

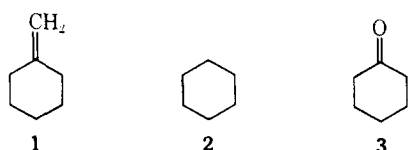
Nuclear Magnetic Resonance Studies of the Conformations of 2-Methylene-*cis*-decalins

J. T. Gerig* and C. E. Ortiz^{1b}

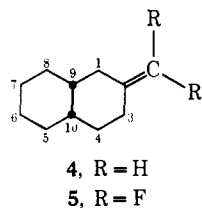
Contribution from the Department of Chemistry, University of California at Santa Barbara, Santa Barbara, California 93106. Received November 7, 1969

Abstract: The proton magnetic resonance spectrum of 1,1,3,3-tetradeuterio-2-methylene-*cis*-decalin has been studied as a function of sample temperature. The vinyl resonances appear as an AB quartet at room temperature and evolve into two overlapping AB quartets at low temperature. Two conformations of this molecule are thus indicated; they are present in a ratio of 69:31 and interconvert with activation parameters, ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger of 12.6 and 11.2 kcal/mol and -6 eu, respectively. This conformational equilibration was also studied in 2-difluoro-methylene-*cis*-decalin by fluorine-19 spectroscopy, with similar results.

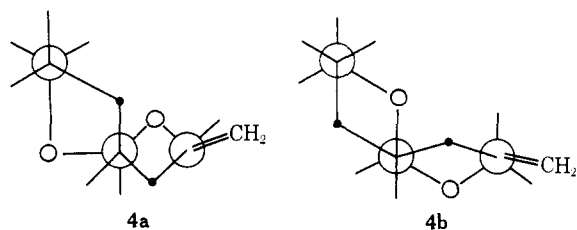
It has been shown that the energy barrier to chair-chair interconversion in methylenecyclohexane (**1**) is considerably lower than the corresponding barrier in cyclohexane (**2**),^{2,3} although not as low as the barrier in cyclohexanone (**3**).^{2,4} It was of interest to determine



if this trend is also prevalent in bicyclic molecules and, as an extension of previous work with methylenecyclohexane, we have examined the conformational attributes of the bicyclic hydrocarbon 2-methylene-*cis*-decalin (**4**)



by nmr spectroscopy. Presuming that the ground state of this molecule is a double-chair form analogous to those found in *cis*-decalin⁵ and *cis*-decal-2-one,⁴ one can see with the aid of molecular models that there are two unique conformations available to the molecule, **4a** and **4b**. These structures can be interconverted



smoothly by a process that involves rotation about the central C₉-C₁₀ bond. Each of these conformers has an

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(1) National Science Foundation Undergraduate Research Participant, Summer 1968. A preliminary report of these results was made to the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 9, 1969.

(2) B. H. Beck and F. R. Jensen, *J. Amer. Chem. Soc.*, **90**, 1066 (1968).

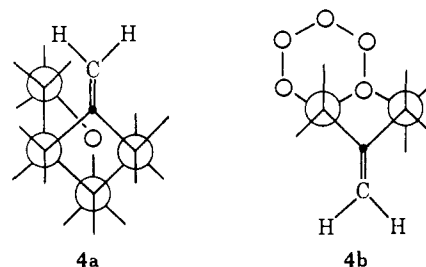
(3) J. T. Gerig and R. A. Rimerman, *ibid.*, **92**, 1219 (1970).

(4) R. E. Lack, C. Ganter, and J. D. Roberts, *ibid.*, **90**, 7001 (1968).

(5) J. T. Gerig and J. D. Roberts, *ibid.*, **88**, 2791 (1966).

enantiomer; **4a** (or **4b**) and its magnetically equivalent enantiomer *cannot* be interconverted, except by breaking this bond. In a nonresolved sample of **4**, there are thus present two families of conformational isomers, each having members analogous to **4a** and **4b**.

A convenient probe for conformational effects in 2-methylene-*cis*-decalin is provided by the vinyl protons of the molecule. This can be seen by viewing structures **4a** and **4b** end-on, as sketched below. In either



conformation, the two vinyl protons are magnetically nonequivalent and thus would be expected to appear in the pmr spectrum as an AB quartet. Furthermore, the vinyl proton environments in **4a** are quite distinct from those in **4b**, so that, in the absence of any rate process which interconverts these conformations, two AB quartets should be present in the spectrum, one quartet for each conformer. At higher temperatures where the rate of interconversion is rapid, a single, averaged AB quartet should be in evidence.

