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New Applications of the Lithiated Phosphinimine $\text{Ph}_3\text{P}=\text{N-Li}$: Synthesis of α,β -Unsaturated Nitriles and $\text{P}=\text{N-P}$ Linked Phosphinimines

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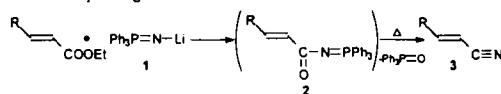
New Applications of the Lithiated Phosphinimine $\text{Ph}_3\text{P}=\text{N}-\text{Li}$: Synthesis of α,β -Unsaturated Nitriles and P=N-P Linked Phosphinimines

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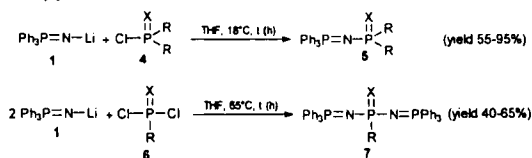
The reaction of $\text{Ph}_3\text{P}=\text{N}-\text{Li}^{(1,2)}$ with various α,β -unsaturated esters gives access to new N-(α,β -unsaturated acyl) phosphinimines, which can undergo intramolecular aza-Wittig reaction (at $65 - 110^\circ\text{C}$) to afford the corresponding nitriles.

The syntheses of novel N-acylphosphinimines have been performed. These last compounds **2** were found to be precursors of nitrile **3** by an intramolecular aza-Wittig reaction. This reaction can be considered as a new direct pathway from α,β -unsaturated esters to the corresponding nitriles⁽³⁾.



R	Me	Et	Ph				
2 Yld (%)	31	25	75	81	53	49	32
3 Yld (%)	93	87	78	89	89	78	79

The reaction of the azayliid **1** with various P^{III} or P^{IV} phosphorus electrophiles, allowed the preparation of mono- or diphosphinimines having P=N-P linkages with satisfactory yields.



The reaction of compound **1** with the electrophiles **4** permits the formation of the desired phosphinimines **5** in mild conditions. However, the formation of diphosphinimines **7** required heating in refluxing THF. We have also attempted to synthesize the triphosphinimines, starting from $\text{X}=\text{PCl}_2$. Our first results have been not yet successful but the reactions are still under further investigations.

References

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- [3] H.-J. Cristau, A. Hammami, E. Torrellles, *Heteroatom Chemistry*, "in press".