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# THE REARRANGEMENT OF 1-NAPHTHYLPHENYLMETHYLSILANE

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## Summary

1-Naphthylphenylmethylsilane has been shown to undergo rearrangement to the 2-isomer when treated with HI in benzene or ether-benzene; protodesilylation also occurs. The rearrangement also takes place when 1-naphthylphenylmethylsilane is heated at 210—220° C.

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In the course of our investigations of the chemistry of silicon-sulphur compounds [1] we undertook the synthesis of 1-NpPhMeSiSH (Np = naphthyl), which we intended to prepare by insertion of sulphur into 1-NpPhMeSiH. The first step was the synthesis of racemic 1-NpPhMeSiH according to the scheme:

$$PhCl_2SiH \xrightarrow{1\text{-NpMgBr}} 1\text{-NpPhClSiH} \xrightarrow{MeMgI} 1\text{-NpPhMeSiH}$$

It was confirmed by GLC that 1-NpPhMeSiH was formed exclusively, but after the reaction mixture had been treated with water, three other products appeared in comparable yields (Fig. 1A). Vacuum distillation of the product mixture gave naphthalene (I), $(PhMeSiH)_2O$ (II), and a mixture of 1-NpPhMeSiH (III) and 2-NpPhMeSiH (IV). Compounds I and III were identified by comparison with authentic samples. Compound II was identified by IR and field desorption (FD) mass spectrometry.

The fraction containing compounds III and IV was subjected to column chromatography to remove any other species. Mass spectral analysis (FD) of the mixture of III and IV then revealed the presence of only one parent ion with *m/e* 248. The IR spectrum was very similar to that of III [2]. The $^1H$ NMR spectrum of III showed a multiplet at 2—3 $\tau$ (12H), a quartet at 4.68 $\tau$ (1H, $J(SiH—CH_3)$ 4 Hz) and a doublet at 9.36 $\tau$ (3H, $J(SiH—CH_3)$ 4 Hz). The spectrum of the mixture of III and IV shows a multiplet at 2—3 $\tau$, two well separated quartets at 4.68 $\tau$ and 4.95 $\tau$ (SiH), and a complex triplet at 9.30—9.46 $\tau$, which consists of two unseparated doublets at 9.36 $\tau$ and 9.42 $\tau$ (resolved as singlets by SiH protons spin decoupling). The proton ratio between

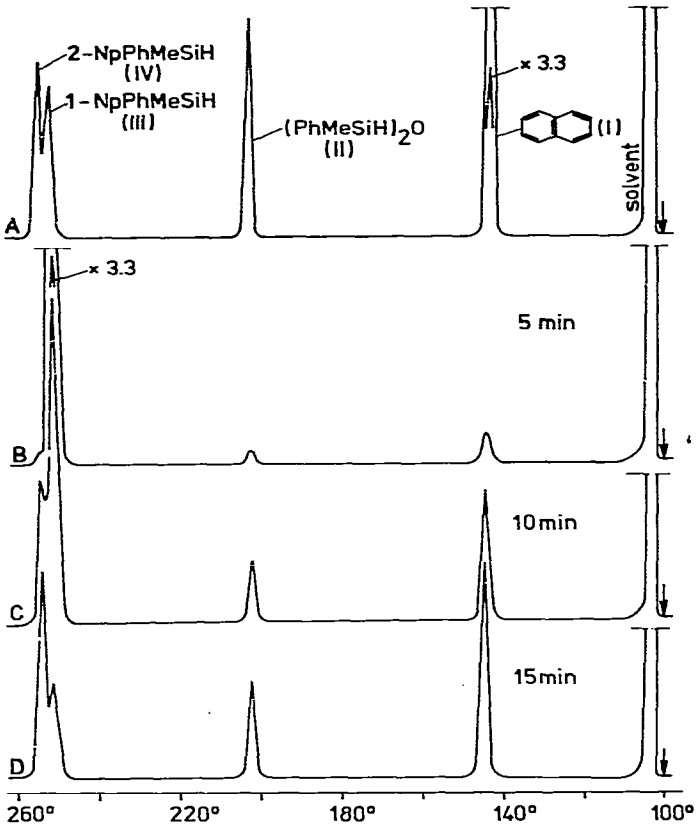



Fig. 1. Rearrangement and protodesilylation of 1-NpPhMeSiH, GLC chromatograms: A, for the quenched reaction mixture; B, C, D, recorded during HI treatment.

quartets and complex triplet was 1 : 3. The results show clearly that the mixture contains IV.

