

STUDY OF THE SYNTHESIS OF 1-TRIALKYLSILYLMETHYL-NITRONAPHTHALENES

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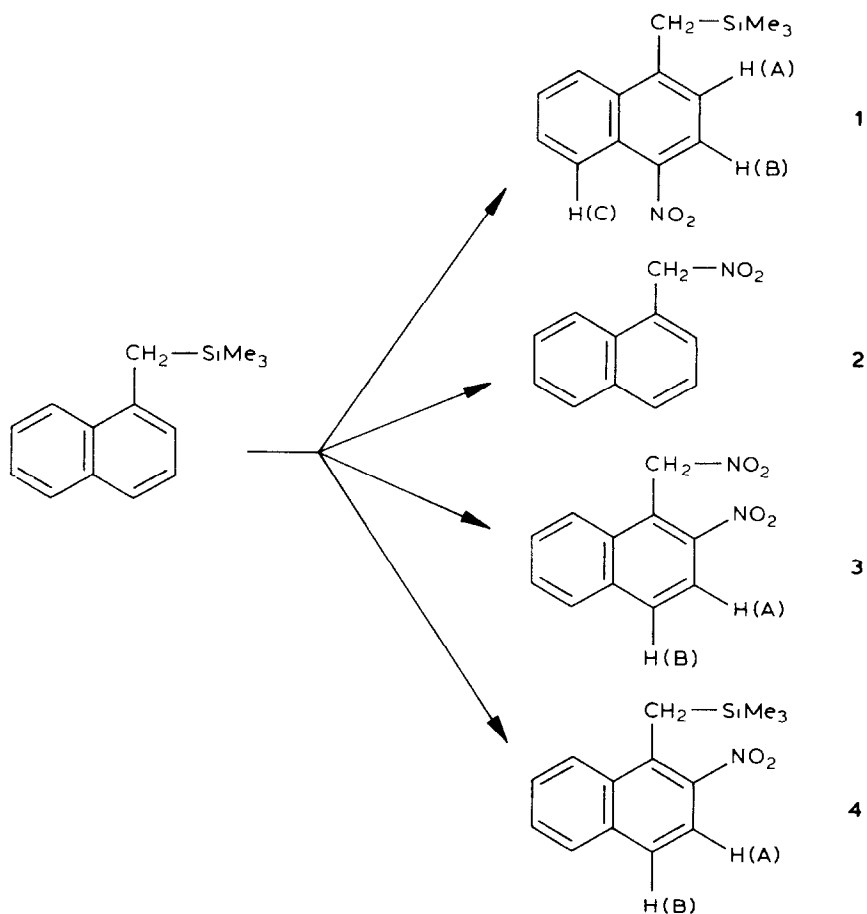
Summary

The preparation of 1-(trimethylsilylmethyl)-4-nitronaphthalene was studied as a function of different nitration agents and temperature. On nitration, 1-trimethylsilylmethylnaphthalene behaved differently from benzylsilane: it undergoes silylation more easily, and a ring-substituted nitro product can be obtained from it only below 0°C.

For the preparation of silicon analogues of the biologically active naphthalene derivatives investigated earlier [1] we needed 1-(trimethylsilylmethyl)-4-nitronaphthalene (SiMNN), which has not yet been reported in the literature. We first attempted to prepare this compound by the method described for the nitration of benzylsilane [2–4]. In comparison to the arylsilanes [5–8], the benzylsilanes are less sensitive to electrophilic reagents, but they can be nitrated [2–4], acylated [9] and chloromethylated [10].

Our efforts to prepare SiMNN under the same conditions as for the nitration of benzylsilane were not successful. We therefore performed a series of experiments using different nitrating agents (HNO₃/Ac₂O, AgNO₃/Ac₂O, Al(NO₃)₃/Ac₂O, Cu(NO₃)₂/Ac₂O, C(NO₂)₄/pyridine and HNO₃/AcOH) at various temperatures. The best result in the preparation of SiMNN was achieved with Cu(NO₃)₂/Ac₂O as nitrating mixture, and, accordingly, we report here only the experiments carried out with this reagent. Under the conditions for the nitration of benzylsilane, only 1-(ω-nitromethyl)-naphthalene (2) and 1-(ω-nitromethyl)-2-nitronaphthalene (3) are formed from 1-(trimethylsilylmethyl)-naphthalene (SiMN), and the desired SiMNN can be obtained with 30% yield only below –10°C (Table 1). The transformation is shown in Scheme 1.

