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CHEMICAL BEHAVIOUR OF A BIFUNCTIONAL ORGANOSILANE: α-NAPHTHYLPHENYLFLUOROSILANE

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Summary

α-Naphthylphenylfluorosilane (α-NpPhSiHF) has been found to react with several reagents possessing a labile H atom in the presence of catalytic amounts of nucleophilic agents. Thus, it reacts with water, alcohols, phenols, thiols and amines, with replacement of either fluorine or the hydrogen atom. With some chlorosilanes halogen exchange occurs, yielding α-naphthylphenylchlorosilane (α-NpPhSiHCl).

A mechanism including nucleophilic assistance to a nucleophilic substitution reaction is proposed, in agreement with results obtained for the racemisation and hydrolysis of chlorosilanes.

Introduction

We previously [1] described the synthesis of the first bifunctional enantiomeric organosilanes. Before studying the stereochemistry of these compounds, it was necessary to determine their chemical behaviour and we describe below some reactions of α-naphthylphenylfluorosilane (α-NpPhSiHF).

Results

α-Naphthylphenylfluorosilane was obtained by treatment of α-naphthylphenylsilane with methanol, in the presence of $(PPh_3)_3RhCl$, followed by the reaction of the methoxysilane obtained with $BF_3 \cdot Et_2O$ (eq. 1).

$$\alpha\text{-NpPhSiH}_2 + CH_3OH \xrightarrow{(PPh_3)_3RhCl} \alpha\text{-NpPhSi}\begin{matrix}H\\OCH_3\end{matrix} \xrightarrow{BF_3 \cdot Et_2O} \alpha\text{-NpPhSi}\begin{matrix}H\\F\end{matrix} \quad (1)$$

Schott et al. [2] showed that phenols react with Si—H bonds. In the presence of

catalytic amounts of a nucleophilic agent (Et_3N: triethylamine, TMEDA: tetramethylethylenediamine, HMPT: hexamethylphosphorotriamide, DMSO: dimethyl sulfoxide), the reaction is faster and can be extended to other reactants (H_2O, R—OH, R_2NH, RSH etc.).

α-Naphthylphenylfluorosilane reacts rapidly with those alcohols and phenols (eq. 2). The corresponding fluoroalkoxysilanes and fluorophenoxysilanes are obtained in good yield ~80% and ~60% respectively.

$$\alpha\text{-NpPhSi}\begin{matrix}H\\F\end{matrix} + ROH \xrightarrow{Et_3N} \alpha\text{-NpPhSi}\begin{matrix}F\\OR\end{matrix} + H_2\nearrow \qquad (2)$$

(ROH = ethanol, benzylalcohol, *l*-menthol *, t-butanol, *o*-cresol, *l*-ephedrine, in which case, the nitrogen atom of *l*-ephedrine suffices to catalyse the reaction)

This reaction can be also catalyzed by other nucleophilic agents and the efficiency increases in the order: DMSO < HMPT < Et_3N < TMEDA.

$$\alpha\text{-NpPhSi}\begin{matrix}H\\F\end{matrix} + \text{t-BuOH} \xrightarrow[\text{benzene}]{Nu} \alpha\text{-NpPhSi}\begin{matrix}F\\O\text{-t-Bu}\end{matrix} + H_2\nearrow \qquad (3)$$

[α-NpPhSiHF] = [t-BuOH] = 1 mol l^{-1}; [Nu] = 10^{-2} mol l^{-1}; *T* 20°C

	Nu			
	TMEDA	Et_3N	HMPT	DMSO
$T_{1/2}$ (h) of formation of the fluoro-t-butoxysilane	17	31	>100	∞

By chromatographic analysis of the reaction mixture it was possible to demonstrate that the alcohol initially replaces either function of the α-naphthylphenylfluorosilane (b) (eq. 4). At the beginning of the reaction, the amount of alkoxysilane (a) is substantial. This compound progressively disappears and eventually the fluoroalkoxysilane (c) is the only monosubstitution product (Fig. 1).

