

The isomerization $7 \rightarrow 8$ is thought to occur as shown in Scheme II. The hexacoordinate phosphorus intermediate is analogous to a compound actually made from pyridine and a spiro-pentaoxyphosphorane.¹⁴

The experiments herein described support the interpretation given for the role of amines in phosphorylation reactions in aprotic solvents.³ Moreover, the observed silyl-transfer from aryl-oxygen to phosphorane-oxygen, $7 \rightarrow 8$, could reflect a significant and more general mechanism in silicon chemistry.¹⁵ The driving force for this isomerization may be provided by a higher stability of the bond $(RO)_4P-O-SiR'_3$ vs. $AR-O-SiR'_3$. This may be true also for $(RO)_2P(O)-O-SiR'_3$, and this point is being investigated further.

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- (7) Equimolar amounts of reactants (**4**, **5**) in ether-hexane (2:1 v/v) at 20° (10 h); **3**: bp ~165° (0.1 mm), τ 9.78 ppm.
- (8) Equimolar amounts of reactants and triethylamine in ether at 0° (5 min). **7**: τ 9.62 ppm; the neat liquid is preserved at -20°; **7** isomerizes to **8** in about 4 h at 25°.
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- (10) Equimolar amounts of reactants and triethylamine in benzene at 10° (25 min), and 20° (1.5 h). **8**: mp 110–112° (hexane); τ 9.85 ppm; $\delta^{13}C$ in ppm⁶ (J in Hz) 0.4 (1.6) and 110.7 (17.4), 122.0, 142.9 (7.4). For the chloro-analogue **9**: $\delta^{13}C$ 111.4 (17.8), 123.2, 142.2 (7.8). For the phenoxy-analogue **10**: 110.8 (17.4), 122.4, 143.1 (10.9), and 120.8 (4.4), 125.3 (2.0), 129.3 (3.8), 151.5 (10.9) (phenoxy group).
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Stabilization of Perpendicular Olefins. The Structures and Rotational Barriers of Singlet and Triplet 1,1-Dilithioethylenes

Sir:

Rotational barriers around carbon-carbon double bonds have been the subject of numerous experimental^{1,2} and theoretical^{3,4} studies. The best available ab initio barriers (63.7^{4a} and 63.2^{4b} kcal/mol) for ethylene itself are in excellent agreement with the experimental value (65 kcal/mol).² The double bond is essentially broken in the perpendicular transi-

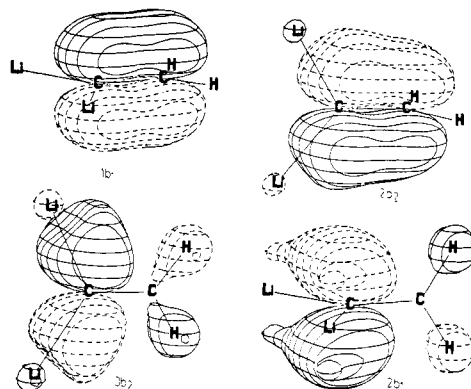


Figure 1. Highest occupied molecular orbitals of **1S** (left side) and **2S** (right side). Note the three-center two-electron bonding ($2b_1$ of **2S**) and the strong hyperconjugation ($2b_2$ of **2S**) leading to the double bond. Since the p orbitals on lithium are diffuse, contours of 0.06 a.u. were employed.

Table I. Optimized Geometries and Dipole Moments (STO-3G) of Dilithioethylenes^a

Structural parameter	Planar forms 1S	Perpendicular forms 1T	Perpendicular forms 2S^b	Perpendicular forms 2T
C-C ^c	1.347	1.368	1.342	1.370
C-Li ^c	1.931	1.987	1.747	1.945
C-H ^c	1.087	1.088	1.092	1.089
Li-Li ^c	3.343	2.326	2.839	2.344
$\angle LiCLi^d$	119.8	71.6	108.8	74.2
$\angle CCLi^d$	120.1	144.2	125.6	142.9
$\angle CCH^d$	124.5	122.4	123.6	122.3
Dipole moments ^e	4.26 ^f	1.08 ^f	1.83 ^g	1.78 ^g

^a C_{2v} symmetry imposed. RHF and UHF procedures were used for the singlet and triplet species, respectively. ^b Removing the C_{2v} constraint and fully minimizing the structure resulted in very little change and negligible alternation in the energy. ^c Bond lengths in Angstroms (Å). ^d Bond angles in degrees. ^e In Debyes. ^f Dipole with the CH_2 moiety negative. ^g Dipole with the CH_2 moiety positive.

