

A STUDY OF THE SILYLATION REACTION OF IMINES WITH TRIMETHYLCHLOROSILANE IN THE PRESENCE OF LITHIUM

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Abstract

A mixture of trimethylchlorosilane (TMS-Cl), lithium and tetrahydrofuran (THF) reacts with imines to produce disilyl compound by addition of two trimethylsilyl (TMS) groups to the double bond of the imine. On hydrolysis the TMS on nitrogen is substituted by hydrogen and yields α -silylamine. In the presence of acetyl chloride (CH_3COCl), benzene and pyridine, the α -silylamine produces the corresponding amides. Finally, the related tertiary silylamines have been prepared.

Introduction

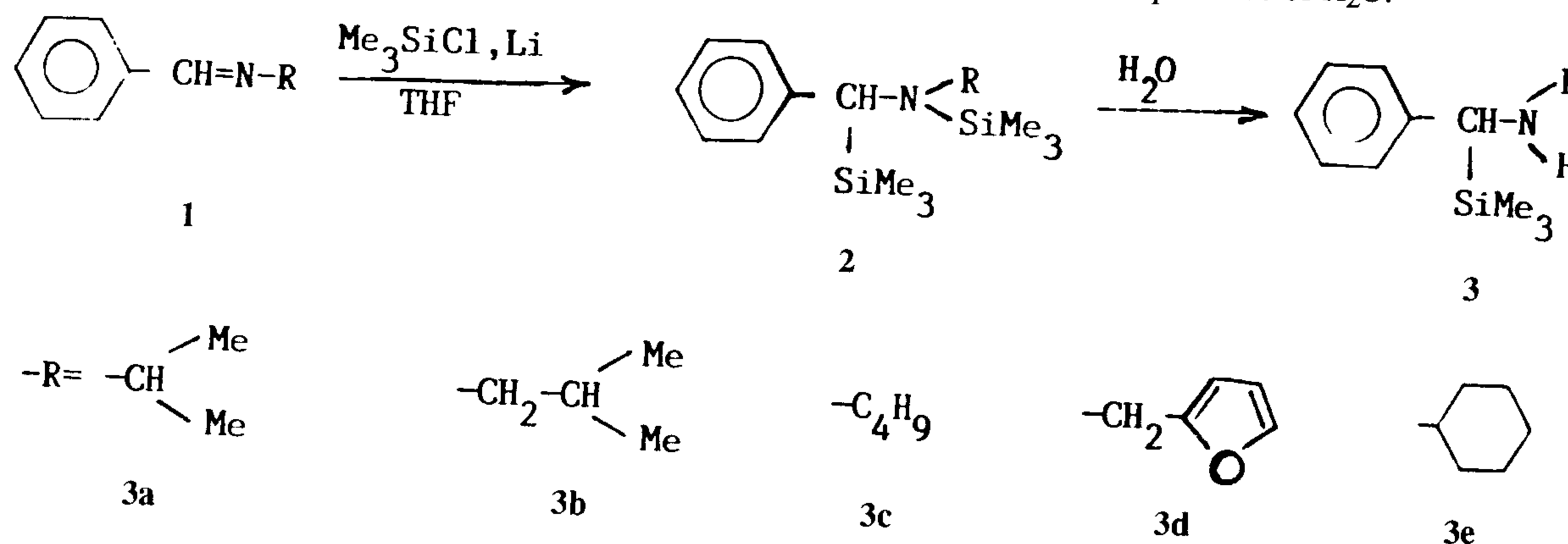
It has been reported earlier [1, 2] that TMS-Cl reacts with some aromatic organic compounds in the presence of magnesium hexamethylphosphotriamide (HMPT) as solvent to give organosilicone compounds.

This has led us to adopt a new method in this study. In this case α -silyl amines have been prepared by the reaction of imines in the presence of lithium and THF as solvent. Furthermore, by this method both α -silyl aromatic amines and the relative aliphatic compounds have been prepared, and the related amides have been synthesized from these

amines. We have also prepared β -silylated amides by a different method from that used previously [3, 4]. The reduction of the former has yielded tertiary silylamines.

