Table I. Optical Rotation for Isophorone Oxide Prepared in a Confined Vortex and Simple Centrifuge[a]

horizontal (centrifuge)[b]		vertical clockwise[b]		vertical counterclockwise[b]	
product rotation 24°, 546.1 nm, mdeg	average rotational rate, rpm	product rotation 24°, 546.1 nm, mdeg	average rotational rate, rpm	product rotation 24°, 546.1 nm, mdeg	average rotational rate, rpm
+0.2 ± 0.3	10 900	+9.0 ± 0.2	8600	−2.6 ± 0.2	10 800
−0.2 ± 0.2	11 500	+5.9 ± 0.2	7700	−2.5 ± 0.2	10 500
−0.3 ± 0.4	10 500	+12.8 ± 0.3	9500	−2.2 ± 0.2	10 600
−0.9 ± 0.4	11 600	+9.8 ± 0.4	8900	−1.0 ± 0.7	10 400
−0.9 ± 0.5	14 300	+17.2 ± 0.6	11000	−3.1 ± 0.7	11 000

[a] Errors are standard deviations for repeated measurements on the same sample. [b] Spinning attitude.

Caution note: A number of tubes exploded during the course of these experiments. Precautions were taken to confine the explosions in a hood.

In a typical experiment[2] isophorone (7.6 g) was mixed with 30% hydrogen peroxide (15.8 mL) and methanol (55 mL) and a total of 6 mL of 6 N NaOH was added in 2-mL aliquots at the start of the reaction and at 20 and 40 min. It was necessary to increase the gas pressure to maintain a constant spinning rate as an emulsion formed roughly 1 h after the reaction was started and the resulting increase in turbulence in the vortex slowed the spinning rate. Small leaks in the Teflon seal for the tube often resulted in a loss of material during the reaction. These losses occurred in all three spinning attitudes.

After a standard cleanup[2] optical rotations for the products were measured as described elsewhere.[3]

Table I presents the product optical rotations and time-averaged rotational rates for five experiments each in the horizontal, vertical clockwise and vertical counterclockwise spinning attitudes.

The optical rotations for the vertical clockwise experiments are well beyond experimental error.

The horizontal spinning attitude is achiral as the axis of the earth's gravitational field and the axis of the momentum due to spinning are perpendicular to each other. The results from these experiments are entirely in accord with bench controls for the same reaction[3] and confirm the notion that achiral physical fields cannot induce asymmetric synthesis.

The optical rotations for the products of the vertical counterclockwise experiments are roughly half an order of magnitude smaller than those of the corresponding clockwise spinning experiments. The motion of molecules in the interior of the clockwise vortex constitutes a *P* helix from the top to the bottom of the tube while the motion of molecules at the walls of the tube describes an *M* helix from the bottom of the tube to the top. This motion is coincident with the motion that would be caused by the combination of *g* or anti-*g* forces and the earth's coriolis force in the Northern Hemisphere. The motion of molecules in the counterclockwise confined vortex is the opposite of this and would be contragradient to the combination of *g* and coriolis forces. This may explain the difference between the results for the clockwise and counterclockwise spinning experiments. If this explanation is correct, the results for the two experiments should reverse on moving to a corresponding latitude in the Southern Hemisphere.

The results reported above demonstrate that it is possible to obtain asymmetric synthesis with chiral gravitational fields alone. Inasmuch as the space-time metric is chiral, it is conceivable that prebiotic organic synthesis could have been partially asymmetric as a result of being conducted in a chiral gravitational field.

Acknowledgment. It is a pleasure to acknowledge useful discussions with J. J. Katz and A. Garay and the technical assistance of J. D. Roberts and P. Bretton.

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Mechanism of Metallotropic Shifts in Fluxional *Monohapto*cyclopentadienyl Metal Derivatives[1]

Sir:

It has been clear for about 10 years that the fluxional character of *monohapto*cyclopentadienyl metal derivatives results from degenerate metallotropic migration. That the latter is intramolecular and is specific (rather than random) remains in no doubt, but, despite all that has been written on the subject,[2] no direct way has been devised for distinguishing NMR resonances due to the two different types of olefinic ring nuclei. Without this differentiation, definitive evidence for a 1,2 (equivalent to 1,5) rather than the alternative 1,3 migration has remained elusive, although the former is strongly indicated by coalescent behavior in ^{13}C NMR spectra of chiral silylcyclopentadienes[3] which show anisochronous behavior among the relevant ring carbon atoms. We believe that we are now in a position to end speculation on this subject.

