Alkali Metal Hydrides: New Metallating Reagents at Silicon

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Summary New procedures for the preparation of organosilyl-sodium or potassium which undergo coupling reactions with alkyl, allyl, and benzyl halides and α-enones, are reported

We report here new procedures for the convenient and easy preparation of silyl anions and especially of Me_3Si^- Triorganosilyl–alkali metal compounds having at least one phenyl group on the silicon atom, can be prepared by cleavage of the silicon–silicon bond of hexaorganodisilanes with alkali metals,[1,2] in contrast, hexa-alkyldisilanes are inert towards metal cleavage

Other syntheses of silyl anions have also been reported [3–6] although the disadvantages of handling mercury compounds[3,4] and the formation of by-products[5,6] make these routes to silyl anions less attractive than expected We therefore sought a convenient and general preparation of organosilyl anions

We found that Si–H and Si–Si bonds are quantitatively cleaved by alkali metal hydrides *e g* reactions (1)—(3)

$$Et_3Si{-}H \xrightarrow{KH} Et_3SiK \tag{1}$$

$$Ph_3Si{-}H \xrightarrow{KH} Ph_3SiK \tag{2}$$

$$Me_3Si{-}SiMe_3 \xrightarrow{KH/NaH} Me_3SiK/Na + Me_3SiH \tag{3}$$

Reaction (1) was carried out in dimethoxyethane (DME) at 40 °C for 12 h or in hexamethylphosphoric amide (HMPA) at room temperature for 6 h Reaction (2) was carried out at 40 °C in DME for 6 h Reaction (3) was carried out using KH in DME at 40 °C for 6 h or in DME with 10% HMPA at room temperature for 6 h and with NaH in tetrahydrofuran (THF)–18-crown-6 at room temperature for 2 h

TABLE

Silyl anion (solvent)	Electrophile	Product	Yield/%
$Et_3Si^-(K^+)$ (DME)	Me_3SiCl[a]	$Et_3Si–SiMe_3$	75
$Ph_3Si^-(K^+)$ (DME)	$PhCH_2Cl$[a]	$Ph_3Si–CH_2Ph$	70
	D_2O[a]	$Ph_3Si–D$	85
	Cyclohex-2-en-1-one[b]	3-Triphenylsilylcyclohexan-1-one	75
$Me_3Si^-(K^+)$[c]	Cyclohex-2-en-1-one[b]	3-Trimethylsilylcyclohexan-1-one	c
$Me_3Si^-(K^+/Na^+)$ (HMPA)	$PhCH_2Cl$[a]	Me_3SiCH_2Ph	12—25
	3-Bromoprop-1-ene[a]	3-Trimethylsilylprop-1-ene	
	Bu^nCl[a]	$Me_3Si–Bu^n$	
	5-Bromopent-1-ene[a]	(Trimethylsilylmethyl)cyclopentane	50
	Ph_3GeBr[a]	$Me_3Si–GePh_3$	80
$Me_3Si^-(Na^+)$ (THF–18-crown-6)	n-$C_{12}H_{25}Br$[a]	$Me_3Si–C_{12}H_{25}$	75

[a] Reaction carried out at room temperature [b] Reaction carried out at −78 °C [c] 55% Yield obtained using DME as solvent, 65% yield obtained using DME/10% HMPA as solvent

Reaction (3) may also be carried out using HMPA with both NaH and KH For instance, to a stirred suspension of the alkali metal hydride (20 mmol) in HMPA, was added slowly hexamethyldisilane (10 mmol) A clear yellow brown solution of trimethylsilylpotassium was obtained instantaneously, in the case of NaH mild heating (30—40 °C) was necessary When the reaction was complete, the excess of hydride was eliminated by centrifugation giving a clear solution of Me_3Si^- which could be titrated by common procedures

The reactions of these anions with various substrates were examined, the results of which are summarized in the Table

It can be seen from the Table that organic halides give substitution products in poor yields when HMPA is used as solvent, suggesting that electron transfer reactions occur predominantly in these cases as indicated previously by Sakurai *et al* [4,5] This is verified by 1-bromohex-5-ene which gives only the corresponding cyclic substitution product In contrast Ph_3GeBr and Me_3SiCl, which are known to have a low ability to add an extra electron,[7] give substitution products in good yields In DME or THF–18-crown-6, the dominant process is a bimolecular nucleophilic reaction Thus organosilyl anions are able to react either by a bimolecular nucleophilic process or by a monoelectronic-transfer one

(*Received, 8th October* 1979, *Com* 1064)

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