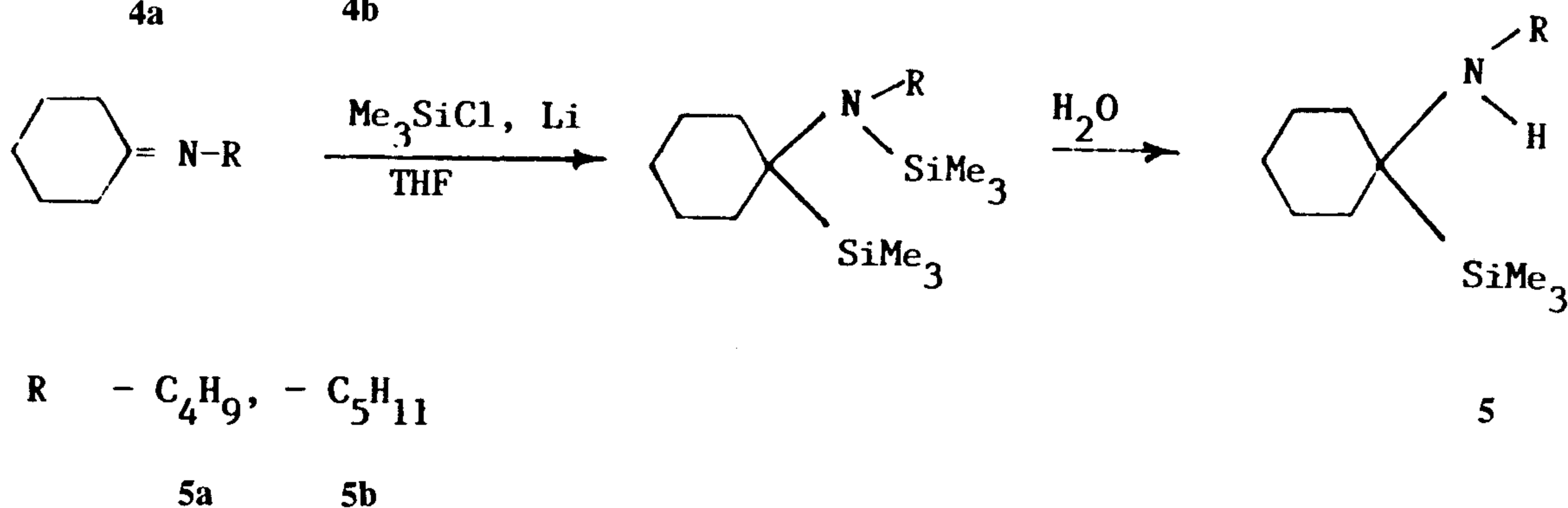
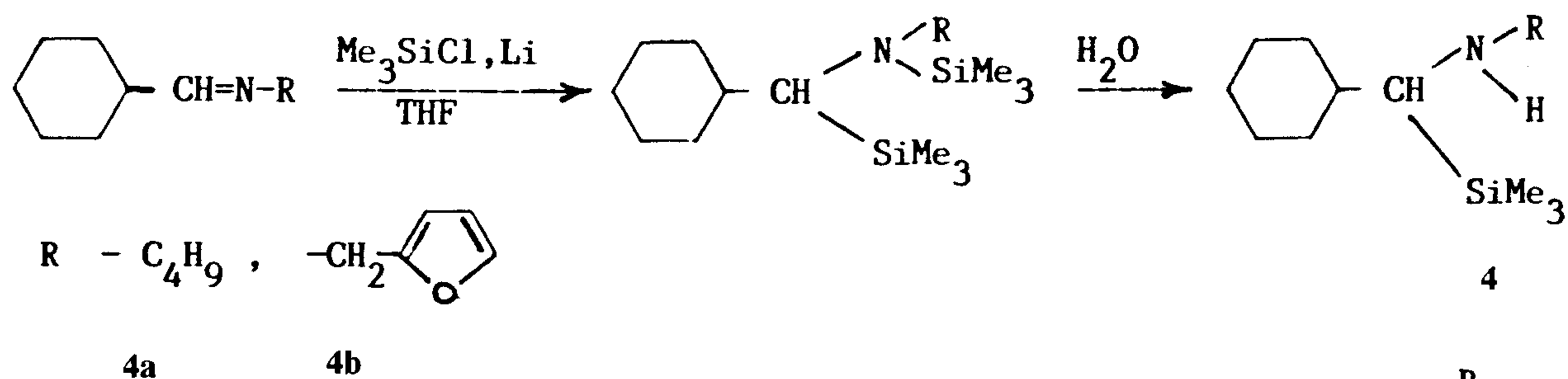
Results and Discussion

a) According to the following reaction, the silylation of (1) with TMS-Cl lithium and THF as solvent leads to the formation of the related disilyl compounds (2). These aromatic compounds can be easily transformed to α -silylamines in the presence of H_2O .

