hydrolyze more slowly than the corresponding chlorides, their hydrolysis being catalyzed by both acid and base. I hydrolyses very slowly in neutral or basic media, but much more rapidly in acid. Susceptibility to neutral or basic hydrolysis, and also sensitivity to heat, increases with replacement of the phenyl groups of I with methyl groups.

These azides also undergo ready photolysis. I is completely decomposed by prolonged ultraviolet irradiation at 30°. Photolysis and thermal decomposition are believed to occur by the same mechanism as for organic azides,[4,5] namely, through the formation of azene intermediates. The photolytic and thermal decomposition products of I are now under study.

I resembles triphenylmethyl azide in forming an isolable complex with triphenylphosphine.[6] This complex is a high-melting solid. Azidotrimethylsilane also forms a solid with triphenylphosphine.

It seems probable that the unexpected thermal stability of I is due to strong dative pi-bonding from the azide group to silicon. Pi-bonding from the degenerate p orbitals of the alpha nitrogen into the de orbitals of silicon may possibly stabilize a linear Si–N–N–N arrangement, in contrast to the bent structure of organic azides. Similar linear configurations have been reported for the Si–N–C–O system in $Si(NCO)_4$,[7] and the Si–N–C–S system in $H_3SiNCS$.[8] Structural studies of silyl azides are in progress.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON 6, WISCONSIN
ROBERT WEST
JOHN S. THAYER

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## CONCERNING THE MECHANISM OF FORMATION OF TRIPHENYLPHOSPHINEALKYLIDENES[1]

*Sir:*

Triphenylphosphinealkylidenes have found widespread application in organic synthesis since the report[2] of their utility in olefin syntheses. The formation of these reagents by the action of bases on triphenylphosphonium salts of type $[(C_6H_5)_3P\text{—}\overset{|}{\underset{|}{C}}\text{—}H]X$ appears generally believed to involve abstraction of the acidic hydrogen atom $\alpha$ to the phosphonium function by the base.[3]

$$[(C_6H_5)_3PCH_2R]Br + R'Li \longrightarrow (C_6H_5)_3P{=}CHR + R'H + LiBr$$

We have investigated the mechanism of triphenylphosphinemethylene formation and have found that two competing reactions can contribute to the generation of this reagent by the organolithium route. Treatment of 11.2 mmoles of methyltriphenylphosphonium bromide with 10 mmoles of methyllithium in ether gave the usual yellow phosphinemethylene solution. The latter was quenched with 48% aqueous hydrobromic acid, and the organic layer was subjected to gas chromatographic analysis. It was found that benzene had been formed in 26% yield, based on the organolithium reagent. In another experiment the phosphinemethylene reagent formed in this manner was treated with an excess of cyclohexanone, and the volatiles from the reaction were analyzed by gas chromatography. The formation of benzene in 21% yield and methylenecyclohexane in 80% yield was demonstrated. Methyltriphenylphosphonium bromide was treated with ethereal *p*-deuteriophenyllithium in another series of experiments. The resulting solutions (Gilman Color Test I negative) were quenched with 48% hydrobromic acid and with cyclohexanone, respectively. In each case the benzene formed was isolated by gas chromatography. Analysis of the latter (mass spectrometry and falling drop method) showed that in the HBr reaction the benzene was composed of 31% $C_6H_6$ and 69% $C_6H_5D$, in the cyclohexanone reaction, of 28% $C_6H_6$ and 72% $C_6H_5D$. These results indicate that in addition to attack by the lithium reagent on the methyl hydrogens, there occurs to a lesser extent attack at the phosphorus atom of the phosphonium salt. If only attack at the hydrogen atoms were to occur, no benzene would be expected in any of these experiments. If, on the other hand, only attack at phosphorus were to occur, the isolated benzene in the second series of experiments would be expected to be a *ca.* 3:1 mixture of $C_6H_6$ and $C_6H_5D$.

The demonstration that in these reactions attack on phosphorus can occur suggested that it should be possible to generate triphenylphosphinemethylene by the reaction

$$[(C_6H_5)_4P]Br + CH_3Li \longrightarrow (C_6H_5)_3P{=}CH_2 + C_6H_6 + LiBr$$

This was found to be the case. When a suspension of 10 mmoles of tetraphenylphosphonium bromide in a 1:5 diethyl ether–tetrahydrofuran solution of methyllithium (10 mmoles) was heated at reflux, the phosphonium salt dissolved completely, and a reddish-brown solution was formed. Cyclohexanone was added, and the resulting solution was refluxed for 18 hr. Distillation and gas chromatographic analysis of the distillate showed that methylenecyclohexane (identified by its infrared spectrum and refractive index) had been produced in 58% yield, and that benzene had been formed quantitatively in the initial reaction.[4]

Two possible mechanisms may be envisioned for phosphinemethylene formation involving attack on phosphorus: (1) formation of a pentacovalent phosphorus intermediate, followed by its decomposition to the observed products

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(1) Studies in Phosphinemethylene Chemistry, Part VI. For Part V see D. Seyferth, J. K. Heeren and S. O. Grim, *J. Org. Chem.*, **26**, 4783 (1961).