Results

2-Methylene-*cis*-decalin. The vinyl portion of the pmr spectrum of **4** at room temperatures appeared as a broad singlet. However, when the four protons at the carbons adjacent to the exocyclic double bond were replaced with deuterium atoms, this part of the spectrum sharpened to an AB quartet which was characterized by the parameters $\delta_{AB} = 7.14$ and $J_{AB} = 2.75$ Hz at 100 MHz. As the temperature of the sample was progressively lowered, the spectrum underwent rather subtle changes, as indicated in Figure 1. At -77° , the vinyl signals do indeed appear as two AB quartets; for one quartet $\delta_{AB} = 9.65$ and $J_{AB} = 2.85$ Hz, while the second quartet is described by $\delta_{AB} = 1.6$ and $J_{AB} = 2.4$ Hz at 100 MHz. The very small chemical-shift difference found in the second "quartet" makes this segment of the spectrum appear essentially as a singlet;⁶ this peak

(6) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 97.

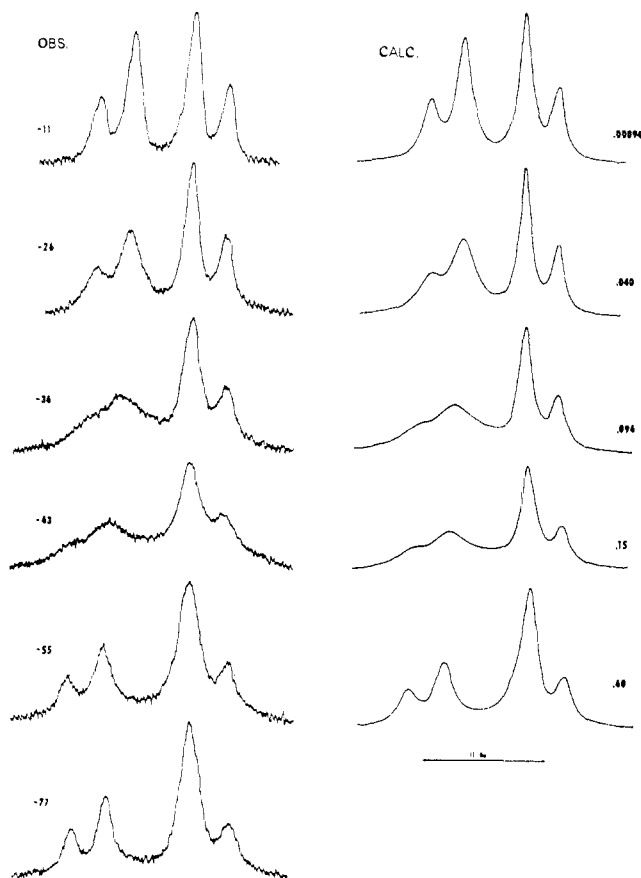


Figure 1. Experimental and computed spectra of 1,1,3,3-tetra-deuterio-2-methylene-*cis*-decalin at various temperatures. The temperatures ($^{\circ}\text{C}$) are indicated on the left while the half-life (τ) of the predominant conformer at each temperature is shown on the right.

fortuitously overlaps a transition in the first AB quartet. In order to obtain the chemical-shift difference and coupling constant that characterize the second conformation, the spectral parameters found at high temperatures were assumed to be average values. Since the spectrum of the major conformation can be determined from the low-temperature data, the desired chemical-shift and coupling constant information for the minor isomer can be calculated.

The behavior of the pmr spectrum of **4** at intermediate temperatures could be simulated by using a computer program which describes the interchange of nuclei between two locations, each of which is characterized by a distinct AB quartet.^{4,6,7} As with 2,2-difluoro-*cis*-decalin,⁵ there are two distinct ways in which the two AB quartets of the spectrum can be averaged as the sample temperature is increased. Only by assuming that the high-field chemical shifts of each quartet (and, therefore, the low-field shifts of each quartet) are interchanged by the conformational process was it possible to generate theoretical spectra which agreed with experimental observations throughout the complete range of temperatures studied. This agreement is illustrated in Figure 1 and provides a strong indication that the assignment of exchanging partners and the analysis for chemical shifts and coupling constant of the less prevalent conformer are correct.