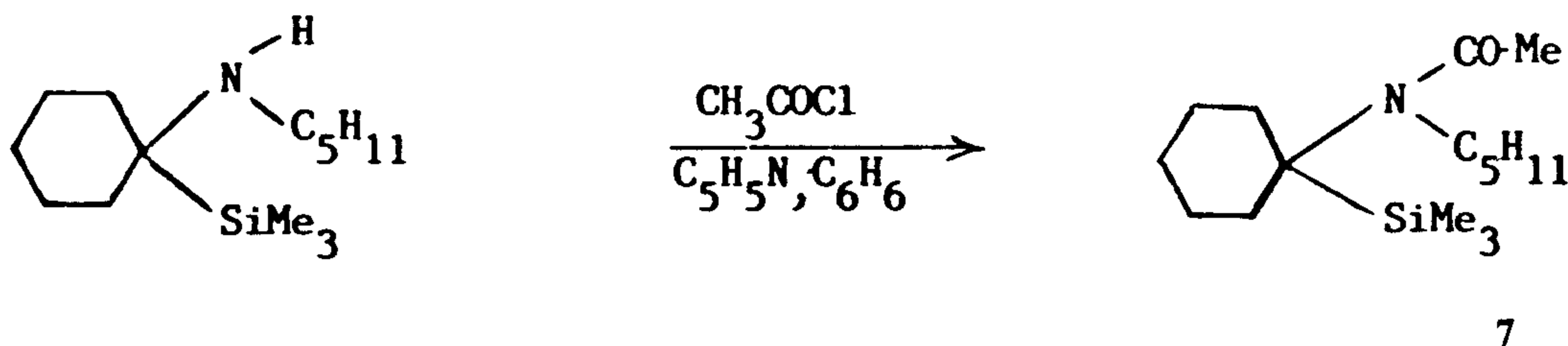
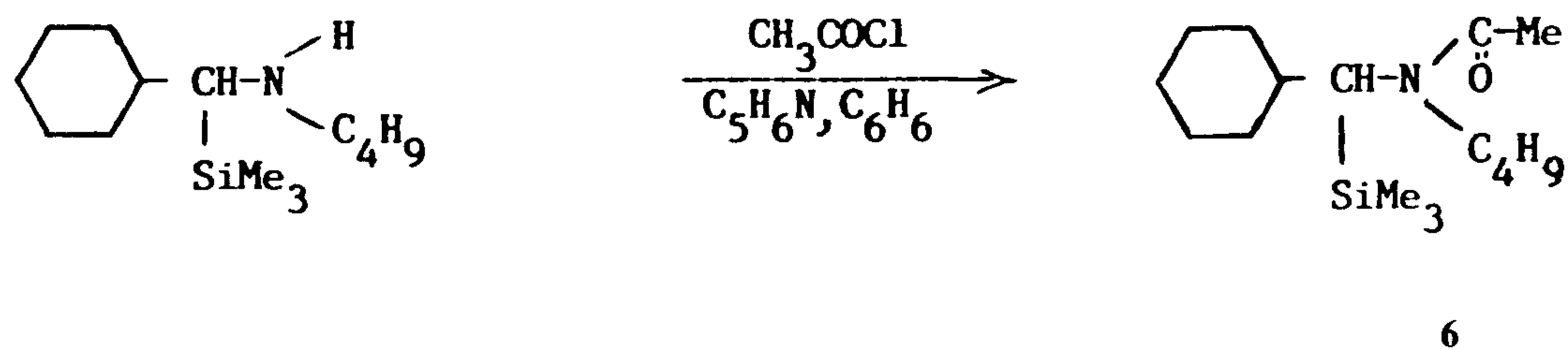


Keywords: Silylation; Imines; TMS

b) Both aromatic and aliphatic compounds can be synthesized by this method.



c) By using CH_3COCl / pyridine these amines are transformed to the corresponding amides.



d) Finally the reduction of the amides leads to tertiary silylamines.