In a chiral compound, $C_5H_5Si^*XYZ$, as well as resulting in diastereotopic shifts among the C_5-ring nuclei[3] it is possible that molecular asymmetry may result in anisochronicity within the migratory group (Si^*XYZ). Indeed we have already reported[3] one such species, $C_5H_5Si(H)(Cl)CH_2SiMe_3$ where the α (methylene) protons of the trimethylsilylmethyl substituent will in principle exhibit such an effect; however the ^{1}H resonances due to these nuclei are completely obscured by the silylmethyl signal. Convinced that identification of such diastereotopic shifts might prove to be the key to resolving the rearrangement mechanism, we have pursued this problem using ^{13}C NMR spectroscopy. Appropriate alkyl substituents at a chiral silicon center include isopropyl (anisochronous methyl carbon atoms) or cyclopropyl and cyclohexyl (anisochronous 2-methylene carbons).

Reaction of isopropylmagnesium bromide with excess methyldichlorosilane over 24 h at 30 °C gave in low yield (~10%) (isopropyl)methylchlorosilane (**1**) which in a reaction with potassium cyclopentadienide at -78 °C afforded[4] (isopropyl)methylsilylcyclopentadiene (**2**, ~75%). The ^{1}H NMR spectrum of this compound at -40 °C consisted of the following signals: τ 3.46, (4, m, aa′bb′), 6.35, (1, br m, SiH), 6.57, (1, br m, x), 8.72, (1, m, $CH(CH_3)_2$), 8.99 (6, $CH(CH_3)_2$), 10.26, (3, d, $SiCH_3$) (where aa′bb′x denote the C_5-ring protons). On warming to ambient temperature successive collapse of the resonances at τ 3.46 and 6.57 occurred to give a broad, averaged low-field signal. During 2 h at 25 °C

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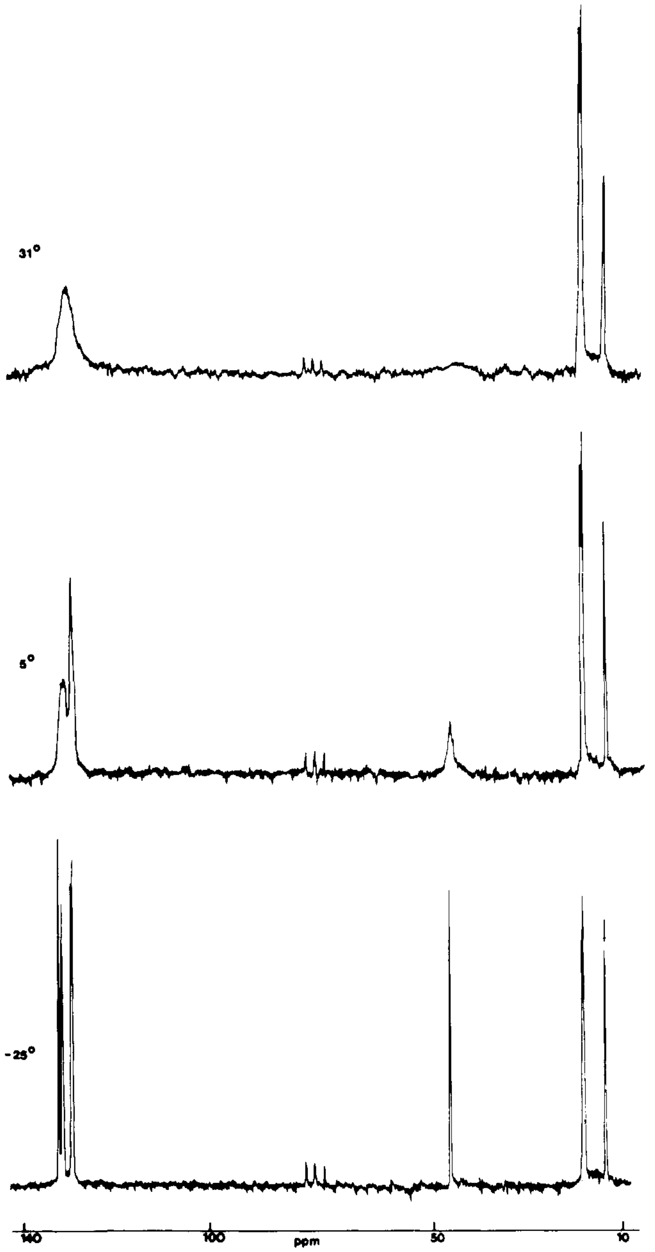