(7) S. Alexander, *J. Chem. Phys.*, **37**, 967 (1963).

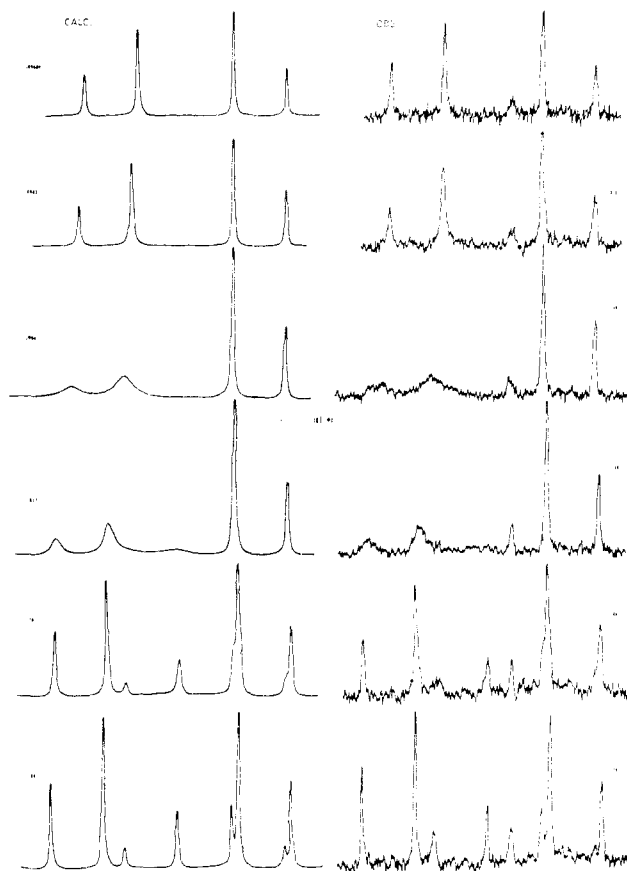


Figure 2. Experimental and computed spectra of 2-difluoromethylene-*cis*-decalin at various temperatures.

Assuming that the rate constant, k , for inversion is given by $1/\tau$ where τ is the mean lifetime of a conformational isomer before inversion as deduced from computed spectra, the kinetic data could be described by the Arrhenius relationship, $k = 7.53 \times 10^{11} \exp[11,700 \pm 370/RT]$, from which the activation parameters ΔG^{\ddagger} , ΔH^{\ddagger} , and ΔS^{\ddagger} were reckoned to be 12.6 and 11.2 kcal/mol and -6 eu, respectively, at -40° for the conversion of the most stable conformer to the less stable form.

The first, large chemical-shift conformer constituted 69% of the bicyclic molecules present in the sample at -77° . The computed spectra at intermediate temperatures were not very sensitive to the relative populations, so that a concentration ratio of 69:31 was assumed at all temperatures.

2,2-Difluoromethylene-*cis*-decalin. In order to confirm the interpretation of the variable-temperature spectrum of 2-methylene-*cis*-decalin advanced above, we also prepared 2,2-difluoromethylene-*cis*-decalin (**5**) and examined the fluorine-19 magnetic resonance spectrum of this material as a function of sample temperature. Qualitatively, the same spectral behavior was found. At room temperature, the proton-decoupled fluorine-19 spectrum was an (averaged) AB quartet with $\delta_{AB} = 166$ and $J_{AB} = 63.5$ Hz and, as the temperature was lowered, this pattern evolved cleanly into two AB quartets (Figure 2). The major conformer, abundant to the extent of 71% was characterized by $\delta_{AB} = 219$, $J_{AB} = 63.5$ Hz at -70° , while the less-favored isomer exhibited $\delta_{AB} = 116$, $J_{AB} = 63.5$ Hz at this temperature. As illustrated in Figure 2, it was possible to reproduce the fluorine

spectrum of **5** at various temperatures, by again assuming that the high-field (and, therefore, the low-field) components of each AB quartet are exchange-related partners. However, an additional complication in interpretation arose with this system since an appreciable temperature dependence was observed for the chemical shifts of the fluorine nuclei of each conformer. The chemical shifts relative to the ethyl trifluoroacetate lock-reference signal appeared to change linearly with temperature and for the major conformational isomer could be described by eq 1 and 2 where the temperature