$$\underset{\text{(b)}}{\alpha\text{-NpPhSi}\begin{matrix}H\\F\end{matrix}} \underset{}{\overset{\text{t-BuOH/Et}_3\text{N}}{\rightleftharpoons}} \underset{\text{(a)}}{\alpha\text{-NpPhSi}\begin{matrix}H\\O\text{-t-Bu}\end{matrix}} + HF$$

$$\text{(b)} \xrightarrow{\text{t-BuOH/Et}_3\text{N}} \text{(c)}$$

$$\underset{\text{(c)}}{H_2\nearrow + \alpha\text{-NpPhSi}\begin{matrix}F\\O\text{-t-Bu}\end{matrix}} \xrightarrow{HF} \underset{\text{(d)}}{\alpha\text{-NpPhSiF}_2} + \text{t-BuOH} \qquad (4)$$

* The reaction of *l*-menthol on α-naphthylphenylfluorosilane leads quantitatively to a diastereoisomeric mixture. It is possible through fractional crystallization to separate one of them ($[\alpha]_D$ — 54.7°, pentane m.p. 99°C). This is the first example of an optically active fluoroalkoxysilane.

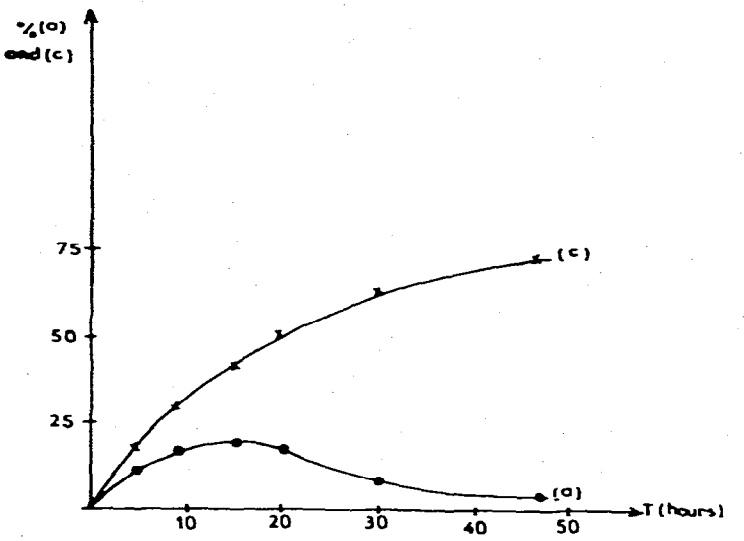


Fig. 1. Formation of a and c (eq. 4). [b] = [t-BuOH] = 1 mol l^{-1}, [TMEDA] = 10^{-2} mol l^{-1}, T = 20°C, solvent: benzene.

After very long reaction times, the formation of α-naphthylphenyldifluorosilane is also detected.

In order to verify the proposed reaction sequence, the action of ammonium fluoride on α-naphthylphenyl-t-butoxysilane (a) was studied. Chromatographic analysis of the mixture showed the formation of b and c. With long contact times, d appears while c progressively decreases and disappears. The direct conversion of a into c seems unlikely, since it was found that the Si—H bond does not react with fluoride anion.

α-Naphthylphenylfluorosilane condenses quickly with water, giving quantitatively bis(α-naphthylphenylfluoro)disiloxane (eq. 5).

