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Preliminary communication

CHEMISTRY OF ORGANOSILICON COMPOUNDS

LXXX* USEFUL MODIFICATIONS IN THE PREPARATION OF TRIMETHYLSILYLSODIUM AND TRIMETHYLSILYLPOTASSIUM

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Summary

New procedures for preparation of trimethylsilylsodium and trimethylsilylpotassium, which gave coupling products with primary and secondary alkyl chlorides in high yields, are reported

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Recently we reported the synthesis of trimethylsilylsodium in hexamethylphosphoramide (HMPA) according to reaction 1 [1] Most of the reactions of the reagent in HMPA are characterized by facile electron transfer to substrates [1, 2]

$$Me_3SiSiMe_3 + NaOMe \xrightarrow{(Me_2N)_3PO} Me_3SiNa + Me_3SiOMe \qquad (1)$$

Consequently, trimethylsilylsodium in HMPA is excellent as an electron transfer reagent especially to produce radical anions from a variety of compounds [3, 4], however, the value of the reagent for a synthetic purpose is somewhat limited since such facile electron transfer often gives a mixture of products For example, the reaction of Me_3SiNa with alkyl halides (RX, X = Cl, Br and I) resulted in the formation of $RSiMe_3$, R—R, RH, and R(−H) [1, 2] We have tried to overcome such difficulties and now wish to report some useful modifications in the preparation of the reagent which may have synthetic utility

The driving force of reaction 1 is apparently the formation of a strong silicon—oxygen bond with an activated methoxide ion Therefore, a strongly basic (coordinating) aprotic solvent is required for the reaction Since trimethylsilylsodium is very nucleophilic and basic, none of the commercially available solvents except HMPA were suitable for the reaction Accordingly,we prepared 1,3-dimethyl-2 imidazolidone (DMI) [5] which was expected to be sufficiently basic and aprotic for the purpose

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* Also part VI of the series Silyl anions for part V see ref 4

TABLE 1

REACTION OF Me_3SiM WITH RX

RX	M	Solvent	Me_6Si_2/RX	Product	Yield (%)
C_4H_9Cl	Na	DMI	1 5	$C_4H_9SiMe_3$	82
C_4H_9Br	Na	DMI	1 5	$C_4H_9SiMe_3$	12
$C_5H_{11}Cl$	Na	DMI	2 0	$C_5H_{11}SiMe_3$	100
$C\ H_{15}Cl$	Na	DMI	1 0	$C_7H_1\ SiMe_3$	72
$C\ H_{15}Cl$	Na	DMI	2 0	$C_7H_{15}SiMe_3$	100
$Me_3Si(CH\ )_3Cl$	Na	DMI	2 0	$Me_3Si(CH_2)_3SiMe_3$	100
$CH_3CHClCH_3$	Na	DMI	1 5	$(CH_3)_2CHSiMe_3$	45
$C_6H_{13}CHClCH_3$	Na	DMI	1 5	$C_6H_{13}CH(CH_3)SiMe_3$	45
C_4H_9Cl	K	CR [a]/benzene	2 0	$C_4H_9SiMe_3$	74
$C_5H_{11}Cl$	K	CR/benzene	2 0	$C_5H_{11}SiMe_3$	61
$C_5H_{11}Cl$	K	CR/THF	1 5	$C_5H_{11}SiMe_3$	99
$C\ H_{15}Cl$	K	CR/benzene	2 0	$C_7H_{15}SiMe_3$	72
$C\ H_{15}Cl$	K	CR/THF	1 5	$C\ H_1\ SiMe_3$	76
$C_8H_1\ Cl$	K	CR/benzene	1 0	$C_8H_1\text{-}SiMe_3$	55
$C_8H_{17}Cl$	K	CR/benzene	2 0	$C_8H_1\ SiMe_3$	74
$C_5H_{17}Cl$	K	CR/THF	1 5	$C_5H_{17}SiMe_3$	88
$C_8H_{17}Cl$	K	CR/ether [b]	1 5	$C_5H_1\ SiMe_3$	39
$Me_3Si(CH\ )_3Cl$	K	CR/benzene	2 0	$Me_3Si(CH\ )_3SiMe_3$	67
$C_6H_{13}CHClCH_3$	K	CR/THF	1 5	$C_6H_{13}CH(CH_3)SiMe_3$	40

[a] 18-Crown 6 [b] The poor result in ether may be partly due to insufficient solubility of MeOK

Hexamethyldisilane can easily be cleaved with sodium methoxide in DMI to give a yellow solution of trimethylsilylsodium The reaction of Me_3SiNa thus formed in DMI with primary alkyl chloride gave the expected alkyltrimethyl silane in high yield In a typical experiment, 0 54 g (10 mmol) of sodium methoxide was suspended in 10 ml of DMI containing 1 35 g (10 mmol) of n-heptyl chloride After the reaction flask was evacuated and filled with argon, 1 46 g (10 mmol) of hexamethyldisilane was added slowly to the mixture Water was then added to the mixture after an additional hour and the mixture was extracted with ether n Heptyltrimethylsilane was obtained in 72% yield (by GLC) DMI can be recovered from the water layer by extraction with chloroform The yield can be improved to almost 100% by using a small excess of hexamethyl disilane Addition of alkyl chlorides to separately prepared solutions of trimethylsilylsodium effected almost identical results Representative results are listed in Table 1

Alkyl bromides and iodides gave substitution products in poor yields Apparently electron transfer reactions occurred dominantly in these cases It was evidenced by ESR spectra that Me_3SiNa can also act as an electron transfer agent to certain substrates However, HMPA facilitates such electron transfer far greater than DMI We will report the role and application of DMI as an aprotic solvent elsewhere

Trimethylsilylsodium in DMI can react even with secondary alkyl chlorides to give substitution products Thus with isopropyl chloride, isopropyltrimethylsilane was obtained in 45% yield Since the reaction of the secondary alkyl Grignard reagents with trimethylchlorosilane usually results in the reduction of trimethylchlorosilane, this one-step preparation of secondary alkyl-substituted silanes may have some synthetic utility

Hexamethyldisilane can also be cleaved with potassium methoxide in common aprotic organic solvents such as THF, benzene and ether in the presence of a crown ether [6] Thus, addition of hexamethyldisilane (1 10 g, 7 5 mmol) in 4 ml of THF to a solution of potassium methoxide (0 53 g, 7 5 mmol) and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6, 1 35 g, 7 5 mmol) [7] in THF (10 ml) resulted in the formation of a yellow solution of trimethylsilylpotassium. Reaction of the reagent with octyl chloride (0 74 g, 5 mmol) in 3 ml of THF gave octyltrimethylsilane in 88% yield Other results are listed in Table 1

$$Me_3SiSiMe_3 + KOMe \xrightarrow[\text{THF}]{\text{18 crown-6}} Me_3SiK + Me_3SiOMe \qquad (2)$$

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