$$\nu_A = 2815 - 0.576t \quad (1)$$

$$\nu_B = 2611 - 0.354t \quad (2)$$

(*t*) is expressed in degrees Centigrade. Chemical shifts for the second, minor conformer changed in a similar way and could be represented by

$$\nu_A = 2724 - 0.576t \quad (3)$$

$$\nu_B = 2624 - 0.354t \quad (4)$$

Thus, the upfield components of each AB quartet are equivalently sensitive to sample temperature while the downfield signals in both quartets likewise change in the same manner but show a greater dependence on temperature. The temperature dependences of these chemical shifts were estimated from spectra recorded at temperatures below those at which chemical exchange appears to modify the spectra and, by extrapolation, gave a good accounting of the averaged chemical-shift difference observed at higher temperatures. Nevertheless, extrapolation of eq 1–4 into the temperature range where chemical exchange introduces significant changes in the appearance of the fluorine spectrum of **5** may introduce some uncertainty with regard to the accuracy of the exchange rates. An Arrhenius plot of the kinetic data was linear with only slightly more scatter than the corresponding plot for **4** and could be summarized by the equation $k = 3.88 \times 10^{17} \exp[-(17,700 \pm 430)/RT]$. The activation parameters ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger for conversion of the major conformer to the minor one were 12.5 and 17.2 kcal/mol and 20 eu, respectively.

Discussion

While consistent with the formulation of the ground state of 2-methylene-*cis*-decalin as a set of equilibrating double-chair conformations, our results do not constitute a proof of this proposition. We assume for the remarks which follow that double-chair forms are the most stable conformers of this molecule; this assumption appears reasonable in view of the close similarity of the ground-state geometries of cyclohexane and methylenecyclohexane³ and the very strong probability that the lowest energy form of *cis*-decalin is the double chair.^{5,8}

An interesting question is the origin of the differences in conformer populations (69–31% for **4** and 71–29% for **5**) in these molecules. A similar ratio of populations, 65–35%, has been found in 6,6-difluoro-*cis*-decal-2-one.⁴ Examination of molecular models suggests an explanation for this effect. We note that in conformations analogous to **4b** there are present three strong cross-ring interactions between the axial pro-

tons at carbons 1, 3, 5, and 7. In structure **4a**, there are only two such interactions, between axial hydrogen atoms at carbon 4, in one ring, and at carbons 6 and 8, in the second ring. The third H–H nonbonded interaction is missing in this latter conformation because a CH₂ group of the ring has been replaced by the exocyclic double bond system. Using Hendrickson's potential energy function (eq 5) for hydrogen–hydrogen inter-

$$V_{\text{H-H}} = 10^4 e^{-4.6r} - 49.2/r^6 \quad (5)$$

action⁹ it can be estimated that one of these cross-ring interactions amounts to a 0.57 kcal/mol increase in potential energy.¹⁰ Taken as free energy, this quantity corresponds to a population ratio of 72:28%, a value close to that observed with both the exocyclic olefins and the ketone.⁴ On this basis we suggest that conformations analogous to **4a** are the favored ones in 2-methylene-*cis*-decalin and *cis*-2-decalone. The small difference in population ratio found with the hydrogen- and fluorine-substituted olefins may reflect solvation differences; it seems unlikely that long range H–H and H–F nonbonded interactions could account for energy differences of the magnitude under consideration here.

A disturbing feature of our results is the considerable difference in the activation parameters for the two bicyclic olefins. The free energies of activation for both compounds are essentially equal but compensating changes in the enthalpy and entropy terms occur. Because the activation entropy of the hydrogen-substituted compound is quite similar to those observed in both the *cis*-decalin^{5,12} and *cis*-decalone⁴ systems, we tend to place more faith in the results with this material. The dependence of the fluorine chemical shifts of **5** on temperature may provide a clue as to the source of this discrepancy. The temperature effect on the upfield signal in each AB pattern amounts to a chemical-shift change of 0.35 Hz/deg. Previous workers have noted effects of this type that ranged between 0.2 and 0.3 Hz/deg¹² so that we do not consider the magnitude of the shifts represented by eq 2 and 4 as unusual. However, the downfield signals in each quartet are considerably more sensitive to temperature, exhibiting a shift of 0.58 Hz/deg. This latter effect appears to be unexpectedly large and may signal unusual solvent–solute interactions in the region of these nuclei that could affect the activation parameters for conformational interconversion. Further work to identify the geometrical position of each fluorine nucleus in each conformer and to examine more closely the effect of solvents on the interversion process will be necessary in order to substantiate this suggestion.