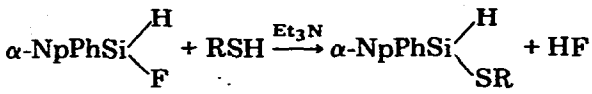
$$2\ \alpha\text{-NpPhSi}\begin{matrix}\diagup\ \mathrm{H}\\ \diagdown\ \mathrm{F}\end{matrix} + \mathrm{H_2O} \xrightarrow{\text{TMEDA}} (\alpha\text{-NpPhFSi})_2\mathrm{O} + 2\ \mathrm{H_2}\uparrow \qquad (5)$$

Primary and secondary amines react very quickly with α-naphthylphenylfluorosilane. The amine is at the same time the reactant and the catalyst. The reaction is identical with those of alcohols. The product formed by reaction at the Si—H bond is obtained, in about 70% yield (eq. 6).

$$\alpha\text{-NpPhSi}\begin{matrix}\diagup\ \mathrm{H}\\ \diagdown\ \mathrm{F}\end{matrix} + \mathrm{R_2NH} \rightarrow \alpha\text{-NpPhSi}\begin{matrix}\diagup\ \mathrm{F}\\ \diagdown\ \mathrm{NR_2}\end{matrix} + \mathrm{H_2}\uparrow \qquad (6)$$

(R_2NH = piperidine, benzylamine)

In the presence of a catalyst thiols also react with α-naphthylphenylfluorosilane. The compound arising from replacement of the fluorine atom (eq. 7) was isolated in about 40% yield.

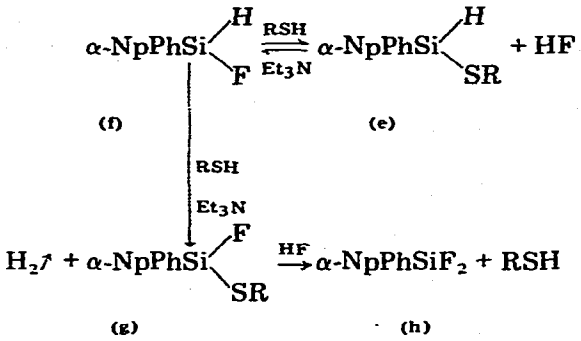


(7)

(RSH = Ethane thiol, thiophenol)

In this case, large quantities of α-naphthylphenyldifluorosilane were also obtained. Chromatographic analysis showed the formation of only e and h which were isolated and characterised.

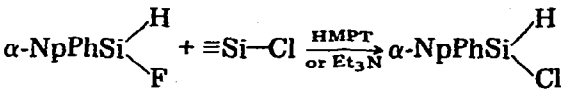
It seems most probable that the reaction sequence, as for amines, is the same as that for the reaction of alcohols with α-naphthylphenylfluorosilane (eq. 8).



(8)

The Si—S bond in g is probably very labile and as soon as it is formed, is attacked by HF to give h. The amount of h is limited by the evolution of HF from the mixture.

α-Naphthylphenylfluorosilane reacts with several chlorosilanes in the presence of a stoichiometric amount of Et_3N or HMPT by an exchange reaction (eq. 9).



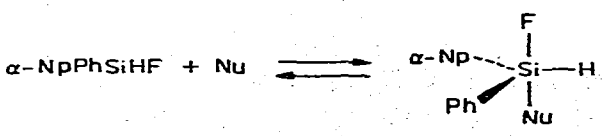
(9)

≡Si—Cl		HMPT		Et_3N	
	Me_3SiCl		68%		0%
	Me_2SiCl_2		100%		82%
	$MeHSiCl_2$		95%		71%
	$HSiCl_3$		—		94%

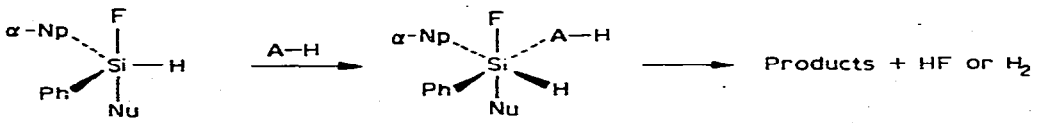
The best yields are obtained for polychlorinated silanes, with HMPT.