We assume that the rearrangement has the mechanism proposed by Seyferth and White [3] for the acid catalyzed $\alpha \rightarrow \beta$ migration in 1,2-bis(trimethylsilyl)-benzene. In 1977 Seyferth and Vick [4] reported that the acid catalyzed rearrangement of 1,8-bis(trimethylsilyl)naphthalene gave 1,7-bis(trimethylsilyl)-naphthalene, but Sjöstrand, Cozzi and Mislow [5] have since shown that the observed rearrangement was in fact; that of 2-(1-naphthyl)-2,4,4-trimethyl-2,4-disilapentane to 2-(2-naphthyl)-2,4,4-trimethyl-2,4-disilapentane.

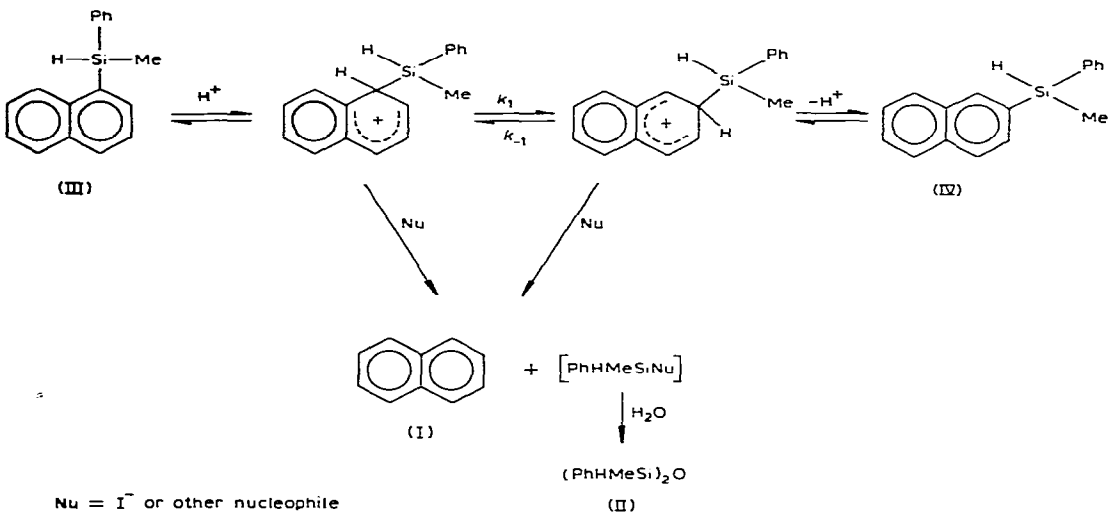
The acid catalyst for our rearrangement is presumably the hydrogen iodide produced by hydrolysis of magnesium iodide. When gaseous HI was slowly bubbled at room temperature through a solution of III, complete elimination of naphthalene had taken place after 10 min. PhMeISiH must be a product of this reaction, but it was not detected by GLC. After addition of water its hydrolysis product II, was found.

In a further experiment water was added to the benzene solution of III and

HI was continuously bubbled through the two layers. The course of both the migration and the protodesilylation could be observed (Fig. 1B—D). The concentration of IV continously increased, showing that the rate of migration is greater than that of protodesilylation of III and IV. The observed protodesilylation of III is faster than that of IV, in agreement with earlier work [6]. Both III and IV were consumed after 40 min HI bubbling. Some protodesilylation of II was also observed; the faster elimination of naphthalene than of benzene is in agreement with earlier data for trimethylsilyl-substituted napthhthalene and benzene [6].

When a benzene solution of III was shaken with concentrated aqueous HI, there was little protodesilylation and no isomerisation was observed. HBr was much less effective then HI as a catalyst for the $\alpha \rightarrow \beta$ migration.

Taking into account the protodesilylation mechanism given by Eaborn [7] and the $\alpha \rightarrow \beta$ migration mechanism given by Seyferth [3], we propose the following reaction pathway:




The $\alpha \rightarrow \beta$ migration also occurs when III is heated at 210—220°C. It is noteworthy that when $Ph_3SiSH$ was added to III and mixture heated at 210—220°C the migration rate decreased.

