$$(\mathbf{M}, \mathbf{G}, \mathbf{B})\, P\, (\mathbf{M}^*, -\mathbf{G}, \mathbf{B})\, T\, (\mathbf{M}^*, \mathbf{G}, -\mathbf{B}) \qquad (2)$$

In principle, the results in (1) and (2) indicate that both types of chiral fields would be capable of perturbing both enantiomeric equilibria and reaction rates.

The amount of energy required to introduce chiral order into a prochiral chemical reaction to the extent of 1-100 ppm depends on the nature of the fields that introduce the order. If the fields are continuous, they must alter the free energies of the *pro-R* and *pro-S* transition states by the amount required to produce the observed enantiomeric excess. In this case classical partition functions can be used to estimate the enantiomeric excess that will be generated for a given field strength. If chiral order were introduced into the *pro-R* and *pro-S* reaction coordinates by a **B** field and a parallel quantal **G** field, classical partition functions will not apply. If the imposed quantal field influenced motion in the reaction coordinate, it would not alter the electronic energy of the system if there was no breakdown of the Born-Oppenheimer approximation. The influence of the field on relative reaction rates would then be found in changes in the frequency for crossing the transition-state barrier.

If we assume that the free energies of the *pro-R* and *pro-S* transition states are the same, as they must be in the magnetic field alone, then it is possible to calculate the amount of energy that would be required to order the *R, S* binary array to the extent of 1-100 ppm. The order-disorder contribution to the entropy of a binary array is given by

$$S = -\left\{\frac{\mathrm{d}A}{\mathrm{d}T}\right\}$$
$$= \tfrac{1}{2}Nk[(1 + s)\ln(1 + s) + (1 - s)\ln(1 - s) - 2\ln 2]$$

where s is the order parameter. The change in entropy associated with 1-ppm ordering corresponds to 3.5×10^{-26} erg/molecule at 255 K. For ordering to the extent of 100 ppm at the same temperature, the energy required is 1.8×10^{-22} erg/molecule. These calculated energies do not take into consideration the fact that the magnetic field only partially orders the *pro-R* and *pro-S* transition states. For a magnetic field strength of 1 T, a transition-state magnetic moment of 2 μ_B which would be realistic for reaction of a solvated electron with a prochiral radical for example, and a temperature of 255 K, the energies above become 2×10^{-24} and 1×10^{-20} erg/molecule for 1 and 100 ppm, respectively. These numbers should be reduced by a factor of 2 because the ordering effect will act equally on the *pro-R* and *pro-S* transition states driving one toward products and one toward reactants. The estimate of the energy required in this case is 1×10^{-24} and 5×10^{-21} erg/molecule for ordering of the extent of 1 and 100 ppm, respectively. Strictly speaking, Boltzman statistics is not applicable to this system because any chiral population is metastable. The numbers above are highly approximate and only indicate general orders of magnitude.

The thermal energy of the reaction system, kT, is of the order of 3.5×10^{-14} erg/molecule at 255 K. The thermal energy is randomly oriented, and any energy producing asymmetric synthesis must be directed. In spite of the fact that the random motions are large compared to the ordering motions, a shift in the centroid of the random motions will be observable as chiral ordering in the reaction products. Prochiral chemical reactions may be one of the most sensitive energy detectors yet devised. The amounts of energy required for observable, asymmetric synthesis in accessible magnetic fields are within the range anticipated for gravitons.

It is possible that the chirality of the prebiotic metric contributed to the selection of the enantiomeric molecules of biology. The effect would have been larger than presently observable if gravitational acceleration has been decreasing with time as suggested by P. A. M. Dirac.

Acknowledgment. It is a pleasure to acknowledge valuable discussions with R. L. Fulton.

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(4) The calculation given in ref 3 omitted a symmetry factor of 2 which would have raised the calculated enantiomeric excess to 0.6 ppm. The nonadiabatic magnetic moment (1 μ_B) and the electric moment (1 eÅ) used in that calculation were both unrealistically large.
(5) Pasteur first investigated the possibility of gravitationally directed, asymmetric synthesis by use of a centrifuge. The experiment was not successful as the motion of molecules in a centrifuge is not chiral.
(6) It is interesting to note that charge inversion, *C*, following *P* and *T* in (2) would produce ($^+\mathbf{M}^*$, **G, B**). The positron enantiomer, $^+\mathbf{M}^*$, would have the same energy in the same field structure as the electron molecule, M. This is not true for charge reflection in (1).

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Asymmetric Synthesis in a Confined Vortex: Gravitational Fields Can Cause Asymmetric Synthesis

Sir:

This paper records the observation of asymmetric synthesis of isophorone oxide which resulted from conducting the reaction in the chiral gravitational field[1] of a confined vortex.

The chiral gravitational field was obtained by placing the reaction mixture in a 30-mm double-walled Pyrex tube which had been capped and placed in a double-ended turbine (Figure 1). The turbine was driven by air at pressures between 37 and 47 psi. The turbine assembly could be oriented so that the tube would spin clockwise or counterclockwise (from the top) when perpendicular to the earth's surface or the tube could be spun parallel to the earth's surface. The rotational rates for the tube varied between 6000 and 14 000 rpm and were generally within the range of 10 000 and 12 000 rpm.

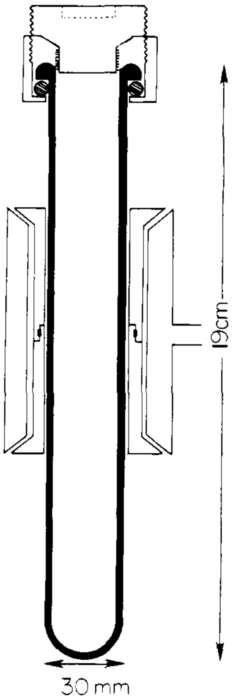

Figure 1. Double-ended turbine spinner assembly. Materials: housing, aluminum; rotor, "Rulon"; plug, "Teflon".

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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.

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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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