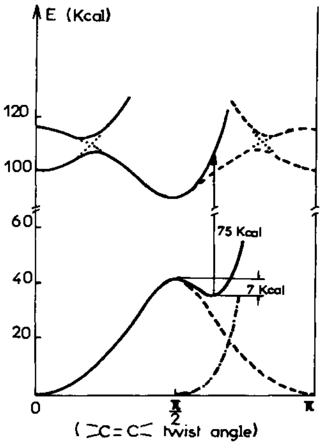

Figure 2. Estimated potential surfaces of 1-phenylcyclohexene (—) constructed as the sum of 1-phenylpropene surfaces (- - -) and of a ring constraint energy curve (------).

vent-stabilized zwitterion B.[8] Hence, in all likelihood, the observed intermediate must be the trans phenylcyclohexene C. It is appreciated that, in the classical sense, the molecule cannot be fully trans. It must be highly twisted and slightly past orthogonality. This hypothesis is substantiated by the increase in transition energy when going from *trans*-phenylcyclohexene to the corresponding *trans*-phenylcycloheptene intermediate, the absorption of which peaks at 305 nm.[9] Approximate potential surfaces of 1-phenylcyclohexene can be obtained as the sum of the ordinary dumbbell curves for cis–trans isomerization and of a steeply rising curve due to ring-strain for twist angles of the double bond above 90°.[10,11] In Figure 2, the dumbbell curves are drawn with the 42 kcal energy barrier in the ground state and 25 kcal energy well in the excited state reported[12] for the 1-phenylpropene. The strain energy curve is empirically adjusted to obtain, on the ground state surface, an energy barrier equal to the energy of activation for return from *trans*- to *cis*-phenylcyclohexene (~7 kcal as calculated from temperature dependence of the lifetime of the transient) and, between the ground state and the excited state surfaces, a 75 kcal energy gap corresponding to the optical absorption of the transient. Of course the equilibrium angle for the trans species depends on the shape of the two dumbbell curves; therefore the value of 115° found in the figure must be considered as tentative.[13]

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References and Notes

(1) We used a frequency doubled neodymium glass laser which provides a pulse of 265-nm light with a duration of about 3×10^{-8} s. The concentration of 1-phenylcyclohexene (K and K) in methanol (Prolabo, U.V. spectroscopic grade) was about 10^{-4} M.
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(3) The first-order rate constant k_r'' is equivalent to the sum of the rates of all processes leading to products such as phenylcyclohexane, dimer of I, 1-hydroxymethyl-1-phenylcyclohexane, etc . . . .
(4) ϕ and ϕ' were measured under continuous illumination by the 2537 Å line of a low pressure mercury lamp, isolated by an interferential filter. The absorbed light flux was measured by actinometry. The rate of disappearance of I was measured by both uv spectroscopy and gas-phase chromatography. The rate of formation of II was measured by gas-phase chromatography after identification by comparison with an authentic specimen prepared by J. P. Desvergnes. Tridecane was used as internal reference in the GC experiments.
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(10) Using Dreiding molecular models, it appears that the strain of the ring remains weak for twist angles up to 90° and rises sharply after.
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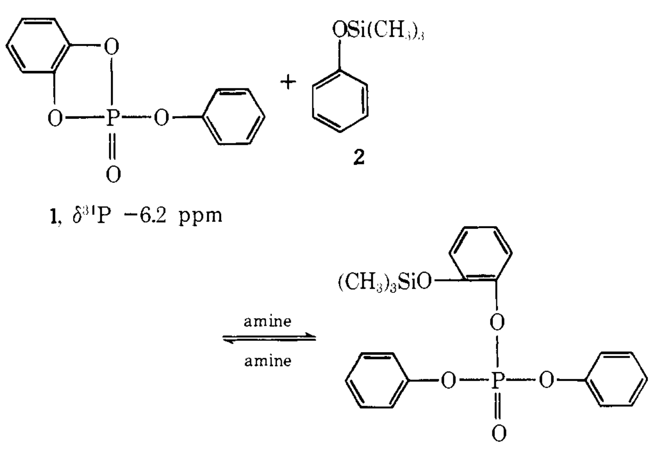
Experimental Evidence in Support of Oxyphosphorane Intermediates in Reactions of Cyclic Phosphate Esters

Sir:

The existence of stable *oxyphosphoranes*[1] is well established. The hypothesis that oxyphosphoranes are formed as transient intermediates in nucleophilic displacements of compounds with tetracoordinate phosphorus has been a fruitful concept in the interpretation of the chemical and stereochemical behavior of phosphonium salts and phosphate esters,[2] and has also led to useful synthetic reactions.[3] However, the direct observation or trapping of such intermediates has remained an elusive goal.[4]

We have carried out reactions of phosphate esters which can be interpreted as proceeding via oxyphosphorane intermediates, and have slightly modified the same phosphate esters in order to trap the postulated intermediates. The results are summarized in this communication.

