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NOVEL POLYHYDRONAPHTHALENIC STRUCTURES

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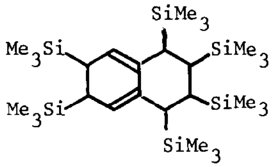
Novel 1,7-dihydro- or 1,2,6,7-tetrahydronaphthalene derivatives were obtained from naphthalene through a polysilylation/oxidation process as well as 1,4,6,7-tetrakis(trimethylsilyl)naphthalene, a regiospecific precursor of 1,4,6,7-tetrafunctional naphthalenes.

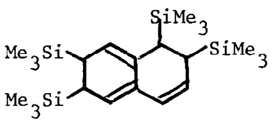
Disilylation of naphthalene using Me_3SiCl in the presence of Li/Et_2O[1], Li or Na/THF[2], Mg/HMPA[3] or K/THF[4] affords organosilicon derivatives having a dihydronaphthalene or tetralin structure. Moreover we have reported the synthesis of a hexasilylated hexalin 1 by direct persilylation of naphthalene under drastic conditions :



1

In this paper, beside an improved synthesis of 1 and the confirmation of its structure, we propose :

a) A short route to compounds 2-4 having apparently novel isotetralin and dialin skeletons :



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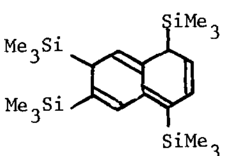

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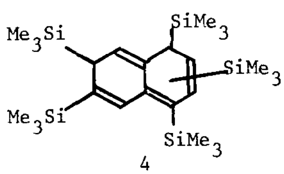

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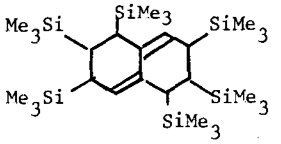
b) A synthesis of 1,4,6,7-tetrakis(trimethylsilyl)naphthalene 5, a regiospecific precursor of 1,4,6,7-tetrafunctional naphthalenes by electrophilic substitution of the trimethylsilyl groups.

Investigations of the polysilylation of naphthalene have given the following results :

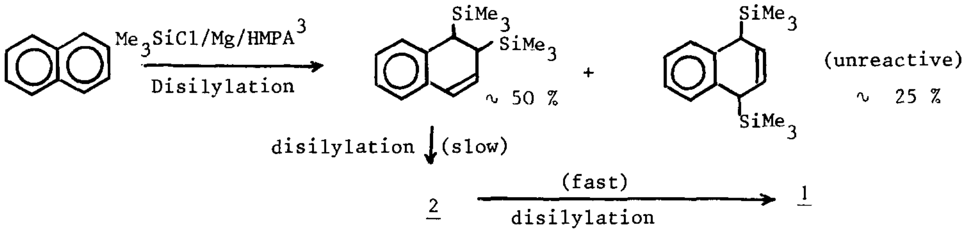
1) Reaction of $Me_3SiCl/Li/THF$ with naphthalene, for 4 h at 5°C, afforded 1 in 50 %

yield (instead of 20-30 % after 3-4 days at 100°C using $Me_3SiCl/Mg/HMPA^3$), as shown by the U.V. data (λ max = 275 mm. ε ≃ 13500), in accordance with the retained structure and not with the alternate formula also previously proposed 1a[5].

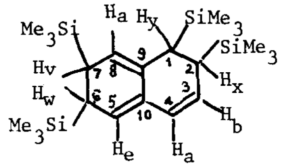


1a

2) With $Me_3SiCl/Mg/HMPA$, the course of the reaction giving 1 was completely elucidated:



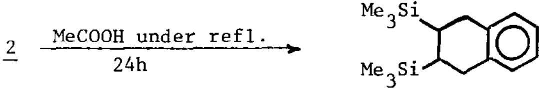
The rapid disilylation of 2 did not permit its isolation in yields higher than 20 %. However 2 easily crystallized (m.p. 122°C) and was unambiguously identified as follows. Mass spectra and analytical data are in accordance with the given formula ; three νC=C absorption bands were observed in IR (Raman) 1643(1644), 1610(1611) and 1583(1585) cm^{-1}. Only the first frequency was absent in the spectrum of 1 ($\nu C_3=C_4$). The frequencies of the conjugated double bonds ($C_8=C_9$ and $C_{10}=C_5$) are apparently coupled with ν_s at 1610 cm^{-1} and ν_a (stronger in IR but weaker in Raman) at 1583 cm^{-1} ; ^1H nmr (at 90 MHz ; CCl_4 as solvent, TMS as internal standard, δppm) 4 s (4 x 9 H) 0.19, 0.20, 0.22, 0.23 (4 $SiMe_3$) ; 1m (4H) centered at 1.90 (allylic protons) ; 2 d (broad) centered at 5.2 and 5.3 (H_c and H_d, not assigned individually ; ab spectrum (2H) centered at 5.65 and 6.02 (H_a and H_b) part b split



up (coupling with Hx). Coupling constants (determined if needed by double irradiation) : J_{ab} = 9.5 Hz ; J_{bx} = 5.5 Hz ; $J_{cw} = J_{dv} \simeq 6$ Hz. ^{13}C nmr : 4 different primary C (0,0.3, 0.7, 1) (4 $SiMe_3$), 4 tertiary allylic C (28.9, 29.3, 31.3 and 33.7) ($C_1 + C_2 + C_6 + C_7$ not assigned individually), 6 ethylenic C (124.4, 125.0, 127.8, 128.4) (4 tertiary $C_3 + C_4 + C_5 + C_8$), 2 quaternary C (131.5, 131.9) ($C_9 + C_{10}$).