It is likely that a chair–boat conformation is an intermediate in the conformational equilibration which occurs in *cis*-decalin and that this process follows an energy–reaction coordinate diagram similar to the one depicted in Figure 3.^{5,13} If the second energy barrier (B) in this sequence is about the same height as the bar-

(9) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537 (1961). This same function was used in previous calculations with the *cis*-decalin system.⁵

(10) An ideal chair–chair conformation was assumed;¹¹ the internuclear distance, *r*, for this interaction is about 1.9 Å.

(11) P. Geneste and G. Lamaty, *Bull. Soc. Chim. Fr.*, 2439 (1964).

(12) (a) R. A. Newmark and C. H. Sederholm, *J. Chem. Phys.*, **39**, 3131 (1963); (b) R. A. Newmark and C. H. Sederholm, *ibid.*, **43**, 602 (1965).

(13) W. A. Thomas, *Annu. Rev. NMR Spectrosc.*, **1**, 44 (1968).

(8) M. I. Davis and O. Hassel, *Acta Chem. Scand.*, **18**, 813 (1964).

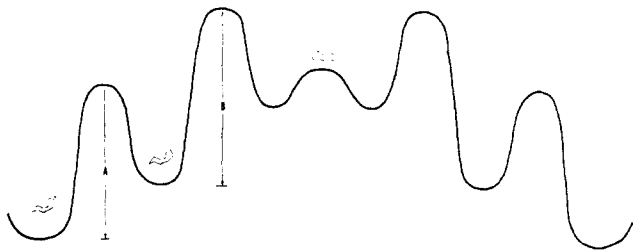


Figure 3. A reaction coordinate diagram from conformational equilibration in *cis*-decalin. A trace impurity appears as a singlet in the experimental spectra. Sample temperatures are 9, 3.5, -19, -30, -45, and -56°, respectively.

rier to ring conversion in cyclohexane (~ 10 kcal/mol) then the free-energy difference between the chair-chair and chair-boat forms of *cis*-decalin should be about 4 kcal/mol, since the overall free-energy barrier to inversion in *cis*-decalin is ~ 14 kcal/mol.¹³ This estimate of the energy difference between the chair-chair and chair-boat forms is in moderately good agreement with the energy difference calculated by Wiberg's technique.^{5,14}

One can devise two simple pathways for the analogous interconversion process in 2-methylene-*cis*-decalin and *cis*-2-decalone. These are represented by the energy-reaction coordinate profiles shown in Figure 4. In the first alternative, path I, the six-membered ring containing the unsaturated group structure flips to a boat form, to give a chair-boat intermediate, which then is converted to a boat-boat intermediate by inversion of the cyclohexane-like part of the molecule. In path II, the opposite order of events occurs; first the cyclohexane ring moves, converting the structure to a chair-boat form and then the part of the molecule with the double bond inverts to produce a boat-boat form. For either pathway, it is presumed that flexion within the boat-boat family occurs,¹¹ eventually leading to interchanged conformations. If the free-energy difference between the double-chair forms and the related chair-boat forms of these unsaturated molecules is nearly the same as that likely present in *cis*-decalin (~ 4 kcal/mol) and if it is assumed additionally that the heights of the free-energy barriers in paths I or II are about the same as those found for inversion of the corresponding six-membered ring, then one concludes that the free-energy barrier to inversion of 2-methylene-*cis*-decalin and *cis*-2-decalone, should both be nearly identical with the barrier found in *cis*-decalin if path I is utilized. That is, if the second barrier (B) corresponds to a flip of the cyclohexyl part of the carbon skeleton, the overall energy barrier for both of these molecules should be about 14 kcal/mol. If itinerary II is more nearly correct, the free-energy barriers to inversion of 4, 5, and *cis*-2-decalone can be calculated to be ~ 12.4 and less than ~ 9 kcal/mol, respectively, using the same assumptions. These values are close to those observed experimentally and suggest that path II is the one followed in the conformational interconversion of 2-methylene-*cis*-decalin and *cis*-2-decalone. The order of energy barriers to conformation exchange for saturated hydrocarbon, exocyclic olefin, and ketone ($>CH_2 > >C=CH_2 > >C=O$) observed with the *cis*-decalin structure is thus

(14) K. B. Wiberg, *J. Amer. Chem. Soc.*, **87**, 1070 (1965).