The data in Table 1 were obtained by thin-layer chromatographic evaluation of the reaction mixtures; the error is ca. ±7%. The structures of the products were elucidated by means of ¹H NMR (Table 1). The assignment of the δ values in Table 1 to structures 1 and 4, was based on the following consideration. Protons A and B



SCHEME 1

(Scheme 1) in both compounds **1** and **4** form spin systems which permit the differentiation of these products. A larger chemical shift can be expected between protons A and B for compound **1** than for compound **4**, since the environment of proton A in compound **1** is aliphatic, while with proton (B) the shielding of the nitro group results in a paramagnetic shift. For compound **4**, the A and B shifts lie closer

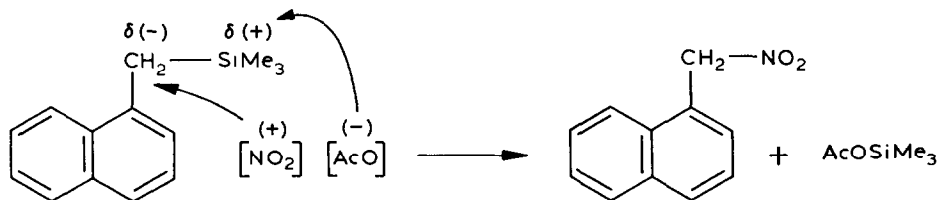
TABLE 1

PERCENTAGE DISTRIBUTION OF COMPOUNDS FORMED ON THE NITRATION OF 1-(TRIMETHYLSILYLMETHYL)-NAPHTHALENE AS A FUNCTION OF TEMPERATURE

Product	Temperature (°C)				δ (ppm)		
	30 to 35	-5 to 0	-15 to -10	-20 to -15	H(A)	H(B)	H(C)
1	-	-	30	30	7.55	8.07	8.70
2	70	60	30	40	-	-	-
3	30	40	35	25	7.82	7.05	8.10
4	-	-	5	5	7.82	7.56	8.10

to each other. The anisotropic shielding effect of the nitro group is exerted here, but in the other case the effect of the aromatic ring holds, in accordance with the α -hydrogens of naphthalene. From the shifts of protons C conclusions can be made on the position of the nitro group, and on the structure **1** ($\delta = 8.7$ ppm) or **4** ($\delta = 8.1$ ppm). The chemical shifts of protons A, B and C in compound **3** are the same as those of the corresponding protons in compound **4**. This, and the signal of the methylene protons ($\delta = 5.77$ ppm) clearly indicate the described structure. Structure **3** is also confirmed indirectly in that its m.p. (144°C) does not agree with that of 1-(ω -nitromethyl)-4-nitronaphthalene (116 – 117°C) [11]. Compound **2** was identified on the basis of literature data [11].

A problem in the preparation of SiMNN is that the substitution of the methyl group of SiMN by a nitro group takes place faster than that of the aromatic ring. Such a difference in nitration between benzylsilane and SiMN is due to the difference in the polarizing effects of the two systems on the C–Si bond. This effect can be assessed indirectly from the ^1H NMR positions of the methylene protons of the two compounds (benzylsilane $\delta = 2.1$, SiMN $\delta = 2.5$ ppm). This indicates a stronger polarity of the naphthyl analogue, since its proton is more acidic. The nucleophilic splitting of the bond proceeds at a higher rate in the more polarized Ar–C–Si bond system. Electrophilic cleavage of the C–Si bond (except the Ar–Si bond) is very rare, and this applies to the benzyl system too. There is no example in the literature of the direct electrophilic cleavage of benzylsilanes [12]. Mention may be made of tetrabenzylsilane, which is converted in the cold with H_2SO_4 to phenylmethylsulphonic acid [13]. It is a general finding that benzylsilanes are also cleaved by nucleophilic, or more or less simultaneous nucleophilic-electrophilic, attack on the Si atom [12]. Hence, the decomposition of SiMN can be described as in Scheme 2.



