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Ketone Hydrosilylation Studies Using a Carbodiphosphorane Catalyst

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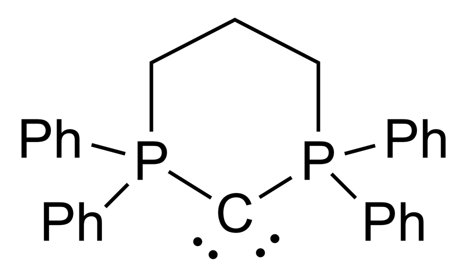
Background

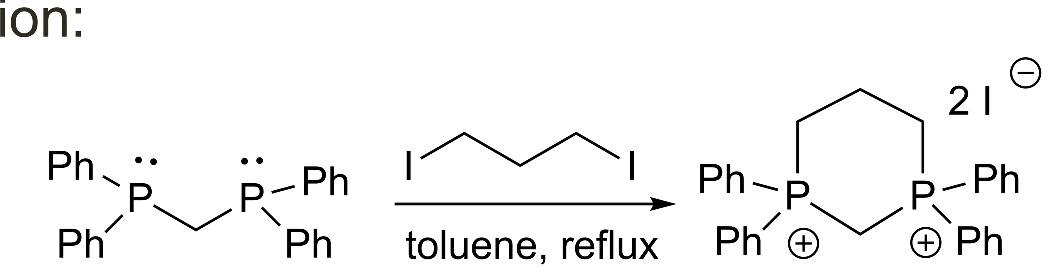
Ketone hydrosilylation is used for the synthesis of alcohol products.

We are investigating a carbodiphosphorane catalyst as a metal-free nucleophilic organic catalyst.

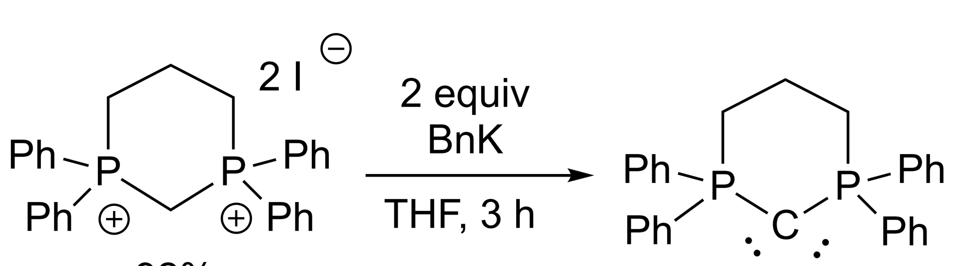


Catalyst Synthesis

Alkylation:

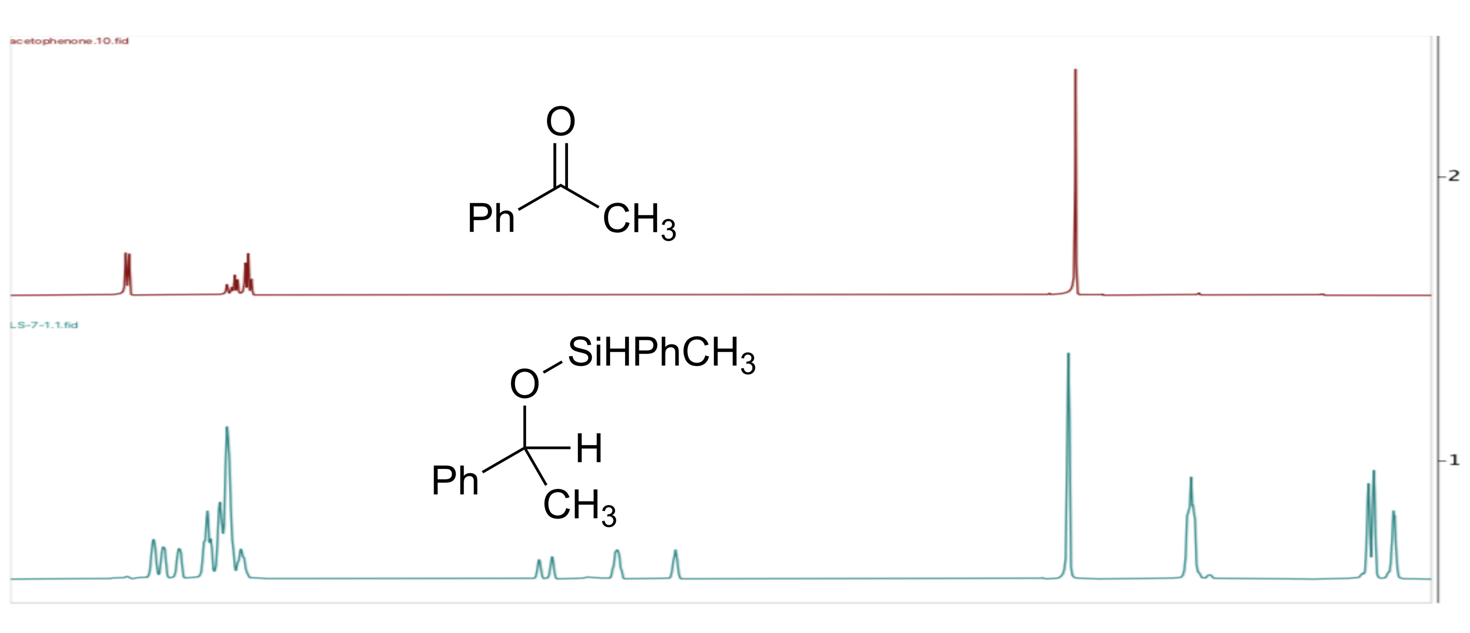


Deprotonation:

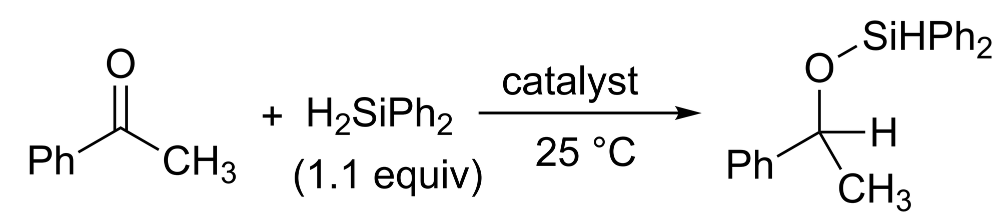


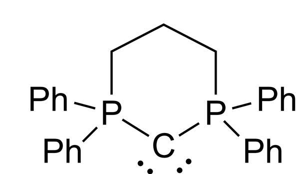
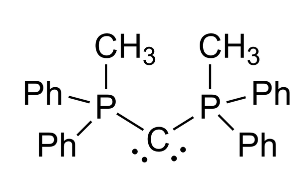
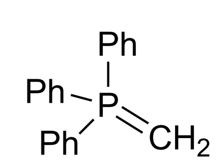
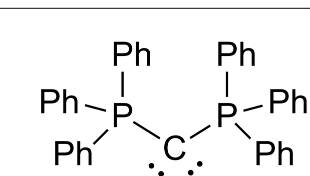
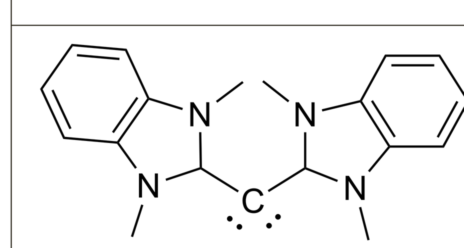
Methodology

^{1}H NMR spectra of the starting ketone were compared to hydrosilylation products to determine the conversion.