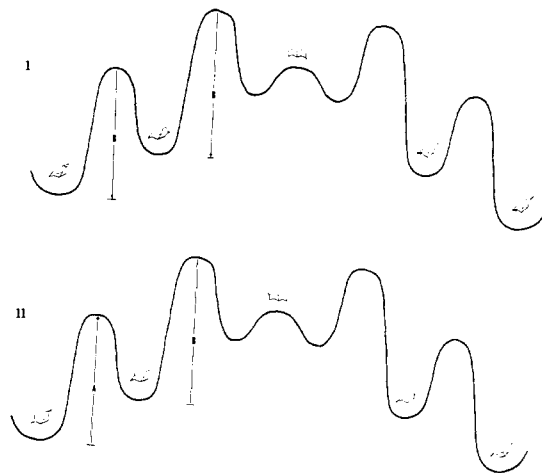


Figure 4. Two possible reaction coordinates for conformational equilibration in 2-methylene-*cis*-decalin or *cis*-2-decalone. The first is initiated by a flip of the six-membered ring containing the sp^2 carbon while in the second pathway the interchange starts with a flip of the cyclohexane ring.

qualitatively the same as that found in the propane and cyclohexane series.³

Experimental Section

cis-2-Decalone was prepared by Jones oxidation of *cis*-2-decalol. Commercially available 2-decalol (Aldrich Chemical Co.) was recrystallized from hexane as a white solid until glc analysis showed that the material was $>98\%$ pure.

cis-1,1,3,3-Tetraduterio-2-decalone was prepared as described previously.⁵

1,1,3,3-Tetraduterio-2-methylene-*cis*-decalin was prepared by a Wittig reaction. A three-necked flask equipped with a drying tube, condenser, a nitrogen inlet, and facilities for magnetic stirring, was flushed with dry nitrogen for 5 min. Dimethyl sulfoxide (10 ml) was added and the flask heated to 65° with an oil bath. Sodium hydride (58% dispersion in mineral oil, 0.41 g, 9.6 mmol) was added. The solution was removed from the bath after 2 hr and 5.33 g (13.2 mmol) of methyltriphenylphosphonium iodide was added. After stirring for 1 hr at room temperature, 1 g (6.58 mmol) of *cis*-2-decalone was added in an equivalent volume of DMSO. The reaction mixture was stirred at 65° for 24 hr and then poured into 50 ml of water. The solution was filtered and extracted twice with 25 ml of hexane. The combined extracts were washed with water until the aqueous phase was neutral. After drying over magnesium sulfate, the organic solvent was removed *in vacuo* to afford a yellow oil. The pure olefin was isolated by preparative glc in about 4% yield. The pmr spectrum consisted of a quartet at δ 4.6 ppm (2 H) and a broad envelope of signals centered at 1.5 ppm (12 H) with TMS as reference. The mass spectrum of the material exhibited a molecular ion at m/e 154.

2-Difluoromethylene-*cis*-decalin was prepared by the method of Fuqua, *et al.*¹⁵

A three-necked flask fitted with a condenser, heated dropping funnel, drying tube, and magnetic stirrer was purged with nitrogen before use. Into the flask were placed 4.5 g (30 mmol) of *cis*-2-decalone, 7 g (35 mmol) of tri-*n*-butylphosphine, and 50 ml of hexamethylphosphoramide (distilled from calcium hydride before use). The mixture was heated in an oil bath to 185° with stirring. A solution of 18 g (121 mmol) of the sodium salt of chlorodifluoroacetic acid in 150 ml of warm (60–70°) hexamethylphosphoramide was added over a period of 2 hr. Pronounced color changes, from dark green to light brown, were observed after the addition was completed, the mixture was stirred for an additional 10 min, and then poured into 2 l. of ice water. The water was extracted with ethyl ether (four 250-ml portions). The extracts were combined and washed with water two 250-ml portions, saturated sodium chloride solution (two 250-ml portions), and again with water. After drying over magnesium sulfate, the ether was removed under vacuum to yield 13 g of a dark oil. Vacuum distillation of

(15) S. A. Fuqua, W. G. Duncan, and R. M. Silverstein, *J. Org. Chem.*, **30**, 1027 (1965).

this residue afforded a fraction, bp 32–70° (1.2 mm). Vapor-phase chromatography of this material showed five components; the third component eluted was collected in a series of preparative experiments. The material exhibited an infrared band at 1750 cm^{-1} and a parent ion in the mass spectrum at m/e 186 (yield 1–2%). The olefin appeared to be quite acid sensitive.

