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Alkali Metal in Silica Gel: A New Route To Access Derivatized Diarylphosphines:

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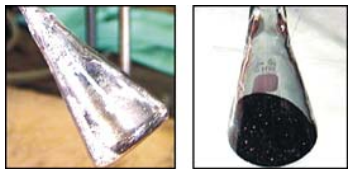
ABSTRACT

Diarylphosphides are important reagents and building blocks for organic and organometallic syntheses and catalysis. This talk will illustrate the application of alkali metal absorbed in silica gel in the reductive cleavage of triarylphosphine and subsequent functionalization of diarylphosphides. The role of electron density on the aromatic rings, different electrophiles, solvent effects will be showcased. In addition the role of ethylenediamine and other electron transporters as catalysts will be described.

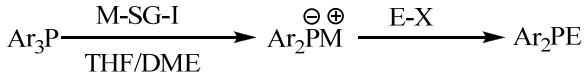
Alkali Metals in Gel (M-G)

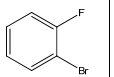
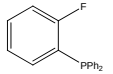
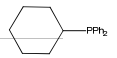
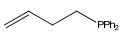


EXPERIMENTAL

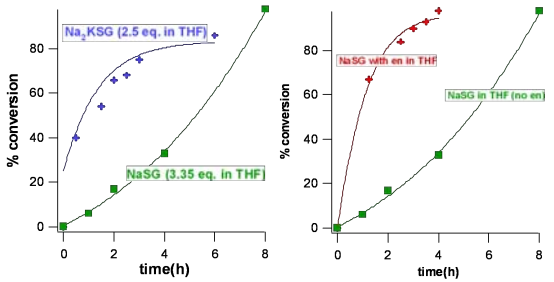
Preparation of M-SG

Material	Metal Used	Procedure
Stage 0	Liquid alloys (NaK, Na_2K, etc.) or liquid Cs	Liquid alkali metal alloy is added to SG at or near room temperature
Stage I	Na, K, Rb, Cs and liquid alloys	Stage 0 or Alkali metal are added to silica gel and agitated for several minutes to hours at a temperature below 160ºC
Stage II	Alkali metals such as Na and K or liquid alloys	Stage I is heated to ~ 400ºC and SiO_2 is partially reduced to silicide



Reactant	Electrophile	Product	Conditions	% Yields
PPh_3	^nBuBr	PPh_2Bu^n	THF, 50°C, 6h	100[a]
PPh_3	MeI	PPh_2Me	THF, 45° C, 6h	75[a]
PPh_3	TMS-Cl	PPh_2TMS	THF, 45°C, 6 h	80[a]
PPh_3			DME, 45°C, 5h	100[a]
$P(tol)_3$	^nBuBr	$P(tol)_2Bu^n$	THF, 45°C, 5h	100[a]
$P(xylyl)_3$	^nBuBr	$P(xylyl)_2Bu^n$	DME, 45°C, 5h	100[a]
PPh_3	*p*-iodo - toluene	PPh_2(*p-tol*)	THF, 45°C, 6h	100[a]
PPh_3	C_6F_6	$PPh_2(C_6F_5)$	THF, 45°C, 6h	70[b]
PPh_3	Cyclohexyl Bromide		THF, 45°C, 6h	100[a]
PPh_3	Homoallyl-bromide		THF, 45°C, 6h	80[a]

a=yield based on ^{31}P NMR, b=isolated yield, in all cases 2.5-3eq. of Na_2K-SG(I) was used



Comparison of Rate of C-P Cleavage: Plot 1: Na-SG(I) vs Na_2K-SG(I)

Plot 2: Catalytic role of Ethylenediamine in the reaction

CONCLUSIONS

Compared with metal dispersions or metal-ammonia solutions:

1. Metal-silica gel is safer, removing the need for dispersions in solvents or in inert oils or cryogenic metal-ammonia solutions.
2. No undesired double cleavage or over reduction (Birch) of aromatic ring observed.
3. Easier to use and commercially available, a free-flowing powder compared to a sticky, pyrophoric soft metal or liquid alloy.
4. Enhanced reactivity due to large surface area, permits many reactions to be performed at room temperature.

REFERENCES

[1] Dye, J. L.; Cram, K. D.; Urbin, S. A.; Redko, M. Y.; Jackson, J. E.; Lefenfeld, M. *J. Am. Chem. Soc.*, **2005,** *127*, 9338.