Figure 1. Temperature dependence of the ^{13}C NMR spectrum of compound **2**, 0–150 ppm. (For experimental details see ref 2 and 3.)

progressive isomerization via prototropic shifts[2] was characterized by accumulation of doublets at τ 9.95 and 9.87 due to $CH(CH_3)_2$ protons in the 2- and 3-silyl compounds, respectively.

The ^{13}C NMR spectrum of compound **2** at −40 °C is summarized in Table I and its temperature dependence is illustrated in Figure 1. The low-frequency region (Figure 2) was unequivocally assigned from a spectrum recorded without proton decoupling on the basis of multiplet structure due to (^{1}H-^{13}C) spin coupling: the pair of lines at δ 18.7 and 18.4 split into overlapping quartets ($^{1}J(^{1}H\text{-}^{13}C)$ = 126.0 and 128.3 Hz), that at 13.5 into a doublet ($^{1}J(^{1}H\text{-}^{13}C)$ = 117.4 Hz), and that at −10.1 ppm into a quartet of doublets ($^{1}J(^{1}H\text{-}^{13}C)$ = 120.7, $^{2}J(^{1}H\text{-}^{13}C)$ = 7.7 Hz). Thus these resonances belong, respectively, to isopropyl β-carbon, (anisochronous pair) isopropyl α-carbon, and silylmethyl carbon atoms. The high-frequency region consisted of four lines due to the $C_{2,5}$ and $C_{3,4}$ pairs of the C_5 ring[5] (diastereotopically shifted by 0.7 and 0.3 ppm). On warming, these signals collapsed asymmetrically with that at δ 47.6 (C_1), but, *during this coalescence, the shift between the two resonances due to the anisochronous pair of β-carbon atoms in the substituent isopropyl group was maintained.* In fact, the low-frequency portion of the spectrum (Figure 2) remain unchanged throughout the temperature range investigated (−50 to +60 °C). We conclude the migration of the silyl group occurs *without inversion at silicon,* the first time the stereochemistry of such a rearrangement has been established.

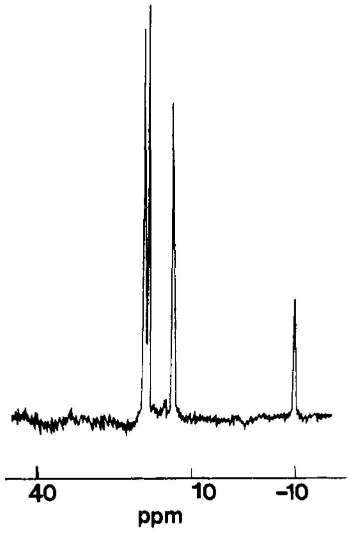

Figure 2. The ^{13}C NMR spectrum of compound **2**, −15–40 ppm.