Our results confirm that acid catalyzed protodesilylation reactions of silylarenes in media of low nucleophilicity can be accompanied by the $\alpha \rightarrow \beta$ migration of the silyl group.

## Experimental

Gas liquid chromatography was used to monitor the reactions and determine the yields; 1 m column, 12.5% SE-30 on Chromosorb NAW 80-100 mesh, programmed temperature 100 → 260°C, 8°/min, FID, argon. Column chromatography was on a 35 cm column of silicagel (Merck) with hexane eluent.

IR spectra were recorded on the Specord 75 IR (Carl Zeiss, Jena). $^1H$ NMR spectra were recorded on Tesla BS467 (60 MHz) and Tesla BS487 (80 MHz)

instruments. Mass spectra (field desorption) were recorded on a Varian 711 Mat spectrometer.

*Synthesis of 1-NpPhMeSiH (III)*

To a solution of $PhCl_2SiH$ (0.18 mol) in benzene was added a solution of 1-NpMgBr (0.18 mol) in benzene-$Et_2O$. After 24 h a solution of MeMgI (0.18 mol) in $Et_2O$ was added. GLC analysis of the reaction mixture indicated that only III was formed (Identification was by addition of an authentic sample). The mixture was placed in an ice bath and water was added dropwise; HI evolution was observed. The two layers were separated, and the organic layer was washed with water and dried over magnesium sulphate, and the solvents were evaporated off in vacuum. The residual oil was analyzed by GLC, and shown to contain four compounds. Vacuum distillation (1 mm Hg) gave I (9 g) (IR spectrum identical to that of an authentic sample), II (b.p. 105—110°C, 8 g) and a fraction (b.p. 170—180°C) which after purification by column chromatography yielded 15 g (30%) of a mixture of III and IV.

When dilute HCl or $NH_4Cl$ solution were used as quenching agents similar results were obtained.

*Reactions of 1-NpPhMeSiH (III) with gaseous HI*

a) 10 mg of III was dissolved in 1 ml of benzene and HI was bubbled slowly through the solution (10 min). The resulting mixture was analyzed by GLC. Only I was detected. After quenching the reaction mixture with water, substantial amounts of II appeared.

b) To a similar solution 1 ml of water was added, and HI was continuously bubbled through the two layers. Every 5 min 0.5 μl samples were taken for GLC (Fig. 1B—D). After 40 min III and IV were consumed and the concentration of II began to decrease. .

*Reaction of 1-NpPhMeSiH (III) with concentrated aqueous HI*

To a solution of 10 mg III in 1 ml benzene 1 ml of concentrated aqueous HI was added, and the mixture was shaken for 15 min. GLC analysis of the benzene layer indicated that less than 5% III was consumed, and that substantial amounts of I and II were formed.

*Reaction of 1-NpPhMeSiH (III) with gaseous HBr*

The experiment was carried out as with gaseous HI. After 10 min about 10% of III reacted giving protodesilylation products I and II, and only traces of IV.

*Thermally induced rearrangement of 1-NpPhMeSiH (III)*

a) 1.24 g (5 mmol) of III was heated at 210—220°C for 23 h under argon. GLC analysis showed that about 60% of III had rearranged to IV. A small amount of I was also formed.

b) A mixture of 1.24 g (5 mmol) of III and 1.46 g (5 mmol) of $Ph_3SiSH$ was heated at 210—220°C during 23 h under argon atmosphere and then analyzed (GLC). About 25% of III had rearranged to IV, and only traces of I were present.

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## References

1 A. Herman, B. Becker and W. Wojnowski, Z. Anorg. Allg. Chem., 450 (1979) 178.
2 L.H. Sommer, C.L. Frye, G.A. Parker and K.W. Michael, J. Amer. Chem. Soc., 86 (1964) 3271.
3 D. Seyferth and D.L. White, J. Amer. Chem. Soc., 94 (1972) 3132.
4 D. Seyferth and S.C. Vick, J. Organometal. Chem., 141 (1977) 173.
5 U. Sjöstrand, F. Cozzi and K. Mislow, J. Organometal. Chem., 179 (1979) 323.
6 C. Eaborn, Z. Lasocki and D.E. Webster, J. Chem. Soc., (1959) 3034.
7 C. Eaborn, J. Organometal. Chem., 100 (1975) 43.