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Stereochemistry of the Base Cleavage of (Dibromomethyl)naphthylphenylmethylsilane

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During the past years a great number of stereochemical data concerning reactions of nucleophilic substitution at silicon have been accumulated [1–3]. Among them, reactions involving carbon leaving groups were studied only to a limited extent [4].

From this laboratory kinetic results were reported on the solvolysis of (α-halomethyl) trimethylsilanes in propanol–water system in the presence of ammonia buffer [5, 6]. The mechanism of one of the two competitive processes, *i.e.* simple base solvolysis catalyzed by solvent conjugate base (eqn. (1)), can be verified by stereochemical studies.

$$\mathrm{RO^-} + \mathrm{Me_3SiCHX_2} \rightleftharpoons \underset{\text{unstable intermediate}}{[\mathrm{Me_3Si(OR)CHX_2}]^-}$$

$$\underset{\text{unstable intermediate}}{[\mathrm{Me_3Si(OR)CHX_2}]^-} \xrightarrow{\text{slow}} \mathrm{Me_3SiOR} + \mathrm{CHX_2}^- \qquad (1)$$

$$\mathrm{CHX_2}^- + \mathrm{ROH} \longrightarrow \mathrm{RO^-} + \mathrm{CH_2X_2}$$

$\mathrm{R} = \mathrm{H}, \mathrm{Pr}; \mathrm{X} = \mathrm{Cl}, \mathrm{Br}, \mathrm{I}.$

It is now known that in all the studied systems removal of α-dibromomethyl group from silicon in optically (+) (dibromomethyl)naphthylphenylmethylsilane proceeds with the inversion of configuration at silicon. The reaction of powdered KOH with NpPhMeSiCHBr$_2$ gave the corresponding silanolate with 95% inversion.

$$\underset{[\alpha]_D\ +14.5}{(+)\mathrm{NpPhMeSiCHBr_2}} + \mathrm{KOH_{(s)}} \xrightarrow[1\,\mathrm{h},\,60\,^{\circ}\mathrm{C}]{\text{xylene}} \underset{[\alpha]_D\ +68}{(+)\mathrm{NpPhMeSiOK}} + \mathrm{CH_2Br_2} \qquad (2)$$

The optical purity of the product was checked according to reaction (3) basing on the known rotation of silanol (20.5) [4].

$$\underset{[\alpha]_D\ +68}{(+)\mathrm{NpPhMeSiOK}} + \mathrm{H_2O} \longrightarrow \underset{[\alpha]_D\ -18.5}{(-)\mathrm{NpPhMeSiOH}} \qquad (3)$$

Other cleavage reactions were carried out in alcohols in the presence of their potassium alkoxides.

$$\mathrm{NpPhMeSiCHBr_2} + \mathrm{ROH} \xrightarrow[20\,^{\circ}\mathrm{C}]{\mathrm{ROK}} \mathrm{NpPhMeSiOR} + \mathrm{CH_2Br_2} \qquad (4)$$

In the reaction with KOH$_{(s)}$ Sommer found that inversion occurred only for the best leaving carbanions Ph$_2$CH$^-$ and Ph$_2$PrC$^-$ of pK_a for their conjugate acids ~34 [7, 9], whereas the majority of the leaving groups gave retention [4].

Judging from the correlation between the rate of base cleavage of the silicon–carbon bond for RSiMe$_3$ compounds and the pK_a of the corresponding RH [8], as well as the fact that Me$_3$SiCHBr$_2$ is about 100 times as reactive as Me$_3$SiC≡CPh [5, 9], one can expect the pK_a for CH$_2$Br$_2$ to be less than 20. Thus it is not surprising that NpPhMeSiCHBr$_2$ gives inversion products, as –CHBr$_2$ is the best leaving organic group among the ones studied.

