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FORMATION OF AMMONIUM YLIDES BY THE CLEAVAGE OF SILICON—CARBON BONDS OF TRIPHENYLSILYLMETHYLAMMONIUM SALTS

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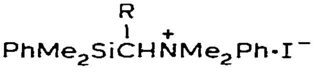
Summary

Treatment of 4-substituted benzyldimethyl(triphenylsilylmethyl)ammonium halides (A) with lithium aluminum hydride afforded a high yield of triphenylsilane and an ammonium ylide intermediate, which was immediately converted into 5-substituted 2-methylbenzyldimethylamines (Sommelet—Hauser rearrangement products), 2-(4-substituted-phenyl)ethyldimethylamines (Stevens rearrangement products), and 4-substituted benzyldimethylamine. Reductive cleavage of nitrogen—carbon bonds of compounds A was a minor process.

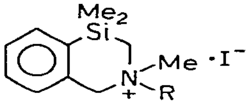
Introduction

We have reported previously that in the reaction of α-silyl substituted quaternary ammonium salts with lithium aluminum hydride, non-cyclic amine methiodides (I) gave demethylation products [1], but cyclic compounds (II and III) formed predominantly ring-opened products by the reductive cleavage of $SiCH_2—N^+$ bounds [2,3]. Thus, the silicon—carbon bonds were not affected in these compounds. However, the silicon—carbon bond in triphenylsilylmethylammonium halides (V) was cleaved by lithium aluminum hydride to give triphenylsilane (VI) and an ammonium ylide intermediate (VII).



$\mathrm{PhMe_2Si\overset{R}{C}H\overset{+}{N}Me_2Ph\cdot I^-}$

(I)



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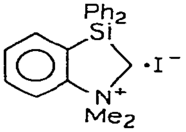
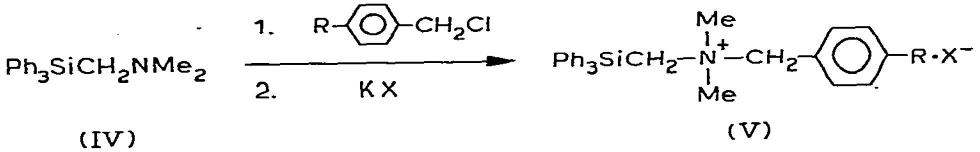


(III)

Results and discussion

The starting compounds, 4-substituted benzyldimethyl(triphenylsilylmethyl)ammonium halides (V), were obtained by treatment of (dimethylaminomethyl)triphenylsilane (IV) with the corresponding benzyl halides (Table 1).



When a mixture of benzyldimethyl(triphenylsilylmethyl)ammonium bromide (Va) and an excess of lithium aluminum hydride in THF was heated at reflux, a high yield of triphenylsilane (VI) and a mixture of basic products were

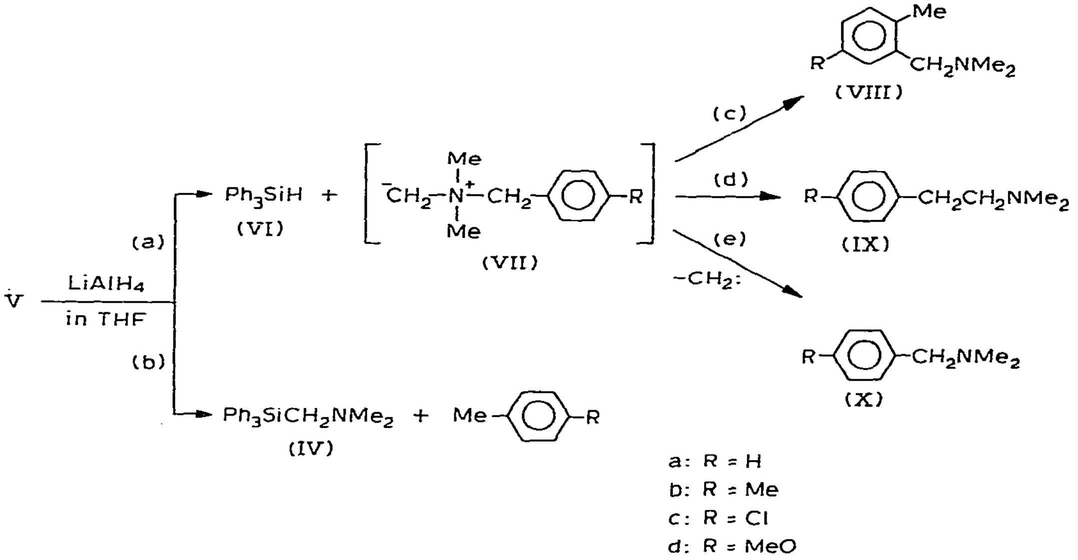


TABLE 1

4-SUBSTITUTED BENZYLDIMETHYL(TRIPHENYLSILYLMETHYL)AMMONIUM HALIDES (V)

