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α -Substituted Silyl and Phosphonyl Phosphonates. An Extensive Study of their Synthesis and Properties

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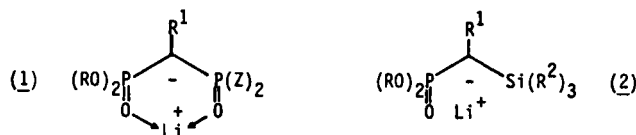
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α-SUBSTITUTED SILYL AND PHOSPHONYL PHOSPHONATES.
AN EXTENSIVE STUDY OF THEIR SYNTHESIS AND PROPERTIES

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Abstract Phosphoryl and silyl chlorides phosphonoalkylation lead to the direct generation of phosphonyl-phosphonyl and phosphonyl-silyl carbanions the properties of which are discussed.

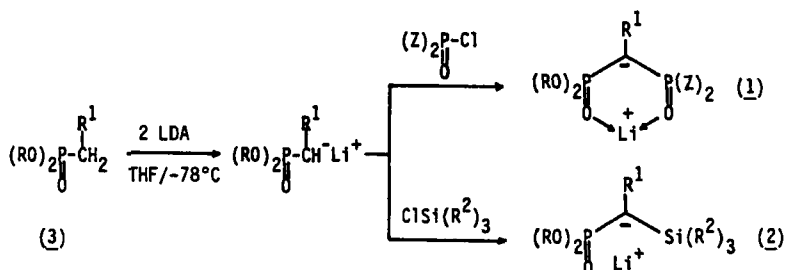
Phosphorus and silicon-containing phosphonates are well-known compounds able to provide useful conversions. The synthetic versatility of the corresponding lithiated carbanions (1) and (2) and the expected chelation or stabilization with modification of chemical reactivity resulting from the direct bonding of phosphorus or silicon to the phosphonic group suggest an extensive examination of the preparation and properties of such intermediates.



Despite their synthetic potential, the lack of general methods to (1) and (2) seriously curtails their approach. The primary reason for this is that the carbanions are obtained through an indirect route involving successively a thermal and an anionic step ; as the first reaction can only deliver symmetrical and unsubstituted structures from not always readily available precursors, both carbanionic species (1) and (2) are limited to a poorly diversified family and of little use. To overcome these limitations a new direct route using a phosphono-alkylation process has been devised.

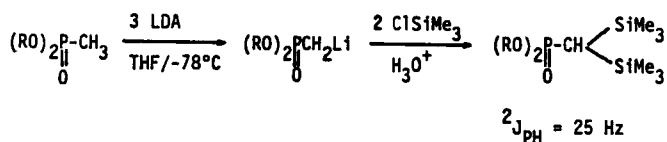
The readily available starting phosphonates (3) are conveniently deprotonated at low temperature with LDA in two fold excess and condensed with a phosphoryl chloride to give quantitatively (1) stabilized at any temperature because of the presence on the carbon atom of two phosphonyl groups. The electrophiles used in this context are phosphates, phosphoramidates and phosphine oxides. Each phosphorus reagent is selected as the most reactive species (electrophilic or nucleophilic) to warrant a coupling in the best conditions. The reaction is limited to the introduction of only one

phosphonyl group.

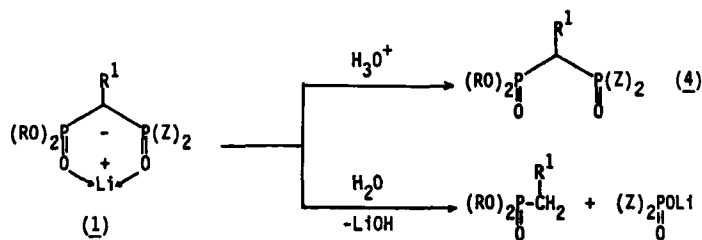


In a similar vein this approach has been extended to the preparation of anions (2) stabilized as well as (1) because of the combined anion-stabilizing properties of silicon and phosphorus. The trialkylsilane normally used in these reactions is ClSiMe_3 but other less common and more crowded silanes have been used ($\text{ClSi}(\text{C}_6\text{H}_5)_3$, ClSiMe_2^+ , ClSiO_2^+ , ClSiEt_3 , ClSiMe_2O) in similar conditions without steric limitations. The two routes do not vary in the ease of preparation with the nature of R^1 (H, alkyl, Cl, O-CH_3 , S-CH_3 , aryl, $\text{S-C}_6\text{H}_5$).

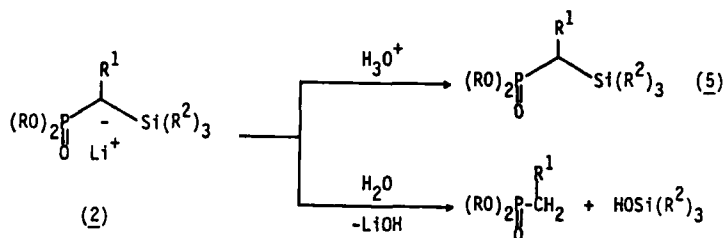
Contrasting with the phosphonyl route the silyl route is not limited to the introduction of only one group; under definite conditions, large excess of LDA and $\text{R}^1 = \text{H}$, two ClSiMe_3 groups can be grafted on the same phosphonate.



When treated with aqueous acid (HCl , 6N) (1) gives tetrasubstituted, symmetrical or unsymmetrical diphosphonates (4) and (2) trialkylsilylmethylphosphonates (5) with each good overall yields (70-95%).



In complete contrast, hydrolysis releases LiOH which has a tendency to act as a nucleophile rather than a base by splitting a P-C bond in (4) or a Si-C bond in (5).



The reaction is notable because it does not occur with symmetrical diphosphonates ($\text{R}^1 = \text{H}, \text{CH}_3$) except when an electron-attracting group is present on the junction carbon atom ($\text{R}^1 = \text{Cl}$); however it has no limitation with unsymmetrical diphosphonates which undergo hydrolysis in all cases. Moreover the reaction is specially exalted by the (Li^+) chelation which liberates the (OH^-) group in the medium. In spite of a lack of chelation, similar results are obtained with compounds (5) in which the Si-C splitting can be a facile reaction. As above it is favoured by the presence of electron attracting group ($\text{R}^1 = \text{Cl}, \text{C}_6\text{H}_5, \text{S-C}_6\text{H}_5$) but much more susceptible to steric effects than for the diphosphonates case. In fact elimination of silanol fails when compounds (5) are bearing a crowded silane group or are disubstituted with two alkyl groups on the junction carbon atom. The oxophilic property of silicon is the driving force here.

The difference in behaviour between (1) and (2) is also striking in alkylation. The two above routes providing a useful unambiguous method for the synthesis of monosubstituted compounds ($\text{R}^1 \neq \text{H}$), dialkylation only has been investigated.

It appears that (1) ($\text{R}^1 \neq \text{H}$) is a poor nucleophile. The alkylation does not occur with sufficient rate and we observe the competing alkylation of $(\text{iC}_3\text{H}_7)_2\text{NH}$; only methylation can be achieved. The carbanions (2) are better nucleophiles and react without drawback in the presence of any R^1 group on the junction carbon atom ($\text{R}^1 = \text{alkyl, aryl, S-C}_6\text{H}_5, \text{Cl} \dots$).