Discussion

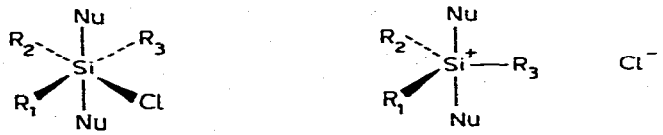
The substitution reactions of α-naphthylphenylfluorosilane, in the presence of a nucleophilic agent can be explained in terms of an extension of the coordination of the silicon atom. We think that the first step is the rapid and reversible attack by a molecule of solvent Nu leading to a pentacoordinated intermediate.



The slow step in the reaction is then the approach of a nucleophilic reactant to this pentacoordinated complex, with substitution of the Si—H or the Si—F bond, after formation of a hexacoordinated intermediate (or transition state).

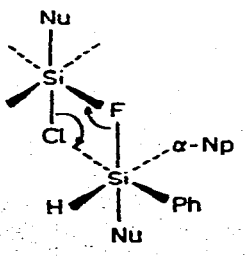


The results cannot be explained solely by an increase in the nucleophilic character of the reagent in the presence of the catalyst. If that were the case, only the ≡Si—F bond would be substituted; it has been demonstrated that nucleophilic reagents (such as Grignard or organolithium reagents) substitute only the ≡Si—F bond [3]. The nucleophilic catalyst must therefore act in another way in promoting the substitution reaction. It is well known that the tendency for silicon to expand its coordination sphere by attachment of additional donor ligands is enhanced by the presence of electron-attracting substituents on the silicon atom. We therefore believe that the role of the catalyst is to coordinate to the silicon atom, so labilising the ≡Si—F and ≡Si—H bonds. A similar mechanism has been proposed for the racemisation of chlorosilane [4,5], which we have shown to proceed at a rate: $v = [\equiv SiCl][Nu]^2$, which corresponds to the slow formation of either a hexacoordinate complex (A) or a pentacoordinate siliconium cation (B).



Furthermore the rate equation for chlorosilane hydrolysis, catalysed by nucleophilic agents (HMPT, DMSO, DMF) is of the form: $v : k\,[\equiv Si—Cl][H_2O][Nu]$ [6]. This corresponds to that obtained for the racemisation and suggests an analogous mechanism. We do not however yet understand why coordination of the nucleophilic agent makes the Si—H bond more labile than the Si—F bond.

The exchange of halogen between α-NpPhSiHF and chlorosilanes catalysed by HMPT or Et_3N, merits discussion. Cartledge [7] has proposed that the epimerisation of chlorosilacyclobutanes in the presence of HMPT occurs by way of a siliconium ion of type B in view of the halogen exchange observed when Me_3SiBr reacts with the chlorosilacyclobutanes. In view of the low reactivity of



(C)

fluorosilanes we prefer in our case the hypothesis of a hexacoordinate complex (C) with concerted transfer of chlorine and fluorine atoms, to that of heterolytic fission of the Si—F bond.

Experimental

Preparation of α-naphthylphenylfluorosilane

α-Naphthylphenylmethoxysilane 50 g (0.189 mol) was dissolved in 100 ml of anhydrous ether under dry nitrogen and 10 ml $BF_3 \cdot Et_2O$ (freshly distilled) was added. The mixture was set aside for 12 h. α-Naphthylphenylfluorosilane (35 g, 0.138 mol) was isolated by distillation after removal of the solvent (b.p. 145 °C/ 0.15 mmHg, yield 74%). Mass spectrum: Found: *m/e* 252. $C_{16}H_{13}FSi$ calcd.: 252. NMR (CCl_4) δ (ppm): >7 (12H, aromatic protons); 6.38—5.48 (1H, Si—H adjacent to fluorine, *J*(H—F) 0.9 Hz).