Compound	R	X	Yield (%)	M.p. (°C) (dec.)	NMR ($CDCl_3$) δ (ppm)		Analysis (Found (calcd.) (%))		
					$SiCH_2$	$ArCH_2$	C	H	N
Va	H	Br	96	263—265	4.05 [a]	4.51 [a]	68.84 (69.14)	6.19 (6.29)	2.87 (3.25)
Vb	Me	I	83	205—207	4.14	5.10	63.38 (63.34)	5.87 (5.79)	2.55 (2.44)
Vc	Cl	I	80	205—206.5	4.27	5.31	59.00 (58.75)	5.13 (5.18)	2.46 (2.43)
Vd	MeO	I	69	195—198 [b]	4.20	5.08	60.62 (60.43)	5.79 (5.65)	2.44 (2.49)

[a] In CD_3OD solution. [b] Semihydrate, $C_{29}H_{32}INOSi \cdot 1/2\ H_2O$.

TABLE 2

REACTION OF 4-SUBSTITUTED BENZYLDIMETHYL(TRIPHENYLSILYLMETHYL)AMMONIUM HALIDES (V) WITH LITHIUM ALUMINUM HYDRIDE

Compound			Reaction time (h)	Yield (%)				
	R	X		VI	VIII	IX	X	IV
Va	H	Br	6	81	31	8	4	4
Vb	Me	I	10	85	15	9	10	2
Vc	Cl	I	10	87	10 + 4 [a]	4	11	4
Vd	MeO	I	10	90	2	18	5	6

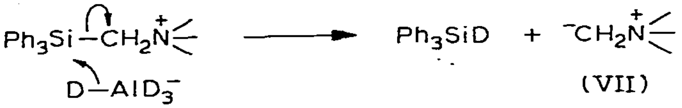
[a] Dechlorinated product.

obtained. Four amines were separated from the mixture and identified by spectroscopic comparison with authentic samples [4]: 2-methylbenzyldimethylamine (VIIIa), 2-phenylethyldimethylamine (IXa), benzyldimethylamine (Xa), and IV. Similar results were obtained with the *para*-methyl, -chloro, and -methoxy substituted analogs (Vb—Vd). The results are shown in Table 2.

The three amines, VIII, IX, and X, are products derived from an ylide intermediate (VII) formed with VI by reductive cleavage of a silicon-carbon bond of V (Scheme 1, path a). Compound VIII is a Sommelet—Hauser rearrangement product (path c), and IX is a Stevens rearrangement product (path d). Benzylamine X also may be produced from VII accompanied by loss of carbene (path e). The possibility of the direct formation of X from V by the cleavage of a nitrogen—carbon bond was negligible, because methyltriphenylsilane was not detected by GLC analysis.

Cope et al. reported that in the reaction of tetrasubstituted ammonium salts with lithium aluminum hydride, methyl or benzyl groups are cleaved faster than other alkyl groups [5]. However, in the case of V, the yield of debenzylation product IV was very low (path b), and demethylation products were not isolated.

Ammonium ylide intermediates usually have been produced by deprotonation of quaternary ammonium salts with strong bases and, in limited cases, by the reaction of tertiary amines with benzyne or carbenes [6]. The ylide formation by the cleavage of silicon—carbon bonds may occur by attack of AlH_4^- on the triphenylsilyl moiety. The transfer of H^- from AlH_4^- to the silicon atom was proved by the use of $LiAlD_4$. The treatment of Va with $LiAlD_4$ gave pure Ph_3SiD and non-deuterated amines VIIIa, IXa, and Xa.



Experimental

Melting points were determined on a Büchi SMP-20 capillary melting point apparatus and are uncorrected. NMR spectra were recorded on a JEOL Model

MH-100 spectrometer. IR spectra were obtained on a JASCO Model IRA-2 spectrometer. GLC analyses were performed on a JEOL Model JGC-1100 chromatograph with FID and TCD detectors. THF was dried by distillation from $LiAlH_4$ just prior to use. Distillation was accomplished by a Büchi GKR-50 Kugelrohr distillation apparatus.