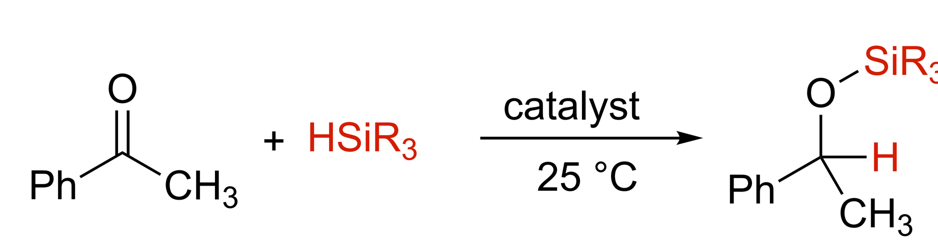


Nucleophilic Catalyst Comparison



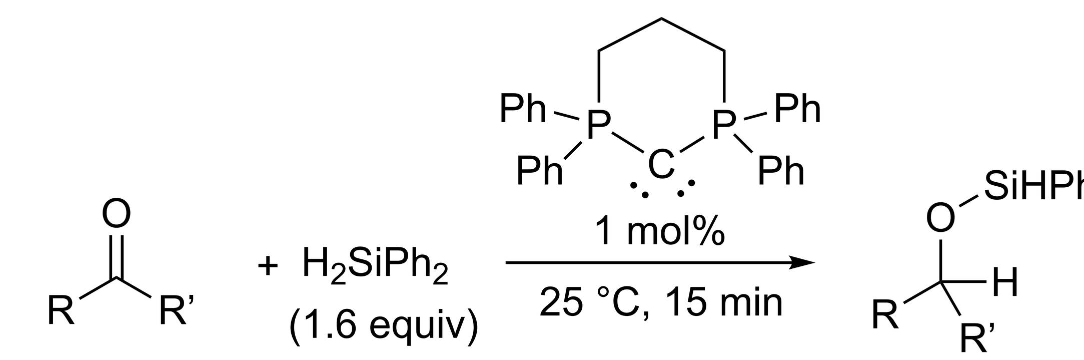
Catalyst	Catalyst Loading	Time	Conversion
	5 mol% 1 mol%	1 h	94% 92%
	5 mol% 1 mol%	1 h	100% 25%
	5 mol%	1 h	53%
	5 mol%	1 h	6%
	5 mol%	1 h	8%

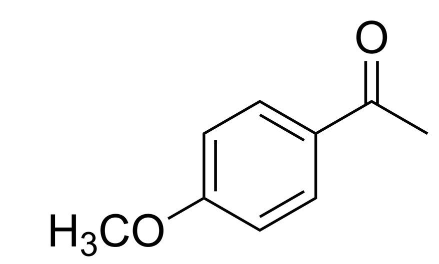
Silane Scope

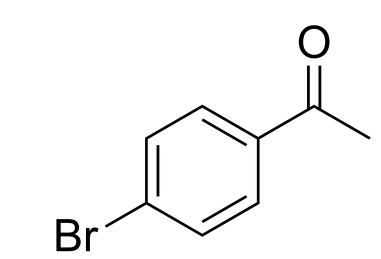


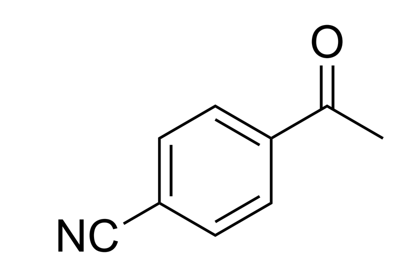
Silane	Conversion
H_3SiPh	89%
H_2SiPh_2	97%
$HSiPh_3$	73%

Ketone Scope




97%


97%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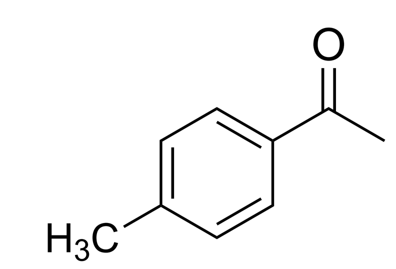
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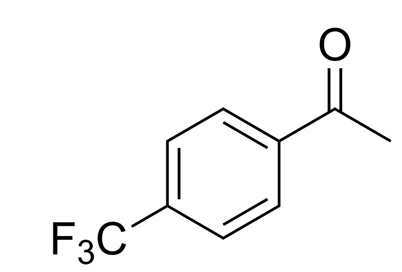
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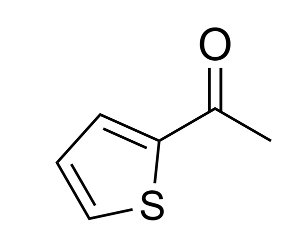
80%

Full ketone substrate scope:

References

(1) Wang, Z.; Fetterly, B.; Verkade, J. G. P(MeNMCH2CH2)3N: An Effective Catalyst for Trimethylsilycyanation of Aldehydes and Ketones. *Journal of Organometallic Chemistry* **2002**, *646*, 161–166.

(2) Wang, Z.; Wroblewski, A. E.; Verkade, J. G. P(MeNCH2CH2)3N: An Efficient Promoter for the Reduction of Aldehydes and Ketones with Poly(Methylhydrosiloxane). *J. Org. Chem.* **1999**, *64*, 8021–8023.

(3) Wu, W.-B.; Zeng, X.-P.; Zhou, J. Carbonyl-Stabilized Phosphorus Ylide as an Organocatalyst for Cyanosilylation Reactions Using TMSCN. *J. Org. Chem.* **2020**, *85*, 14342–14350.

Acknowledgements

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