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A NEW DIRECT SYNTHESIS TO OXAZAPHOSPHOLIDINES

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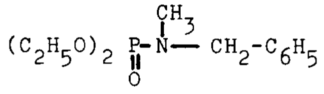
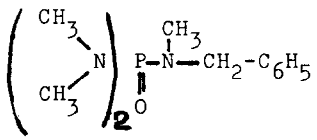
Although five membered heterocycles containing phosphorous,nitrogen and oxygen atom have received much attention, the synthetic approaches to these compounds are relatively few in number and for the most part of limited applicability (1). We wish to report a direct synthesis of oxazaphospholidines (V) in a very simple way.

In previous work, we have shown that the reactivity of



$(C_2H_5O)_2\underset{O}{\overset{\|}{P}}-\overset{CH_3}{N}-CH_2-C_6H_5$

and



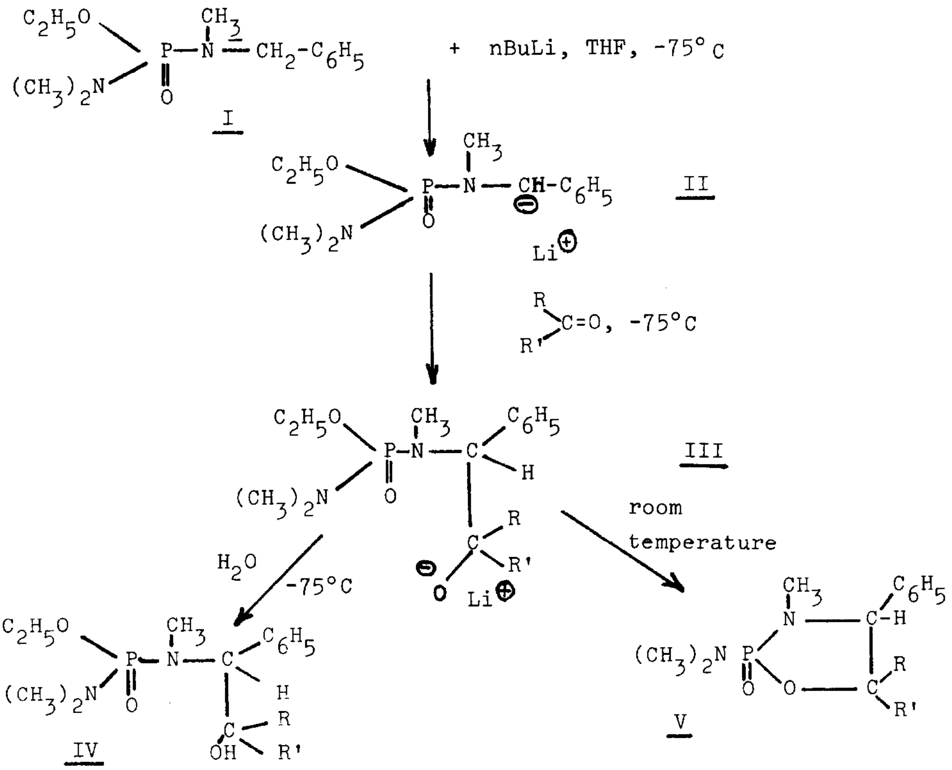
when treated with strong bases (R-Li, R_2N-Li) is very different. The former affords an elimination reaction whereas the latter gives a stable carbanion whose reactivity is being investigated.

Such different behaviour coming from the effect of substituents on the phosphorous atom prompts us to investigate the phosphoramide (I) under the same experimental conditions.

Surprisingly (I) gives a stable carbanion (II) at -75°C whose hydrolysis regenerate (I);upon condensation with electrophiles as ketones or aldehydes, (II) afford two products (IV or V) which depend upon the experimental conditions.

This reaction presumably involves intermediate formation of the alcoholate(III) which undergoes rapid cyclisation to the compound (V) with ejection of lithium ethylate.Yields of cyclisation products are high and there is no side reaction.

This reaction does not show any stereoselectivity; there are three asymmetric centers in each cyclic molecule and the ^1H NMR spectra are too complicated to effect any conformational analysis of the mixture of diastereoisomers we obtain (3).



V(R,R',%) H,$C(CH_3)_3$, 65; H,C_6H_5,68; H,$pClC_6H_4$,70; H,$oMeOC_6H_4$, 38; $pMeOC_6H_4$,39; C_6H_5,C_6H_5,80;$-(CH_2)_5-$41;

Assignment of the oxazaphospholidines is done unambiguously, the alcohol (IV) showing a $\delta^{31}P$ at -18ppm from H_3PO_4 whereas $\delta^{31}P$ of the ring is -26ppm.

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