Reaction of α-naphthylphenylfluorosilane

1. Ethanol

Anhydrous ethanol (1.3 ml) was added to α-naphthylphenylfluorosilane (4.94 g, 1.96×10^{-2} mol) under a dry nitrogen stream. The mixture was cooled to 0°C and 5 mg of triethylamine were added. After 1 h the mixture was distilled, to give α-naphthylphenylfluoroethoxysilane (5.05 g, 1.70×10^{-2} mol, b.p. 153°C/ 0.2 mmHg, yield 87%). Mass spectrum: found: *m/e* 296. $C_{18}H_{17}FOSi$ calcd.: 296. NMR (CCl_4) δ (ppm): >7 (12H, aromatic protons); 3.95 (2H, Si—O—$C\underline{H}_2$—CH_3, quadruplet); 1.27 (3H, Si—O—CH_2—$C\underline{H}_3$, triplet).

2. Benzyl alcohol

A procedure identical to that described under *1* was used with α-naphthylphenylfluorosilane (4 g, 1.58×10^{-2} mol), freshly distilled benzylalcohol (1.71 g, 1.58×10^{-2} mol) and 5 mg of triethylamine; after 30 min distillation gave α-naphthylphenylfluorobenzyloxysilane (4.7 g, 1.31×10^{-2} mol; b.p. 195°C/0.2 mmHg, yield 83%). (Found: C, 76.96; H, 5.46; F, 5.34; Si, 7.32. $C_{23}H_{19}FOSi$ calcd.: C, 77.06; H, 5.34; F, 5.30; Si, 7.83%.) NMR (CCl_4) δ (ppm): >7 (17H, aromatic protons); 4.92 (2H, Si—OCH_2—singulet).

3. l-Menthol

A similar procedure was used with α-naphthylphenylfluorosilane (5.5 g, 2.18 $\times 10^{-2}$ mol) and *l*-menthol (3.4 g, 2.18×10^{-2} mol) in 3 ml of anhydrous benzene containing 5 mg of triethylamine. After 3 h removal of the solvent a residue was left which was allowed to crystallize in pentane. Crystals corresponding to one of the two diastereoisomers of α-naphthylphenylfluoromenthoxysilane were obtained in good yield, 3.2 g, 36%; $[\alpha]_D$ — 54.7° (*c* 32, pentane); m.p. 99°C. (Found: C, 76.59; H, 7.48; F, 5.02; Si, 6.55. $C_{26}H_{31}FOSi$ calcd.: C, 76.80; H, 7.68; F, 4.67; Si, 6.91%.) NMR (CCl_4) δ (ppm): >7 (12H, aromatic protons); 3.4—4 (1H, tertiary proton of the menthoxy group); 0.3—2.7 (18H, aliphatic protons).

4. t-Butanol

A similar procedure was used with α-naphthylphenylfluorosilane (3.9 g, 1.54

$\times 10^{-2}$ mol), t-butylalcohol 1.45 ml and 5 mg of triethylamine. After 24 h, α-naphthylphenyl-t-butoxyfluorosilane (4.8 g) was obtained by distillation (b.p. 165°C/0.4 mmHg, yield 96%). (Found: C, 74.05; H, 6.47; F, 6.22; Si, 8.45. $C_{20}H_{21}FOSi$ calcd.: C, 74.00; H, 6.23; F, 5.85; Si, 8.65%) NMR (CCl_4) δ (ppm): >7 (23H, aromatic protons); 1.33 (9H, singulet for aliphatic protons).

5. o-Cresol

A similar procedure was used with α-naphthylphenylfluorosilane (5.39 g, 2.13×10^{-2} mol), molten, freshly distilled *o*-cresol (2.6 ml) and triethylamine (5 mg). After 3 h all trace of Et_3N were removed and the mixture was allowed to crystallize in pentane, to give α-naphthylphenylfluorocresoxysilane, 4.4 g, yield 58%; m.p. 48°C). (Found: C, 77.04; H, 5.43; Si, 7.95. $C_{23}H_{19}FOSi$ calcd.: C, 77.06; H, 5.34; Si, 7.83%.)