Due to the applied low concentration of alkoxides in respective alcohols it was even possible to find the stereochemical effect for the reactions carried out in methanol and ethanol. At higher base concentrations the product racemize too quickly as a result of reactions of alkoxy groups exchange [4]. Thus the cleavage reactions shown in Table I are probably even

TABLE I. Cleavage of NpPhMeSiCHBr$_2$ in protic solvents at 20 °C

Solvent	Alkoxide (ROK) concentration (M)	Reaction time	$[\alpha]_D$ of alkoxides[a]	Predominant stereochemistry
t-BuOH	0.05	30 h	+19.6	85% INV
cyclo-C$_6$H$_{11}$OH	0.05	24 h	+5.6	81% INV
i-PrOH	0.01	6 h	+3.1	75% INV
EtOH	0.01	10 min	−3.7	68% INV
MeOH	0.01	3 min	−3.5	60% INV

[a] Measured in pentane. The rotations of the optically pure alkoxysilanes are given in the literature [1, 10].

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more stereospecific. They were stopped at the moment when GLC analysis revealed that the cleavage was completed. During that time, however, racemization must have occurred to some extent, particularly in the case of the reactions carried out in lower alcohols.

The stereochemical results obtained for the removal of the $CHBr_2$ group, both with the earlier observed [6] lack of primary isotope effect, should be considered as evidence in favour of the stepwise S_N2-Si mechanism of the substitution as it is presented in (eqn. (1)). The higher apicophilicity and polarizability of the dibromomethyl group, compared to that of the carbon leaving groups studied earlier [4], results in the back-side attack of the nucleophile and formation of the unstable five coordinate intermediate.

Experimental

(Dibromomethyl)naphthylphenylmethylsilane

($NpPhMeSiCHBr_2$) was prepared according to the literature [11] and further purified by molecular distillation to give yellow oil, $[\alpha]_D$ +14.5 (*c* 4.2 in pentane). MS; *m/z* 422 (M^+).

Cleavage of $NpPhMeSiCHBr_2$ *in xylene with powdered KOH*

3 g (0.0071 M) of (+)α-$NpPhMeSiCHBr_2$ $[\alpha]_D$ +14.5 (*c* 4.2 in pentane) and xylene (20 ml) were placed in a 100 ml flask under nitrogen and treated with potassium hydroxide (4 g). The reaction mixture was kept at 60 °C for 1 h. The GLC analysis (10% OV 101 on Chromosorb Q) revealed no α-$NpPhMeSiCHBr_2$ after that time. The mixture was then cooled and the decanted solution was placed in a polarimeter tube. It showed $[\alpha]_D$ +68 (*c* 11.2 in xylene). The value is based on the quantitative yield of potassium silanolate. Then the product was hydrolyzed with 3% hydrochloric acid after the addition of 50 ml of diethyl ether. The organic layer was washed five times with water and dried ($CaCl_2$). The solvent was removed under vacuum to give (–)α-NpPhMeSiOH $[\alpha]_D$ –18.5 (*c* 2.5 in diethyl ether). The IR spectrum of the product was typical for pure silanol with strong absorption for free Si–OH at 3690 cm^{-1} and a broad band corresponding to hydrogen bonded Si–OH at 2900–3100 cm^{-1}.

Reactions of $NpPhMeSiCHBr_2$ *with alcohols*

All the reactions were carried out at 20 °C in the presence of the corresponding alkoxide. The typical procedure for the reaction in methanol is given below:

(+)α-$NpPhMeSiCHBr_2$ (2 g, 0.0048 M) $[\alpha]_D$ +14.5 (*c* 4.2 in pentane) was treated with 10 ml of 0.01 M solution of KOMe in MeOH. The reaction was stopped after 3 min by neutralization with hydrochloric acid in n-hexane (40 ml). GLC analysis of the sample taken after that time revealed that the cleavage was completed. The mixture was filtered and evaporated under vacuum (10^{-3}) to give 1.12 g (0.0045 M) of (–)α-NpPhMeSiOMe $[\alpha]_D$ –3.5 (*c* 2.0 in pentane), MS; *m/z* 278 (M^+).

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