The implications of this observation seem to us to be far reaching. Configurational stability at the silicon center during migration is consistent only with a concerted process. A heterolytic dissociative mechanism provides access to inversion which would result in loss of anisochronicity while lack of rate dependence on concentration or solvent precludes the corresponding homolytic dissociation. Identification of a 1,2 (equivalent to 1,5) shift with retention in compound **2** provides a compelling comparison with the characterization by Slutsky and Kwart[6] of a thermal [1,3] rearrangement of allylsilanes with inversion at temperatures above 500 °C. Invoking well-known arguments based on the criteria of Woodward and Hoffmann[7] for sigmatropic transformations, in a cyclopentadiene system[8] a [1,5] shift results in retention of configuration whereas inversion accompanies the alternative [1,3] migration. Anastassiou has emphasized the significance of frontier orbital symmetry in describing sigmatropic migrations in odd-membered monocyclic π systems in terms of distortions from regular polygonal geometry in corresponding radicals.[9] This approach leads to the same conclusion since the symmetry properties of the pertinent orbital ψ_3 for the five-membered ring system imply no change of configuration during a [1,5] shift with inversion for the [1,3] alternative. Thus we suggest that the mechanism resulting in the fluxional nature of com-

Table I. Proton Noise-Decoupled ^{13}C NMR Spectrum of (i-Pr)(Me)(H)SiC$_5$H$_5$ (**2**) at 233 K

chemical shifts, ppm[a]			
C (olefinic)	C (tertiary)	C (isopropyl)[b]	C (methyl)[b]
133.4 (74) 132.7 (64) [c]	47.6 (61)	18.7 (69) 18.4 (73) [c]	−10.1 (17)
130.6 (100) 130.3 (97) [c]		13.5 (65)	

[a] CDCl$_3$ used as solvent and reference throughout; relative peak heights are shown in parentheses. [b] Assigned through (^{1}H-^{13}C) spin-coupling characteristics in nondecoupled spectrum; see text. [c] Resonances due to anisochronous pairs of ^{13}C nuclei; see text.

pound **2** (and indeed perhaps all related *monohapto*cyclopentadienyl metal compounds[10]) is correctly termed a concerted [1,5] metallotropic rearrangement with conservation of orbital symmetry.

Acknowledgment. We thank the National Research Council, Canada, and the University of Victoria for financial support and Mr. G. Trump for experimental assistance.

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(5) Assignment of the pair of lines at higher frequency and showing the larger diastereotopic splitting to $C_{2,5}$ is consistent with our earlier conclusions:[2,3] thus chlorine substitution at Si to give $(R(H)(Cl)Si^*C_5H_5$[3] results in a diamagnetic shift of $C_{2,5}$ to a position of low frequency of $C_{3,4}$. It can be seen from the comparison of the present data with those of ref 3 that replacement of alkyl by chlorine at Si also magnifies anisochronous effects. It follows that the unsymmetrical collapse in this region shown in Figure 1 is in accordance with a 1,2 (or 1,5) shift.

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^{1}H NMR Assignment of the C-5′ Protons of B_{12} Coenzyme and the Synthesis of B_{12} Coenzyme Chirally Labeled in the C-5′ Position

Sir:

In the course of our study on the mechanism of action of the coenzyme B_{12} dependent enzyme dioldehydrase, we synthesized B_{12} coenzyme chirally labeled in the C-5′ position, To confirm the synthesis of chiral B_{12} coenzyme and subsequently to follow its fate in the enzymatic reactions, it was essential to have the correct NMR assignments for the C-5′ protons. These protons are directly involved in the enzymic reaction. Unfortunately, some uncertainty exists in the literature regarding these assignments. Based on model compound studies, Cockle et al.[1] have tentatively assigned these two protons to be at 0.6 and 0.9 ppm from DSS in D_2O. Brodie and Poe[2] have assigned these two protons to broad resonances at ~0.57 and 1.1 ppm in $(CD_3)_2SO$. However, in a study of the ^{1}H NMR of [5′-^{13}C]adenosylcobalamin, Hogenkamp[3] was unable to observe the expected $^{13}C-^1H$ spin-spin coupling. From this data, he concluded the peaks at 0.6 and 1.1 ppm are not due to the C-5′ protons.

To aid in the assignments, we have used [5′,5′-$^2H_2$]adenosylcobalamin.[4] The spectrum of that compound, as well as that of nonisotopically labeled cobalamin, is shown in Figures 1A and 1B. The spectrum of the nonisotopically labeled coenzyme shows a triplet at 0.6 and a doublet at 1.56 ppm which are not present in the spectrum of the deuterated coenzyme. It is, therefore, reasonable to assign these peaks to the C-5′ protons.