Variable-temperature pmr spectra were recorded with a Varian Associates HA-100 spectrometer using samples that were approximately 10% olefin and 5% TMS (v/v) in trichlorofluoromethane. For fluorine spectroscopy the operating frequency was 94.6 MHz. A capillary of ethyl trifluoroacetate was used to provide a lock signal for the fluorine experiments. Samples were degassed and sealed under vacuum. Sample temperatures were estimated by replacing the sample tube with another tube containing solvent and a copper-constantan thermocouple which was connected to a Digitec

Model 504 digital thermometer. Sample temperatures are believed to be accurate to $\pm 1^\circ$.

Theoretical spectra were generated using an IBM 360/75 computer and a version of the two-site AB exchange program previously described.⁶ The rate constants derived by visually fitting theoretical spectra to experimental spectra are believed to be accurate to better than 10%.

Acknowledgment. This work was supported in part by Grant No. GP-8166 from the National Science Foundation. We are indebted to Professor J. D. Reinheimer (on leave from the College of Wooster, Wooster, Ohio) for preliminary assistance in the analysis of the fluorine spectra.

Structural Implications of Nuclear Magnetic Resonance Studies on 1-R-1-Phospha-2,6-dioxacyclohexanes

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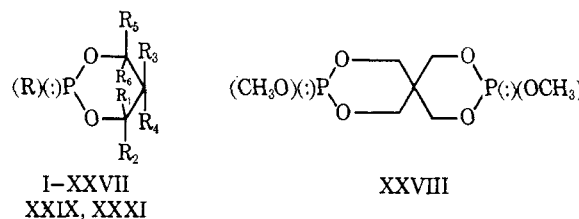
Abstract: ^1H and ^{31}P nmr spectra of 15 1-R-1-phospha-2,6-dioxacyclohexanes have been examined, in which R = OCH_3 , $\text{OC}(\text{CH}_3)_3$, SC_6H_5 , C_6H_5 , F, Cl and Br. Two methyl substituents were present in the ring at C_3 and C_5 or at C_4 . Spectra of several 4-methyl-4-chloromethyl systems were also studied as well as 3,9-dimethoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane. The bulk of the nmr evidence is consistent with the presence of one very dominant chair conformer. The question of the stereochemistry at phosphorus in these systems is examined in the light of present evidence. An intermolecular halide exchange mechanism is proposed to account for the broadening of the ^1H nmr lines with increasing temperature of several of the 1-chloro and 1-bromo derivatives. The order of the 1-R exchange rates appears to be $\text{OCH}_3 < \text{F} < \text{Cl} < \text{Br}$.

The syntheses of many 1-R-1-phospha-2,6-dioxacyclohexanes have been reported in the last 20 years,^{3–6} but attempts to study the stereochemistry of these systems have not been made until recently.^{7–19} Although a few of the stereochemical investigations have been reviewed,²⁰ we briefly summarize here pre-

vious conclusions pertinent to the new results we describe in this paper. The rings of I; IIIa,b; IVa,b; VII; VIIIa,b; IXa,b; Xa; XIIa,b; XIIIa,b; XIV; XV; XVII; XIXa; XXa; XXIIa; XXIIIa,b; and XXVI, shown in Table I, were assigned chair conformations on the basis of their ^1H nmr spectra.^{9, 12–15, 17, 18} In two cases, IIIb¹⁵ and VIIIb,⁹ rapid equilibria between two chair conformers have been postulated, but in all of the others one conformer has been concluded

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to be very dominant under the conditions of observation. Conflicting stereochemistries at phosphorus have been deduced for several of the above derivatives. An axial R, equatorial electron lone-pair stereochemistry has been assigned for IIIa;¹⁵ VIIIa;¹⁰ IXa,b;¹⁸ XXIIIa,b;¹⁴ and the dominant conformer of VIIIb.¹⁰ In contrast, an equatorial R, axial lone-pair stereochemistry has been assigned for VII;¹² Xa;¹³ IVa,b;¹⁴ XIIa,b;¹⁴ and the dominant conformer of IIb at -30° .¹⁵

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