6. l-Ephedrine

A similar procedure was used with α-naphthylphenylfluorosilane (4.76 g, 1.88×10^{-2} mol) and *l*-ephedrine (3.1 g) dissolved in 3 ml of anhydrous benzene. The amine was added at the same time as the reagent and the catalyst. After 2 h the solvent was removed. The product was not distilled because of the danger of polymerisation or cyclisation. Mass spectrum: found: *m/e* 415. $C_{26}H_{26}SiFNO$ calcd.: 415. NMR (CCl_4) δ (ppm): >7 (17H, aromatic protons); 4.9 (1H, doublet, Si—O—C<u>H</u>⟨); 2.6 (1H, multiplet, Si—O—CHPh—CH⟨NHMe / Me⟩); 0.7—1.1 (3H, two doublets, Si—O—CHPh—CH⟨NH—Me / <u>Me</u>⟩).

7. Piperidine

Freshly distilled (under dry nitrogen) piperidine (1.37 ml) was added to 3.40 g (1.34×10^{-2} mol) of α-naphthylphenylfluorosilane. The mixture was kept at 0°C. The reaction was very exothermic and gas evolution was vigorous. After 2 h the mixture was distilled to give 3.2 g of α-naphthylphenylpiperidinofluorosilane (b.p. 150°C/0.2 mmHg, yield 72%): Mass spectrum: found: *m/e* 335.146. $C_{21}H_{22}FNSi$ calcd.: 335.150. NMR (CCl_4) δ (ppm): >7 (12H, aromatic protons); 2.7—3.2 (4H); 1.2—1.8 (6H).

8. Benzylamine

α-Naphthylphenylfluorosilane (5.27 g, 2.09×10^{-2} mol) and 2.28 ml of the freshly distilled amine were allowed to react for 1 h. Distillation gave 5 g of α-naphthylphenyl(benzylamino)fluorosilane (b.p. 180°C/0.35 mmHg, yield 67%). Mass spectrum: found: *m/e* 357.5 $C_{23}H_{20}FNSi$ calcd.: 375.5. NMR (CCl_4) δ (ppm): >7 (12H, aromatic protons) 3.82—4.12 (2H, benzylic protons); 1.8—2.3 (1H, Si—NH—).

9. Ethanethiol

Freshly distilled ethanethiol (2.3 ml) was added to α-naphthylphenylfluorosilane (7.75 g, 3.07×10^{-2} mol) in 15 ml of anhydrous benzene. A slight evolu-

tion of gas occurred when 100 mg of triethylamine was added under dry nitrogen. After 2 h, distillation gave α-naphthylphenyl(thioethyl)silane (3 g, yield 37%, b.p. 168°C/0.4 mmHg). Found: C, 73.38; H, 6.11; S, 10.90; Si, 9.54. $C_{18}H_{18}SSi$ calcd.: C, 73.41; H, 6.16; S, 4089; Si, 9.54%. NMR (CCl_4) δ (ppm): >7 (12H, aromatic protons), 5.89 (1H, singulet, Si—H); 2.48 (2H, quadruplet Si—S—CH_2—CH_3); 1.17 (3H, triplet Si—S—CH_2—CH_3).

10. Thiophenol

α-Naphthylphenylfluorosilane (3.52 g, 1.39×10^{-2} mol), freshly distilled thiophenol (1.2 ml) and 50 mg of triethylamine were allowed to react for 16 h. Distillation gave α-naphthylphenyl(thiophenyl)silane (2.1 g, yield 44%, b.p. 180°C/0.1 mmHg). Mass spectrum: found: *m/e* 342. $C_{22}H_{18}SSi$ calcd.: 342. NMR (CCl_4) δ (ppm): >6.6 (17H, aromatic protons); 5.97 (1H, singulet, Si—H).

