The isomerization **7 → 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 spiropentaoxyphosphorane.[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 → 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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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-
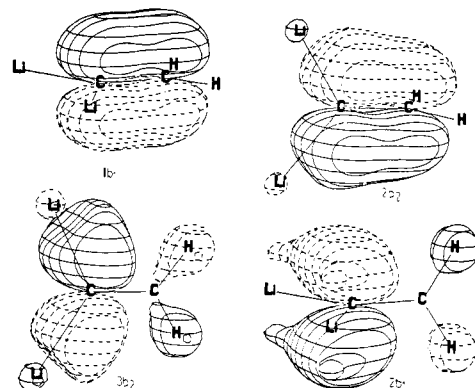

Figure 1. Highest occupied molecular orbitals of **1S** (left side) and of **2S** (right side). Note the three-center two-electron bonding ($2b_1$ of **2S**) and the strong hyperconjugation ($2b_2$ of **2S**) leading to the double bond. Since the p orbitals on lithium are diffuse, contours of 0.06 a.u.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

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

| Structural | Planar forms | | Perpendicular forms | |
parameter	1S	1T	2S[b]	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 programs[8] 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]
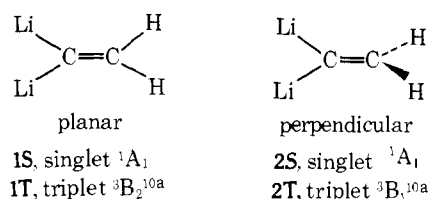
The energy differences between the planar and the perpendicular forms are small for both the triplets and the singlets. The relative energies of **1S** and **2S** vary from −9.9 kcal/mol

Table II. Total and Relative Energies for the Planar Singlet (1S) and Triplet (1T), Perpendicular Singlet (2S) and Triplet (2T), and the Partially Rotated Singlets (3S) and Triplets (3T) of 1,1-Dilithioethylene

| Compound[a]	θ[b] (degrees)	Total energies (hartrees)		Relative energies (kcal/mol)	
		STO-3G	4-31G	STO-3G	4-31G
1S ($^1A_1$)	0	−90.495 48	−91.555 19	0.0	0.0
1T ($^3B_2$)	0	−90.550 68[c]	−91.606 80[c,d]	−34.6	−32.4
2S ($^1A_1$)	90	−90.511 33[e]	−91.553 99	−9.9	+0.8
2T ($^3B_1$)	90	−90.553 95[c,f]	−91.608 64[c]	−36.7	−33.5
3S	25	−90.494 56		+0.6	
3S	45	−90.498 46		−1.9	
3S	60	−90.504 47		−5.6	
3T	20	−90.551 05[g]		−34.9	
3T	45	−90.552 18[g]		−35.6	
3T	70	−90.553 16[g]		−36.2	

[a] Geometry minimized at the STO-3G level imposing a C_{2v} symmetry for **1** and **2** and a C_2 symmetry for **3S**. [b] The dihedral angle LiCCH. [c] Using the unrestricted Hartree–Fock procedure for open shell systems.[12] [d] Convergence achieved by using direct descent techniques (R. Seeger and J. A. Pople, *J. Chem. Phys.*, in press). [e] See Table I, footnote *b*. [f] An energy of −90.538 54 was obtained using the restricted Hartree–Fock procedure for open shell systems.[16] [g] A rigid rotation using the geometry of **1T**.

(RHF/STO-3G)[9a,b] to +0.8 kcal/mol (RHF/4-31G)[9c,d] with the basis set. Addition of limited configuration interaction (3 × 3 CI)[5] to the STO-3G calculations caused an insignificant change in the total energies and in the relative energies of **1S** and **2S**.[11] The triplet perpendicular form (**2T**) is more stable (by 2.1 kcal/mol at UHF/STO-3G and 1.1 at UHF/4-31G)[12] than the planar geometry (**1T**). The two triplets, **1T** and **2T**, are almost identical in bond lengths and bond angles (Table I), energies of corresponding molecular orbitals, and population analyses. The perpendicular form is the only minimum found on the rotational surface. The structures of **1S** and **2S** differ significantly, and both are distinct energy minima but with a barrier (at a rotational angle of 25° from **1S**) of only 0.6 kcal/mol (RHF/STO-3G).

planar

1S, singlet $^1A_1$
1T, triplet $^3B_2$[10a]

perpendicular

2S, singlet $^1A_1$
2T, triplet $^3B_1$[10a]