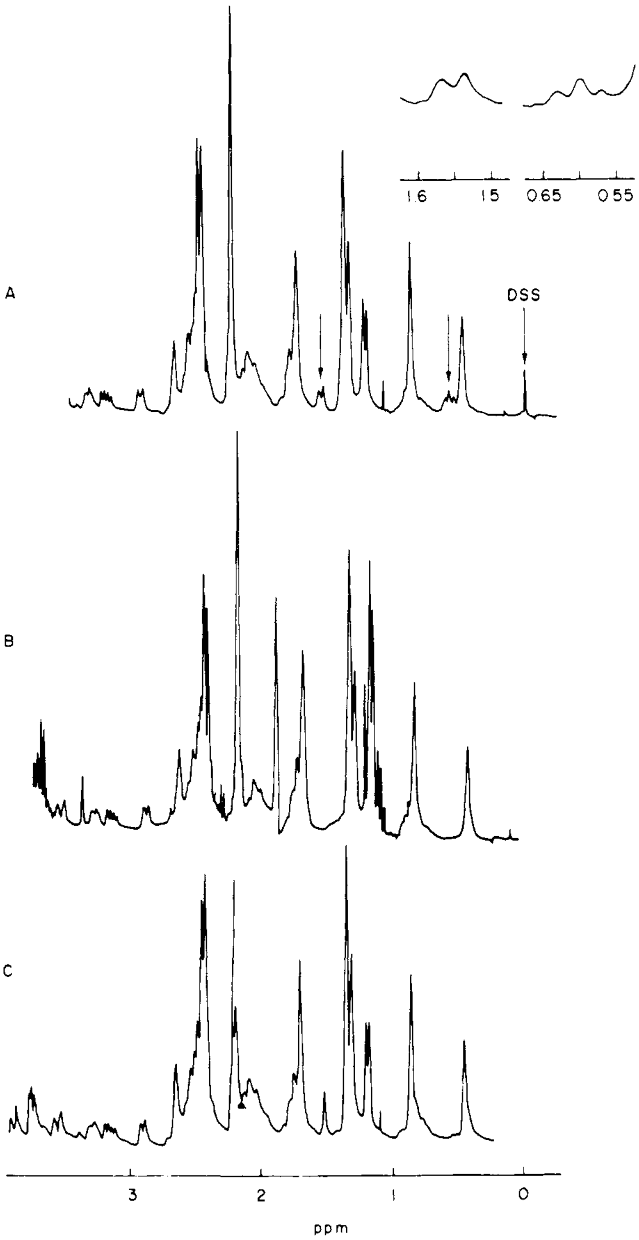

Figure 1. A: 2 mM adenosylcobalamin in D_2O. B: 2 mM [5′,5′-$^2H_2$]adenosylcobalamin in D_2O (it contains contaminants from paper chromatography). C: 2 mM 5′-chiral [5′-^{2}H]adenosylcobalamin in D_2O. The insert in the upper right-hand corner is an expanded spectrum (5.4×) showing the regions of the C-5′ protons. The NMR spectra were taken with a 270-MHz NMR spectrometer at a probe temperature of 20 °C built by A.R.[12]

To confirm these assignments, we have undertaken decoupling experiments. Irradiation at 0.6 ppm changes the doublet at 1.56 ppm into a singlet, and, conversely, irradiation at 1.56 ppm changes the triplet at 0.6 ppm into a doublet. This finding clearly indicates the two peaks in question are spin-spin coupled with each other. With decoupling techniques, we are also able to assign the C-4′ proton. Irradiation at 2.6 ppm causes the triplet at 0.6 ppm to change into a doublet. This suggests the C-4′ proton resonates at 2.6 ppm. These results then confirm our assignment for the two prochiral C-5′ hydrogens.

Figure 1C shows the spectrum of the coenzyme synthesized from (5′-*R*)-[5′-^{2}H]adenosine.[5,6] The absorption at 0.6 ppm is missing and there is now a singlet at 1.56 ppm. These results establish that no significant racemization occurred during the

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