Phenyl *o*-phenylene phosphate[4a] (**1**) reacts with *O*-trimethylsilylphenol[5] (**2**) in aprotic solvents, under amine catalysis, to form diphenyl (2-trimethylsilyloxy)phenyl phosphate[6] (**3**).



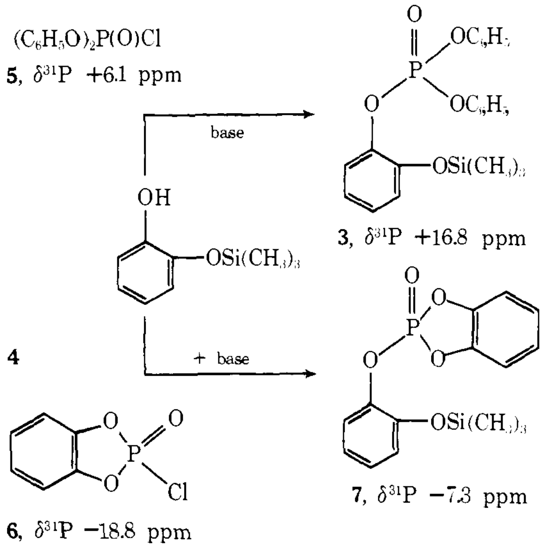
1, $\delta^{31}P$ −6.2 ppm

2

3, $\delta^{31}P$ +16.8 ppm

This novel reaction is reversible, and reaches a state of equilibrium between the two reagents and the product. The ratio of cyclic **1** to acyclic **3** phosphates is about 2/1 at 35° in a 1.5 M CDCl$_3$ solution, when the cyclic phosphate **1**, the silylphenol **2**, and the amine are combined in equimolar amounts. The equilibrium position is shifted in favor of the acyclic phosphate **3**, when an excess of silylphenol **2** is added (ca. 1/2 with 3 mol equiv of **2**, under comparable conditions). The catalytic efficiency of the amines seems to be related mainly to their steric requirements, as follows (figures in parentheses are the approximate times for attainment of equilibrium in the experiments with equimolar reagents, **1** + **2**, and amine): imidazole (5 min) > 1-methylimidazole (35 min) > pyridine (1.5 h) > quinuclidine (4.0 h) > γ-collidine (15 h) > triethylamine (36 h) ≫ no amine (estimated ~9 days). The course of the reaction is conveniently followed by a combination of ^{31}P and ^{1}H NMR spectrometry (the singlet from the silyl group protons of **3** is about 1 Hz to high field of the singlet from **2**). In control experiments, neither the cyclic phosphate **1** nor the silylphenol **2** is noticeably affected by the tertiary amines in the absence of the second reagent.

An authentic sample of the acyclic phosphate **3** was synthesized[7] from diphenyl phosphorochloridate (**5**) and *O*-trimethylsilylcatechol[5] (**4**). The addition of 1 mole equiv of imidazole (or pyridine) to a 1.5 M CDCl$_3$ solution of **3** reestablishes the same equilibrium, cyclic **1**/acyclic **3** ~ 2/1 in about 1 min at 35°. The silylphenol **2** can be separated from the cyclic phosphate **1** by distillation when equimolar amounts of imidazole and the acyclic phosphate **3** are kept 15 min at 55° and 0.75 mm.