SCHEME 2

The fact that compound **3** is formed in a relatively high proportion may be connected with the fact that a large amount of AcONO_2 , a reagent favouring nitration in the α -position, promotes the formation of compound **3** or the analogous Si compound. The latter, however, is rapidly transformed into **3**, as illustrated in Scheme 1. This appears to be proved by the circumstance that 1-(trimethylsilylmethyl)-2-nitronaphthalene could not be isolated from the reaction mixture. On the other hand, SiMNN seems to be stable under the conditions of the reaction, as we did not succeed in detecting its decomposition product, 1-(ω -nitromethyl)-4-nitronaphthalene.

Experimental

The purity of the products was controlled by m.p., elemental analysis, ^1H NMR spectroscopy and TLC. Melting points were measured in a Koffler-block system.

The ^1H NMR data were taken on a JEOL/60 Mc apparatus in CDCl_3 , with TMS or CHCl_3 as reference. Thin layer chromatography was performed on DC-Alufolien Kieselgel 60F₂₅₄, with n-hexane/benzene (50/15) as eluent.

Nitration of 1-(trimethylsilylmethyl)-naphthalene

a) A nitrating mixture of 18.6 g of $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and 100 ml of acetic anhydride was added dropwise with stirring during 1 h to a solution of 26.0 g (0.12 mol) of 1-(trimethylsilylmethyl)-naphthalene [14] in 50 ml of acetic anhydride at 30–35°C. Stirring was continued for an additional 3 h at the same temperature. The reaction mixture was then poured on to 300 g of ice, neutralized with diluted ammonia and extracted with 3×75 ml of ether. The combined extracts were washed 2 or 3 times with water, and dried over Na_2SO_4 . After evaporation of the ether, the residual 22.7 g (72.2%) of crude product (a reddish-brown oil) crystallized on standing. Recrystallization from petroleum ether yielded 20.6 g of 1-nitromethyl-naphthalene. M.p.: 72.5°C. (lit. [11] 72–73°C) δ : 5.77 ppm (CH_2).

b) Nitration below -10°C : The preceding experiment was repeated between -10 and -15°C . Thin-layer chromatography verified that the crude product contained compounds 1–4 in the distribution shown in Table 1. (The proportions were calculated from the areas of the spots). 7.3 g of the crude product was chromatographed on a Kieselgel G nach Stahl column (length: 20 cm, diameter: 5 cm) under an overpressure of 1.5 atm (N_2). For elution n-hexane/benzene (50/15) was used, fractions of 100 ml being collected. The following fraction combinations were evaporated.

Fractions 1–3: 0.7 g of 1-(trimethylsilylmethyl)-naphthalene. Identified by means of a control sample. R_f : 0.8.

Fractions 4–7: 0.5 g of 1-(trimethylsilylmethyl)-2-nitronaphthalene (4). Slightly brownish liquid, R_f : 0.5, identified from the ^1H NMR spectrum: $\text{H}(3)\delta = 7.82$, $\text{H}(4)\delta = 8.07$, $\text{H}(5)\delta = 8.10$, $\text{CH}_2\delta = 2.95$ ppm. Found: C, 65.10; H, 6.45; N, 5.80. $\text{C}_{14}\text{H}_{17}\text{NO}_2\text{Si}$ calcd.: C, 64.84; H, 6.60; N, 5.40%.

Fractions 8–10: 2.0 g of 1-(trimethylsilylmethyl)-4-nitronaphthalene (1). Brownish liquid, R_f : 0.4 (decomposed during distillation). Identified by ^1H NMR: $\text{H}(2)\delta = 7.55$, $\text{H}(3)\delta = 8.07$, $\text{H}(5)\delta = 8.70$, $\text{CH}_2\delta = 2.62$ ppm. Found: C, 64.50; H, 6.55; N, 5.65. Calculated values as for fractions 4–7.

Fractions 11–17: 3.4 g of 1-nitromethylnaphthalene (2). M.p.: 72.5–73°C; (lit. [11] 72–73°C); R_f : 0.25.

Fractions 18–23: 1-nitromethyl-2-nitronaphthalene (3). M.p.: 144°C. Identified by ^1H NMR: $\text{H}(3)\delta = 7.50$, $\text{H}(5)\delta = 8.10$, $\text{CH}_2\delta = 5.77$ ppm. R_f : 0.10. Found: C, 56.40; H, 3.27; N, 11.84. $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4$ calcd.: C, 56.90; H, 3.47; N, 12.6%.

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