11. Water

A violent reaction occurred when 0.5 ml of water and 5 mg of tetramethylethylendiamine (TMEDA) were added to α-naphthylphenylfluorosilane (1.0 g, 0.4×10^{-2} mol). Reaction was complete in 5 min. Preparative thin layer chromatography (Kieselgel PF 254 Merck, solvent system benzene/pentane 30/70) gave bis(α-naphthylphenylfluoro)disiloxane (850 mg). Mass spectrum: found: *m/e* 518. $C_{32}H_{24}Si_2OF_2$ calcd.: 518. NMR (CCl_4) δ (ppm): >7 (aromatic protons).

12. Exchange with chlorosilanes

General method: Stoechiometric amounts of α-naphthylphenylfluorosilane, the chlorosilane, and the nucleophilic solvent (HMPT or Et_2N) were allowed to react under dry nitrogen for 12 h. Distillation of the mixture α-naphthylphenylchlorosilane (b.p. 150°C/0.2 mmHg) in varying yields. Mass spectrum: found: *m/e* 269. $C_{16}H_{13}SiCl$ calcd.: 269. NMR (CCl_4) δ (ppm): >7 (12H, aromatic protons); 6.07 (1H, singulet Si—H). The NMR spectrum of the purified product was identical to that of an authentic sample, prepared directly by chlorination of α-naphthylphenylsilane.

In each of the following cases, the yield of α-naphthylphenylchlorosilane is derived from the NMR spectrum after removal of the volatile chloro- and fluorosilanes.

α-NpPhSiHF 0.920 g, Me_3SiCl 0.46 ml, HMPT 0.45 ml; yield 68%.
α-NpPhSiHF 0.920 g, Me_3SiCl 0.46 ml, Et_3N 0.5 ml; no exchange after 24 h of contact.
α-NpPhSiHF 1.00 g, Me_2SiCl_2 0.48 ml, HMPT 0.49 ml; yield 100%.
α-NpPhSiHF 0.820 g, Me_2SiCl_2 0.39 ml, Et_3N 0.45 ml; yield 82%.
α-NpPhSiHF 0.600 g, $MeHSiCl_2$ 0.25 ml, HMPT 0.29 ml; yield 95%.
α-NpPhSiHF 0.500 g, $MeHSiCl_2$ 0.21 ml, Et_3N 0.27 ml; yield 71%.
α-NpPhSiHF 0.500 g, $HSiCl_3$ 0.24 ml, HMPT 0.24 ml; products not identified.
α-NpPhSiHF 0.500 g, $HSiCl_3$ 0.24 ml, Et_3N 0.27 ml; yield 94%.

Chromatography and other reactions

Apparatus: Chromatograph Girdel 75. Column SE 30, carrier gas N_2. Temperature 240°C. Internal standard Ph_3GeEt (8.49 g/l Et_2O).

This apparatus was used to observe the progress of the reaction of the α-

naphthylphenylfluorosilane with t-butanol in the presence of various nucleophilic agents (TMEDA, Et_3N, DMSO, HMPT).

Standard route: 5 ml of benzene, 7.1 m*M* of α-naphthylphenylfluorosilane, 7.1 m*M* of t-butanol, 0.1 m*M* of catalyst. Regular sampling revealed the progress of the reaction, and gave the value of $t_{1/2}$ and the order of efficiency of the catalysts. (Sample for injection: 0.2 ml of mixture in 5 ml of standard solution.)

Preparation of α-naphthylphenyldifluorosilane: α-Naphthylphenyldimethoxysilane (7 g, 2.38×10^{-2} mol) was dissolved in 30 ml of anhydrous ether under dry nitrogen. 3 ml of freshly distilled $BF_3 \cdot Et_2O$ were added, and the mixture set aside for 12 h. After removal of the solvent, distillation gave α-naphthylphenyldifluorosilane (4.23 g) (b.p. 145°C/0.6 mmHg, yield 66%; m.p. 54°C). Mass spectrum: found: *m/e* 270. $C_{16}H_{12}F_2Si$ calcd.: 270. NMR (CCl_4) δ (ppm): >7 (12H, aromatic protons). The signal corresponding to $Si—(OCH_3)_2$ disappeared.

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