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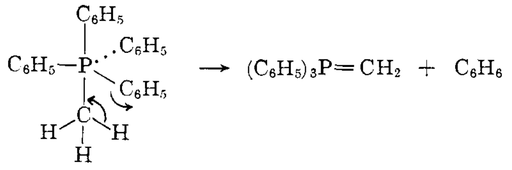
(4) It has been reported[2] that this reaction did not occur when these reactants were shaken at room temperature in diethyl ether alone during 4 months. Our conditions (maintaining the 5:1 tetrahydrofuran–diethyl ether solvent system at reflux and high speed stirring) apparently were sufficiently different to allow this reaction to proceed.

$$[(C_6H_5)_4P]Br + CH_3Li \longrightarrow (C_6H_5)_4PCH_3 + LiBr$$
$$(C_6H_5)_4PCH_3 \longrightarrow (C_6H_5)_3P{=}CH_2 + C_6H_6$$

or, (2) an exchange reaction giving the methyltriphenylphosphonium ion, followed by α hydrogen abstraction from the latter

$$[(C_6H_5)_4P]^+ + CH_3Li \longrightarrow [(C_6H_5)_3PCH_3]^+ + C_6H_5Li$$
$$[(C_6H_5)_3PCH_3]^+ + RLi \longrightarrow (C_6H_5)_3P{=}CH_2 + RH + Li^+$$

Wittig and Rieber[5] have demonstrated the easy formation of pentaphenylphosphorane by the reaction of tetraphenylphosphonium bromide with phenyllithium in ether. Thus it seems likely that any organolithium reagent should react with this phosphonium ion in this manner, although the $P^V$ product need not be stable in all cases. Furthermore, the removal of a phenyl anion from pentaphenylphosphorane is relatively easily accomplished, as demonstrated by its reaction with triphenylborane to give tetraphenylphosphonium tetraphenylboron,[6] as well as by other reactions.[2,5] A concerted loss of benzene from a trigonal bipyramidal methyltetraphenylphosphorane intermediate by a cyclic mechanism thus seems easily possible. An attempt to demonstrate the intermediacy of phenyllithium in the methyltriphenylphosphonium bromide–methyllithium reaction gave a negative result. When this reaction mixture was quenched with trimethylchlorosilane immediately after mixing, not even trace amounts of trimethylphenylsilane could be detected.



Indirect evidence favoring a pentacovalent intermediate in the tetraphenylphosphonium bromide–alkyllithium reaction was obtained by a consideration of relative reactivities. Since the experimental procedure used involved adding all of the lithium reagent at one time to the phosphonium salt, the results observed (*i.e.*, quantitative formation of benzene) could only have been obtained *via* the exchange mechanism if the phenyllithium formed were extremely highly favored over methyllithium in the reaction with methyltriphenylphosphonium bromide. If this were not the case, and if the exchange mechanism were operative, then much lower yields of benzene would be expected. Since methyllithium is among the less reactive organolithium reagents,[7] the much more reactive ethyllithium was allowed to react with tetraphenylphosphonium bromide in the same manner. Again, benzene was obtained in nearly quantitative (92%) yield, and ethylidenecyclohexane in 67% yield. Since it is unlikely that the phenyllithium formed in an exchange reaction could complete this successfully with the initially large excess of ethyllithium, the exchange mechanism lacks support, and most likely a pentacovalent ethyltetraphenylphosphorane intermediate is involved.

It should be pointed out that the other extreme in behavior, attack only at the α hydrogen atom of an alkyltriphenylphosphonium salt, is possible. Thus the reaction of methyllithium with benzyltriphenylphosphonium bromide, giving triphenylphosphinebenzylidene, resulted in not even a trace of benzene. Experiments designed to relate the relative importance of the two possible mechanisms to structural factors in the phosphonium salt and the organolithium reagent are in progress.

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DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS
DIETMAR SEYFERTH
JAMES K. HEEREN
WILLIAM B. HUGHES, JR.

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## LARGE SECONDARY INTERMOLECULAR KINETIC ISOTOPE EFFECTS IN NON-EQUILIBRIUM SYSTEMS. ENERGIZATION BY PHOTOSENSITIZATION

*Sir:*

The occurrence of very large *normal* secondary intermolecular kinetic isotope effects in non-thermally activated unimolecular systems has been described.[1] So far, illustration of this general effect has been given only for systems in which the non-equilibrium distributions of energized molecules has been realized by chemical activation.[1,2] In principle, other experimental techniques such as electron impact, radiation, *etc.*, may be used. We wish to point out the occurrence of the phenomenon for an energization technique other than chemical activation.

In some interesting work by Callear and Cvetanovic[3] collisions of the second kind, $Hg(^3P_1)$ photosensitization at 25°, were used to excite ground state (*N*) ethylene molecules which underwent unimolecular decomposition to split off hydrogen molecules

$$C_2H_4(N) + Hg(^3P_1) \longrightarrow C_2H_4(T) + Hg(^1S_0)$$
$$C_2H_4(T) \longrightarrow H_2 + C_2H_2 \qquad (d_0)$$

Similarly

$$C_2D_4(T) \longrightarrow D_2 + C_2D_2 \qquad (d_4)$$

The nature of the excitation process and decomposition reaction as presented in these equations was described by earlier workers.[4] The excited ethylene species is believed to be both vibrationally and electronically excited to the lowest triplet state (T) of ethylene. The low experimental temperature, together with the operation of the Franck–Condon principle, ensures that the internal energy distribution is highly peaked, *i.e.*, that the excited species are, relatively, vibrationally monoenergetic. Decomposition (if it arises from the excited T state)

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