5, δ^{31}P +6.1 ppm

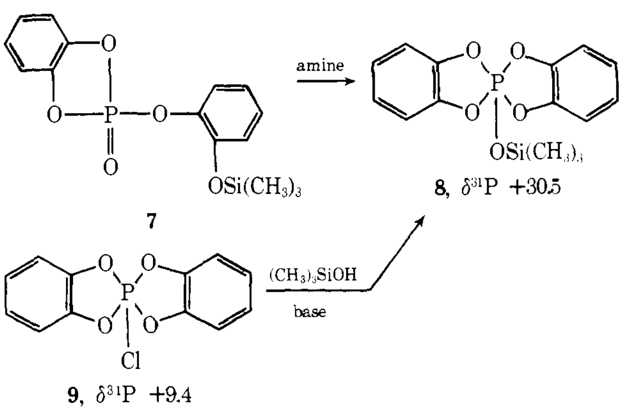
3, δ^{31}P +16.8 ppm

4

6, δ^{31}P −18.8 ppm

7, δ^{31}P −7.3 ppm

To test the hypothesis that the establishment of the amine-catalyzed equilibrium: **1** + **2** ⇌ **3** involves oxyphosphorane intermediates, (2-trimethylsilyloxy)phenyl *o*-phenylene phosphate[6] (**7**) was synthesized[8] from *o*-phenylene phosphorochloridate[9] (**6**) and the silylcatechol, **4**. The cyclic catechol phosphate derivative, **7**, undergoes a complete isomerization into the spirodicatechol-(trimethylsilyloxy)phosphorane[6] (**8**) in aprotic solvents, under amine catalysis. The effect of various amines is qualitatively similar in the isomerization **7** → **8** and in the reaction **1** + **2** ⇌ **3**. The following sequence is observed at 28° in a 0.55 M CDCl$_3$ solution containing the phosphate **7** and 10 mol % of amine (figures in parentheses are the approximate times at which [**7**] = [**8**]): imidazole (4 min) > 1-methylimidazole > pyridine (15 min) > quinuclidine (25 min) > γ-collidine (7.5 h) > triethylamine (8.5 h) >> no amine (estimated 39 h). The isomerization is followed by ^{31}P and ^{1}H NMR spectrometry (the singlet from the silyl group protons of **8** is 13 Hz to high field of the singlet from **7**). An authentic sample of the oxyphosphorane **8** was synthesized[10] from the spirodicatecholchlorophosphorane[11] (**9**) and trimethylsilanol.

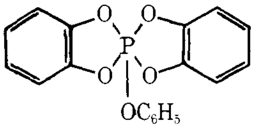


7

8, δ^{31}P +30.5

9, δ^{31}P +9.4

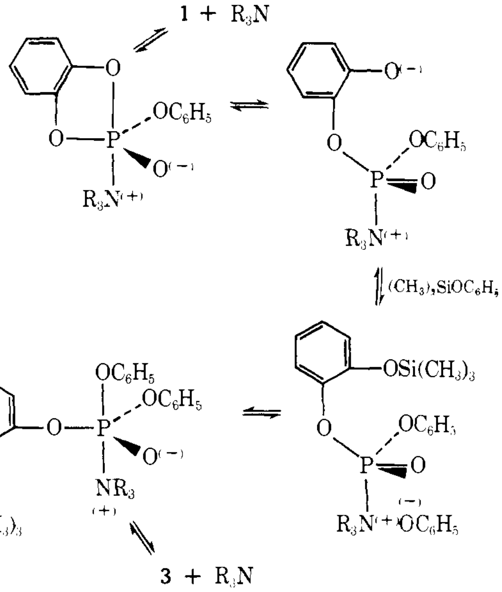
The molecular structure of spirodicatecholphenoxyphosphorane[11] (**10**) has been confirmed by x-ray crystallography.[12]



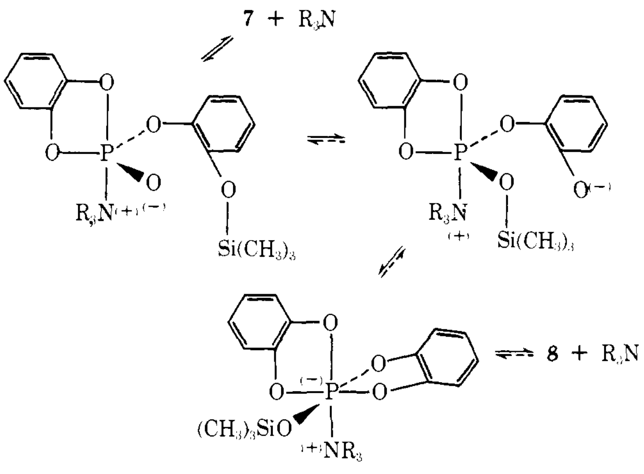
10, δ^{31}P +30.2 ppm

The following mechanism (Scheme I) is proposed for the amine-catalyzed reaction **1** + **2** ⇌ **3**. Entropy, as well as enthalpy, factors seem to be important in the control of this equilibrium.[13]

Scheme I



Scheme II



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 $(RO)_4P\text{-}O\text{-}SiR'_3$ vs. $AR\text{-}O\text{-}SiR'_3$. This may be true also for $(RO)_2P(O)\text{-}O\text{-}SiR'_3$, 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 ppm[6] (*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 transition 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]

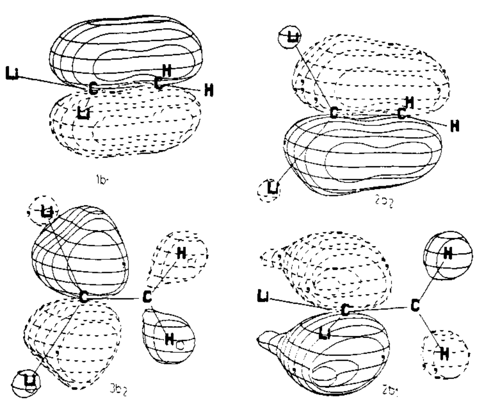

Figure 1. Highest occupied molecular orbitals of **1S** (left side) and of **2S** (right side). Note the three-center two-electron bonding ($2b_1$ of **2S**) and the strong hyperconjugation ($2b_2$ of **2S**) leading to the double bond. Since the p orbitals on lithium are diffuse, contours of 0.06 a.u.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

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

Structural parameter	Planar forms **1S**	**1T**	Perpendicular forms **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
∠ LiCLi[d]	119.8	71.6	108.8	74.2
∠ CCLi[d]	120.1	144.2	125.6	142.9
∠ 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.

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