

SYNTHETIC APPLICATION OF AMINOSILANES
SELECTIVE FORMATION OF SECONDARY AMINES WITH AMINOSILANES

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Aminosilanes readily react with alkyl halides in the presence of sodium methoxide under mild conditions to give N-alkylamines in good yields

Although the most straightforward route to an amine is alkylation of ammonia or another amine with an alkyl halide, the reaction with it shows the possibility of further alkylation and can not be expected to stop at any specific stage on the basis of intrinsic differences in amine nucleophilicity. Recently, a mild and efficient method for the N-alkylation of amines was described based on the oxidative coupling of lithium alkylcopper amide but the yields for secondary amines were relatively low.¹⁾ The use of haloamine or hydroxylamine derivatives was one of the solutions to this problem.²⁾

We wish to report herein a selective and simple preparation of secondary amines using aminosilanes with alkyl halides. In the direct reaction of aminosilanes with alkyl halides, silylammonium salts are not formed, probably because of their low basicities by the interaction of the free electrons pair of nitrogen with the d-orbitals of silicon. However, aminosilanes such as cyclohexylaminotrimethylsilane (1) and anilinotrimethylsilane (2) were found to react readily with primary alkyl halides in the presence of sodium methoxide in THF-diglyme (5:1) under mild conditions to afford selectively the corresponding N-alkylcyclohexylamines and N-alkylanilines in good yields, respectively.



The formation of N,N-dialkylamines as by-products was not observed. Representative results are summarized in Table 1.

The simplicity of the present procedure is illustrated by the following example. Anilinotrimethylsilane (2) (1.65 g, 10 mmol), sodium methoxide (0.54 g, 10 mmol), allyl bromide (1.21 g, 10 mmol), and dry THF (25 ml)- diglyme (5 ml) were combined, and stirred for 18 hr at 40°C. The mixture was quenched with water and extracted with hexane. The organic layer was washed several times with water, dried over magnesium sulfate and the solvents evaporated. The residue was column-chromatographed (silica-gel, benzene) to afford pure N-allylaniline (0.95 g, 72% yield).

Table 1. Selective Conversion of Primary Amines to Secondary Amines Using Aminosilanes with Alkyl Halides

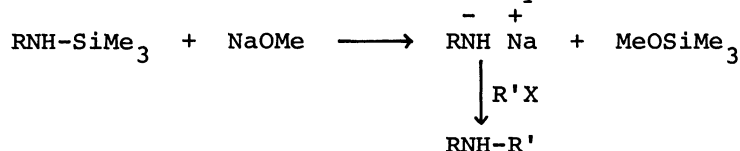
Aminosilanes	Alkyl Halides	Temp(°C)	Time(hr)	Product ^{a)}	Yield(%) ^{b)}
cyclo-C ₆ H ₁₁ NHSiMe ₃	EtBr	40	15	cyclo-C ₆ H ₁₁ NH-Et	64
cyclo-C ₆ H ₁₁ NHSiMe ₃	n-PrBr	40	18	cyclo-C ₆ H ₁₁ NH-Pr-n	56
cyclo-C ₆ H ₁₁ NHSiMe ₃	n-BuBr	40	18	cyclo-C ₆ H ₁₁ NH-Bu-n	53
cyclo-C ₆ H ₁₁ NHSiMe ₃	CH ₂ =CHCH ₂ Br	40	15	cyclo-C ₆ H ₁₁ NHCH ₂ CH=CH ₂	68
cyclo-C ₆ H ₁₁ NHSiMe ₃	PhCH ₂ Br	40	18	cyclo-C ₆ H ₁₁ NH-CH ₂ Ph	67
PhNHSiMe ₃	EtBr	r.t.	20	PhNH-Et	43
PhNHSiMe ₃	EtI	40	18	PhNH-Et	64
PhNHSiMe ₃	n-PrBr	40	20	PhNH-Pr-n	48
PhNHSiMe ₃	n-BuBr	40	18	PhNH-Bu-n	55
PhNHSiMe ₃	CH ₂ =CHCH ₂ Br	40	24	PhNH-CH ₂ CH=CH ₂	72
PhNHSiMe ₃	PhCH ₂ Br	c)	5	PhNH-CH ₂ Ph	84

a) Identity was confirmed by comparison with an authentic sample.

b) Isolated yield by column chromatography.

c) THF only, reflux.

A probable mechanism for this selective N-alkylation is shown as follows.



The nucleophilic attack of a methoxide anion on a silicon atom forms methoxysilane, and amide anion species which subsequently reacts with the alkyl halide to yield a secondary amine.

Since aminosilanes can be prepared quantitatively from appropriate amines and trimethylchlorosilane,³⁾ this approach offers a simple and highly selective way of converting primary amines to secondary ones in two successive steps.

References

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