tion state, calculated to have a C-C bond length of 1.48 Å vs. the value in the planar form of 1.33 Å.^{4a} The high barrier can be reduced significantly by π -donor and π -acceptor substituents, which will preferentially stabilize either the diradical or especially the dipolar configuration of the perpendicular form by electron delocalization.^{1,5} Bulky substituents destabilize the planar ground state. In extreme cases, a partially rotated structure is found to be the most stable, but the double bond is severely disrupted.⁶ The same should be true for the highly strained anti-Bredt bridgehead olefins.⁷

We have discovered by theoretical calculation a simply substituted ethylene remarkable in several ways. The rotational barrier not only is very low, but also the perpendicular form may actually be more stable than the planar. The C=C bond length is essentially double, and does not change significantly during rotation! A new mode of stabilization of perpendicular ethylenes is indicated by these results.

The structures (Table I) and energies (Table II) of the planar (**1**), perpendicular (**2**), and partially rotated forms (**3**) of 1,1-dilithioethylene in their singlet and triplet configurations were calculated using the ab initio SCF-MO GAUSSIAN 70 series of programs⁸ using the standard molecular exponents.⁹ For the triplet, rigid rotation was assumed while for the singlet a full geometry search was performed for each rotational angle within the constraints of C_2 symmetry.^{10b}

The energy differences between the planar and the perpendicular forms are small for both the triplets and the singlets. The relative energies of **1S** and **2S** vary from -9.9 kcal/mol

of unoccupied low energy σ -type orbitals on lithium,¹⁸ which allow the additional α electron to occupy a bonding orbital. This should be contrasted with planar triplet ethylene ($^3B_{1u}$), where an electron occupies the π^* antibonding orbital.

We hope that these findings and the synthetic availability of closely analogous molecules such as 1,1-dilithio-2-methylpropene¹⁹ will encourage experimental work on the determination of the structures and rotation barrier of ethylenes geminally substituted with electropositive groups.²⁰ Extension of our research to other polyolithioethylenes, as well as to polyolithiated methanes,¹³ acetylenes, allenes, imines, and azo compounds has also revealed startling structural features, and these results will be presented in future publications.

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refer to isolated molecules in the gas phase. The known tendency of organolithium compounds to associate or to be solvated²¹ must be taken into account in experimental work in condensed phases. In addition, our calculated dipole moments indicate that **1S** should be stabilized relative to **1T** and **2** in polar solvents. Note Added in Proof: Dr. K. Krogh-Jespersen (private communication) has now discovered a boron-substituted ethylene which behaves like **1S** and **2S**.

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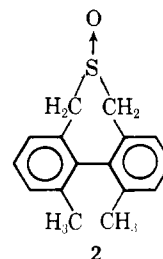
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Evidence on Internal Return from Isotope Effects in the Hydrogen-Deuterium Exchange of Benzyl Sulfoxides. A Caveat re Interpretation of Isotopic Exchange Rates

Sir:

In 1965 the report by Rauk, Buncel, Moir, and Wolfe¹ describing a highly stereoselective hydrogen-deuterium exchange of the diastereotopic methylene protons of benzyl methyl sulfoxide, **1**, has stimulated extensive studies on the mechanism of this interesting reaction. Effects of orientation of the developing anion with respect to the asymmetric sulfur atom on selectivity have received wide attention² as have effects of solvent^{2,3} and ion-pairing.⁴ In addition, ab initio MO calculations of anion stability as a function of stereochemistry were carried out.⁵ A comparison of the results of H-D exchange with those calculated (for the gas phase) led one of us^{2f} to conclude that agreement was lacking "presumably because of strong solvation effects". At the same time it was pointed out that *internal return*,⁶ which could invalidate the use of kinetic data to assess carbanion stability, remained to be examined. Recent additional studies on several thiolane *S*-oxide derivatives^{2a} have produced results which the authors termed "difficult to organize in a unique coherent pattern". Such ambiguous accumulating data emphasize the need for knowing if internal return occurs during the exchange process. In this paper we provide evidence on internal return by measurement of the primary isotope effects k_H/k_T and k_D/k_T in the isotopic exchange of (a) each diastereotopic proton of benzyl methyl sulfoxide and (b) two of the benzylic protons of the bridged biaryl sulfoxide, **2**.^{2f} The results show that internal return is negligible in the former case but dominant in the latter.



The pioneering research of Cram and co-workers first established the presence of internal return in an isotopic exchange reaction involving carbanion intermediates.⁹ The pathway for