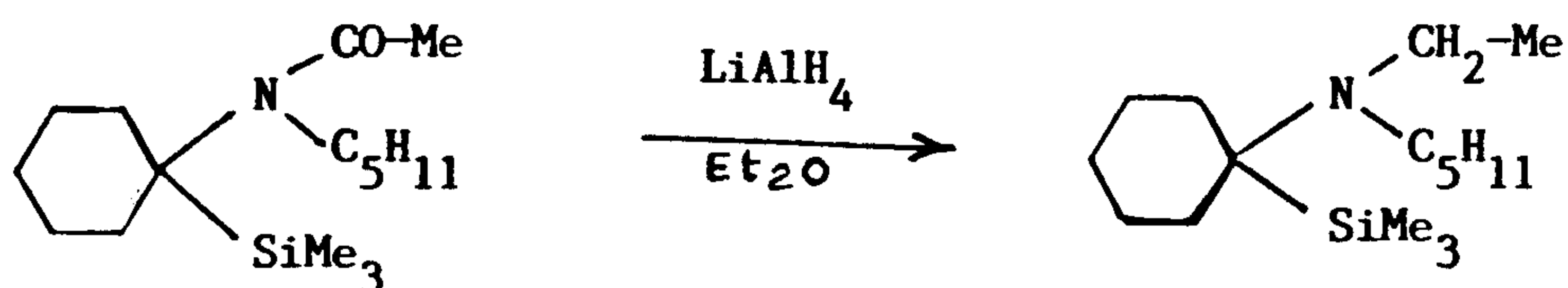


Table 1

Product	Yield(%)	M.P. ($^{\circ}$ C)	B.P. ($^{\circ}$ C)	NH Cm^{-1}	C=O Cm^{-1}	C-Si Cm^{-1}
3a	75		75-76 1 mm Hg	3300-3400		1250,845
3b	70		72-74 1 mm Hg	"	-	"
3c	70		84-87 0.7 mm Hg	"	-	"
3d	65		130-132 2 mm Hg	"	-	"
3e	70		129-132 2 mm Hg	"	-	"
4a	50		100-103 2 mm Hg	"	-	"
4b	40		100-102 0.5 mm Hg	"	-	"
5a	45		72-75 1 mm Hg	"	-	"
5b	60		80-85 0.5 mm Hg	"	-	"
6	40	170		-	1645	"
7	50	158		-	1645	"

Silylation of the imines can be interpreted according to the mechanism proposed for the silylation of aldehydes and ketones by means of the $\text{Me}_3\text{SiCl}/\text{Mg}/\text{HMPT}$ reagents. [1, 5, 6].

Experimental Section

A 250 ml three-neck round bottom flask was taken and 80ml of dry THF was poured into it. A mechanical stirrer was placed in the center neck, a 125ml dropping funnel was attached to one of the sidenecks and a condenser together with a CaCl_2 tube were connected to the other side-neck.

The solution was cooled to $2-3^{\circ}\text{C}$ and 0.2 mole of lithium filings and 0.2 mole of TMS-Cl were added to the flask. Imine (0.1 mole) was dissolved in 30ml of dry THF and was poured into the dropping funnel. The imine was added dropwise to the flask while the solution was stirred.

The reaction was continued for 24 hrs at $0-10^{\circ}\text{C}$ after addition of the imine. It was noted that lower temperatures were more suitable for aromatic compounds ($0-10^{\circ}\text{C}$ for 24 hrs), whereas the reaction of aliphatic compounds ($7-9^{\circ}\text{C}$ for 36 hrs) took more time than the aromatic ones. Hydrolysis of the compounds was carried out with satu-

rated NaHCO_3 solution. The aqueous layer (containing LiCl and THF) was extracted three times with ether. The ethereal layer was dried over anhydrous sodium sulphate and the solvent evaporated, this was followed by the distillation of the liquid products.

Acetyl chloride and pyridine were used for the synthesis of amides with benzene as solvent. The amides were reduced to tertiary silylamines by LiAlH_4 .

Conclusion

The following results were achieved from the silylation reaction of the imines with good yield (Table 1):

1. A new method of formation of carbon-silicon bonds is presented, using imines.
2. Novel organosilicone compounds were synthesized.
3. As a result silylamides and tertiary silylamines were formed.

References

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