The high stability of **2S** is due to the special combination of σ-donor and π-acceptor character of lithium, the operation of which can be understood by considering the formal zwitterion structure (**2a**) for the perpendicular form. The anionic part of the zwitterion is stabilized by the delocalization of the two p_y electrons in a cyclopropenium-type aromatic system (similar to that found in cis-planar CH_2Li_2[13a]) formed by three p orbitals, two on the lithium atoms and one on the carbon C_1. This shortens the C–Li bond length and the Li–Li distance of **2S** relative to **1S**. The cationic center is stabilized by very strong hyperconjugation of the p_x orbital on C_2 across the C–C bond with the two coplanar C–Li bonds (the C–C$^+$ rotational barrier in $LiCH_2CH_2^+$ is 53 kcal/mol at the RHF/STO-3G level).[14] The short C=C bond length in **2S** (1.342 Å) results. Although the STO-3G basis set tends to overemphasize the role of p orbitals on lithium, it is our experience that leaving out these p orbitals give results not consistent with large basis set calculations near the Hartree–Fock limit.[13] Figure 1[13c] illustrates the special features that stabilize **2S**.

2a
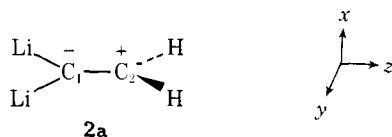
The same factors stabilize perpendicular triplet **2T** which can be visualized as having transferred one of the p_y electrons on C_1 in **2a**, with spin inversion, to a σ orbital ($7a_1$) which bonds the two lithium atoms. Similarly the planar triplet (**1T**) involves an electron transfer from the singlet HOMO (a $3b_2$ σ orbital, bonding the two lithium atoms to C_1 but having antibonding character between the two lithium atoms) to another σ bonding orbital ($7a_1$) which has a bonding character between the two lithium atoms. A further shortening of the Li–Li distance in **1T** and **2T** results (Table I). For both **1T** and **2T** the π-type orbitals, $1b_1$ and $2b_2$, respectively, representing the carbon–carbon double bonds are lower in energy and remain doubly occupied.

We stress that a description of perpendicular 1,1-dilithioethylene by **2a** is misleading, and **2S** or **2T** actually is a better representation. The C–C bonds (1.34–1.37 Å) in **1S**, **1T**, **2S**, **2T**, and **3S** are all essentially double in length. The strong back-donation accompanying the hyperconjugation with the C–Li bonds causes a transfer of 0.866 electrons in **2S** and 0.811 electrons in **2T** into the formally empty p orbital on the β carbon and thus balances the transfer of electrons from C_1 to the lithium atoms.[15] As a result, **2** is only slightly polarized and the net charge on the $=CH_2$ moiety is only +0.039 for **2S** and +0.087 for **2T**. As the $=CH_2$ groups in both **1S** and **1T** are negatively charged, there is an interesting reversal of the dipole moments on rotation (Table I). Alternative explanations for the behavior of $CH_2=CLi_2$ in terms of an ionic structure, $2Li^+C=CH_2^{2-}$, are not consistent with the Mulliken populations,[15] which indicate only very small net charges on Li (in the range +0.01 to +0.06 for all species, **1S**, **2S**, **1T**, and **2T**).

The triplet states of both the planar (**1T**) and the perpendicular (**2T**) conformations are calculated to be more stable than the corresponding singlets by 34.6 kcal/mol (STO-3G) and 32.4 kcal/mol (4-31G) for **1S** and by 26.8 kcal/mol (STO-3G) and 34.3 kcal/mol (4-31G) for **2S**. The UHF triplet states show considerable contamination from higher multiplicity spin states ($\langle S^2 \rangle$ = 2.46 for **1T** and 2.41 for **2T**). However, this contamination cannot account for the large singlet–triplet energy differences since **2T** is calculated to be 17.1 kcal/mol more stable than **2S** using the RHF/STO-3G procedure.[16] It is known that the stability of triplet methylene over singlet methylene is overestimated by 14 ± 6 kcal/mol by unrestricted single determinant theory.[17] Since the singlet–triplet separations here are significantly larger, **1** and **2** probably have *triplet ground states*. This surprising result, especially for planar conformation **1**, arises from the presence

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-methylpropene[19] 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 polylithioethylenes, as well as to polylithiated 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 solvated[21] 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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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 Wolfe[1] 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 attention[2] 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.

2
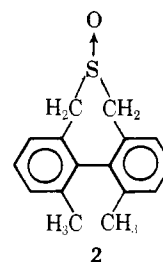
The pioneering research of Cram and co-workers first established the presence of internal return in an isotopic exchange reaction involving carbanion intermediates.[9] The pathway for