment. We wish to thank the National Science Foundation for support of this research.

[11] National Science Foundation Cooperative Fellow, 1965–1967; Stauffer Fellow, 1967–1968.

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Formation of the Bridgehead Free Radical 1-Adamantyl by Perester Decomposition[1]

Sir:

The most favorable geometry of aliphatic free radicals remains an unsolved problem, since existing data are consistent with a geometry which is either pyramidal and rapidly inverting, or planar but easily deformed.[2-4] One approach to the problem is generation of the radical at a bridgehead of a bridged bicyclic system. For planar geometry, a stability order such as the following, well established for carbonium ions,[5] is predicted (the numbers are relative rates of alkyl bromide solvolysis): *t*-butyl > 1-adamantyl > 1-bicyclo[2.2.2]octyl ≫ 1-norbornyl, 1.0, 10^{-3}, 10^{-6}, and 10^{-14}, respectively. From their aldehyde decarbonylation study, however, Applequist and Kaplan concluded that 1-adamantyl and 1-bicyclo[2.2.2]octyl were appreciably more stable than *t*-butyl.[3] To reach this conclusion, they had to assume that the rates of capture of acyl radicals by CCl_4 were the same for all the alkyl groups studied.

We have attempted to assess the relative stabilities of 1-adamantyl and *t*-butyl radicals more directly by comparing the rates of thermal decomposition of the corresponding *t*-butyl peresters. We take advantage of the well-documented concerted two-bond scission (eq 1),

$$\mathrm{RCO_3\text{-}}t\mathrm{\text{-}Bu} \xrightarrow{\Delta} \mathrm{R\cdot} + \mathrm{CO_2} + \mathrm{\cdot O\text{-}}t\mathrm{\text{-}Bu} \qquad (1)$$

I, R = 1-adamantyl
II, R = *t*-butyl

obtaining whenever the stability of R· is equal to or greater than that of isopropyl or *t*-butyl; $\Delta H^{\ddagger} \leqslant 32$ kcal/mol and $\Delta S^{\ddagger} \leqslant 11$ eu in such cases.[6] The rates of formation of the radicals should therefore be directly measurable. We now report our study of the decompositions of peresters I and II.[7-10]

Both peresters I and II were prepared by known methods, and were free of hydroxylic or carbonyl-containing impurities, as judged from their infrared spectra. I, prepared from the acid chloride (Aldrich Chemical Co., mp 52–54°, lit.[3] 48.5–52.0°) and anhydrous sodium *t*-butyl peroxide[11] in dichloromethane at 0°, was purified by column chromatography on silica gel. It was a clear oil freezing at 0°, showed $\lambda_{\max}$ 5.69 μ in the infrared, and evolved 85–90% CO_2 on thermal decomposition in degassed cumene solution at 85°.[12] By nmr analysis, ~5% dichloromethane was detected in a sample of I. II, which has been reported,[13,14] was prepared either from (a) acid chloride, *t*-butyl hydroperoxide, and pyridine or (b) anhydride and hydroperoxide, washed with dilute aqueous ammonia, and distilled, bp 30–35° (0.05 mm). It showed $\lambda_{\max}$ 5.65 μ in the infrared. Samples of II prepared using sodium *t*-butyl peroxide were apparently more difficult to purify than those prepared by methods a and b, since their decomposition rate constants tended to decrease with increasing initial perester concentration.

Kinetics of decomposition of I and II in undegassed cumene were followed at the temperatures indicated in Table I, perester concentration being monitored by infrared spectra at the carbonyl maximum. First-order plots were linear to at least three half-lives, and rate constants were independent of initial perester concentration (0.07–0.5 *M* for I; 0.2–1.0 *M* for II) within the stated limits. Activation parameters, calculated *via* the Eyring equation, are as follows: for I, $\Delta H^{\ddagger} = 27.9$ kcal/mol, $\Delta S^{\ddagger} = +4.9$ eu; for II, $\Delta H^{\ddagger} = 27.6$ kcal/mol, $\Delta S^{\ddagger} = +3.6$ eu.

Table I. Kinetics of Decomposition of Peresters I and II

	10^5k, sec^{-1} [a]		
Temp, °C	I	II	$k_{\mathrm{I}}/k_{\mathrm{II}}$
64.6	6.87 ± 0.10	5.81 ± 0.10	1.18
74.6	24.4 ± 1.0	18.7[b]	1.30
75.6		21.0 ± 0.7	
84.6	77.8 ± 1.5	59.4 ± 1.5	1.31

[a] Each value is the average of the least-squares *k*'s of four runs. [b] Extrapolated from 75.6°.

The products of decomposition of I, besides CO_2, included *t*-butyl alcohol (45%), adamantane (47%), *t*-butyl 1-adamantyl ether (15%), and dicumyl (73%). Carbonyl-containing products were absent. The products of decomposition of II in cumene included[15] CO_2 (98%), *t*-butyl alcohol (79%), isobutylene (40%), isobutane (30%), dicumyl (68%), and di-*t*-butyl ether (2%). Carbonyl-containing products were again absent.

Peresters I and II evidently decompose in cumene *via* spontaneous, concerted two-bond scission, without induced decomposition, as judged by the first-order kinetics, absence of carbonyl-containing products, and low activation parameters. The rate constants therefore reflect the radical stabilities, and it is clear from Table I that the 1-adamantyl and *t*-butyl radicals are

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[1] Taken in part from the A.M. Thesis of S. D. C., 1968.

[2] W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966; *cf.* literature cited in ref 3.

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[6] (a) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem Soc.*, 80, 1398 (1958); (b) C. Rüchardt, *Fortschr. Chem. Forsch*, **6,** 251 (1966); (c) these activation parameters now appear to vary strongly with solvent; P. D. Bartlett and F. Herkes, private communication; (d) P. D. Bartlett and L. B. Gortler, *J. Am. Chem. Soc.*, **85,** 1864 (1963).

[7] We have also prepared the *t*-butyl perester precursor to 1-apocamphyl radical and found it to decompose *ca.* 500 times more slowly than I and II.

[8] R. C. Fort, Jr., and R. E. Franklin, *J. Am. Chem. Soc.*, **90,** 5267 (1968); Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 11–15, 1967, No. S-165.

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[12] The vacuum line technique is described in ref 6a.

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[14] T. Koenig and R. Wolf, *ibid.*, **89,** 2948 (1967).

[15] J. P. Lorand, Ph.D. Thesis, Harvard University, 1964.