4-Substituted benzyldimethyl(triphenylsilylmethyl)ammonium halides (Va—Vd)

A solution of (dimethylaminomethyl)triphenylsilane [7] (IV 5.00 g, 15.8 mmol) and 30 mmol of 4-substituted benzyl chloride (R = H, Me, Cl, or MeO) in 60 ml of ethanol (or THF for 4-methoxybenzyl chloride) was heated at reflux for 5 h. After removal of the solvent, 50 ml of ethyl acetate was added to the residue. The precipitated crystals were filtered and dissolved in a hot solution of KBr or KI (30 g) in methanol (300 ml). After being allowed to cool for 1 h, the solvent was evaporated in vacuo and the residue was extracted with hot chloroform. The chloroform was evaporated and ethyl acetate was added to give bromide Va or iodides Vb—Vd. The yield and analytical data are summarized in Table 1.

Reaction of 4-substituted benzyldimethyl(triphenylsilylmethyl)ammonium halides (Va—Vd) with lithium aluminum hydride

A mixture of 10 mmol of V and 20 mmol of lithium aluminum hydride in THF (100 ml) was heated at reflux with stirring for 6—10 h under a nitrogen atmosphere. The reaction mixture was poured into ice-water and extracted with ether. The ether solution was extracted with 10% HCl. The ether layer was dried, concentrated, and distilled giving triphenylsilane (VI, b.p. 140—145°C/1 mmHg).

The acid extract was neutralized with NaOH and extracted with ether. After removal of the solvent, the residue was distilled under reduced pressure. Low boiling distillate (b.p. 140°C/15 mmHg) was analyzed by GLC using a 3 mm × 2 m stainless steel column filled with 10% Tergitol NP-35 on Celite 545 AW. The chromatogram showed the presence of 5-substituted 2-methylbenzylmethylamine (VIIIa—VIIId) [4], 2-(4-substituted-phenyl)ethyldimethylamine (IXa—IXd), and 4-substituted benzyldimethylamine (Xa—Xd). Samples of each product were isolated by preparative GLC on a 6 mm × 2 m, 30% Tergitol NP-35 column with a helium flow rate of 150 ml/min. High boiling distillate (b.p. 190°C/0.01 mmHg) was analyzed by GLC using a 10% Silicone XE-60 column and separated by preparative TLC (silica gel/ethyl acetate) to give IV.

All isolated products gave satisfactory elemental analyses and spectroscopic data. The yields of IV, VIII, IX, and X were determined by GLC and are shown in Table 2.

The same procedure as described above using $LiAlD_4$ (CEA, 99.0%, 0.5 g, 12 mmol) and Va (3.00 g, 6.1 mmol) gave Ph_3SiD (1.13 g, 70%), VIIIa (27%), IXa (6%), and X (2%). Ph_3SiD: b.p. 140°C/1 mmHg; NMR ($CDCl_3$): δ 7.2—7.7 ppm (m, aromatic protons), not observed SiH; mass spectrum: *m/e* 261 (M^+), 259, 184; IR (neat): 1545. 593 cm^{-1} (SiD).

Acknowledgement

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References

1 Y. Sato, T. Toyo'oka, T. Aoyama and H. Shirai, J. Org. Chem., 41 (1976) 3559.
2 Y. Sato, Y. Fukami and H. Shirai, J. Organometal. Chem., 78 (1974) 75.
3 Y. Sato, Y. Ban, T. Aoyama and H. Shirai, J. Org. Chem., 41 (1976) 1962.
4 W.Q. Beard, Jr. and C.R. Hauser, J. Org. Chem., 25 (1960) 334; W.R. Brasen and C.R. Hauser, Organic Syntheses, Coll. Vol. 4, Wiley, New York, 1963, p. 585.
5 A.G. Cope, E. Ciganek, L. Fleckenstein and M.A.P. Meisinger, J. Amer. Chem. Soc., 82 (1960) 4651.
6 A.R. Lepley and A.G. Giumanini, in B.S. Thyagarajan (Ed.), Mechanisms of Molecular Migrations, Vol. 3, Wiley—Interscience, New York, 1971, p. 297; A.W. Johnson, Ylid Chemistry, Academic Press, New York, 1966, p. 251.
7 Y. Sato, Y. Ban and H. Shirai, J. Organometal. Chem., 113 (1976) 115.