Vicinal trimethylsilyl groups are situated in *trans* position, but the complete structure was not elucidated.

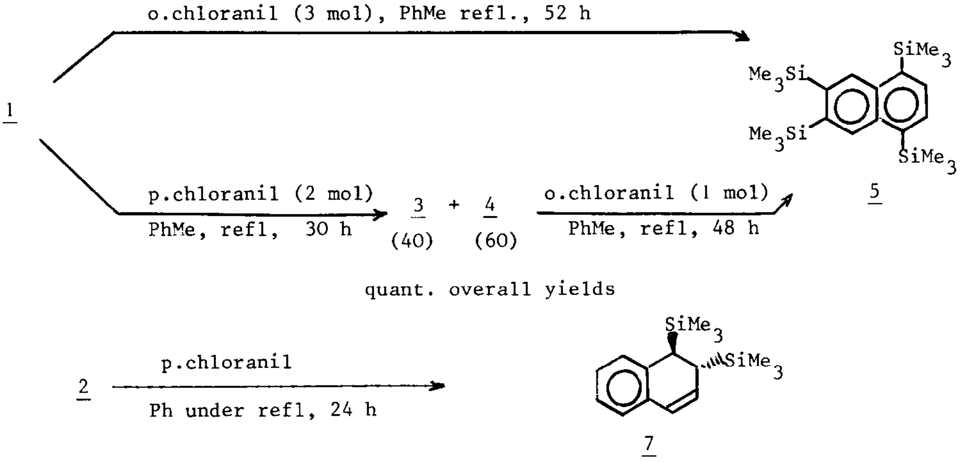
Protodesilylation converted 1 into tetralin (100 %) and 2 into 6 (which has not allylic trimethylsilyl groups) :



6 (80 %)

6 was identified by mass spectroscopy and ^{1}H nmr δ(solvent)ppm ; -0.1 (s ; 18H) (2 $SiMe_3$) ; 1.2 (m ; 2H) (2 CH-Si) ; 2.7 (m ; 4H) (C_{ar}-CH_2) ; 7.0 (m ; 4H) (aromatic protons).

Aromatization of 1 and 2 using different conditions are summarized in the following scheme :



These results suggest the following comments :

- Complete aromatization of 1 required the use of o-chloranil, but similar treatment of 7 led to a mixture of unidentified products.

- The mixture (3 + 4) exhibits a strong blue fluorescence ; 3 and 4 were separated by HPLC. They were identified by mass spectroscopy (chemical ionisation with methane : presence of the mol. peak + 1) and ^{1}H nmr data 3 4s (4 x 9 H) : 4 $SiMe_3$ at - 0.15, - 0.05, 0.18 and 0.23 ppm, 2m (2H), 2 CH-Si with 2 peaks at 2.0 and 2.2 ppm and 1 m (4 H) 4=CH- between 6.4 and 7.1 ppm.

4 5s (5 x 9H) 5 $SiMe_3$ at - 0.15, - 0.05, 0.20, 0.26 and 0.33 ppm, 1 m complex (2H) 2 CH-Si with 2 peaks at 2.0 and 2.2 ppm., 1m (2H) 2=CH- at 6.7 ppm and 1m (1H) 1=CH- at 7.1 ppm.

3 is unstable and was rapidly autoxidized to 5.

4, more stable was also identified by ^{13}C nmr : 5 types of primary C (5$SiMe_3$), -1.9,-1.1, -1.1, -0.5 and 0.1, 2 allylic C (not assigned)^6, 8 ethylenic C (5 quaternary C, 133.4, 136.6, 137.7, 140.2 et 143.3), (3 tertiary C, 133.7, 135.9 et 136.9).

5, m.p. 162°C, (EtOH) was identified by mass spectrom. (molecular peak at 416) ; ^{1}H nmr 1s, (18H), 0.34 (2 $SiMe_3$), 1s (18H), 0.47, (2 $SiMe_3$). 1s, (2H), 7.55, (2H β), 1s, (2H), 8.05, (2H peri).

Experimental procedure 1 was synthesized from naphthalene and Me_3SiCl/Li/THF according to the general procedure previously described^7. We obtained a mixture of 1 and 1,4-bis(trimethylsilyl)1,4-dihydronaphthalene (1/1 mol). The latter was separated by distillation (b.p.$_{11}$: 141°). 1 was recrystallized from boiling EtOH (m.p. 116°).

2 was prepared as follows : naphthalene (12.8 g, 0.1 mol) was dissolved in anhydrous HMPA (20 ml) and was added dropwise to a mixture of Mg (6.5 g, 0.27 mol), and Me_3SiCl (54 g ; 0.5 mol) in HMPA (200 ml) at 60-70° with vigorous stirring under N_2. After 30 h at 60-70°

the reaction mixture was hydrolyzed under acidic conditions, extracted with Et_2O, neutralized, dried and the low boiling products were evaporated. From the remaining yellow viscous oil 2 precipitated (white needles) and was recrystallized from ethanol : 4-8 g (10-20 %).

Tetralin or 6 were formed by heating (reflux, 36 h) 5 g of 1 or 2 respectively in MeCOOH (25 ml) followed by hydrolysis under basic conditions, extraction with ether, neutralization and drying. When the solvent was removed tetralin was separated by distillation or 6 was purified by filtration on a silica column using pentane as eluent.

7 was synthesized by heating under reflux for 24 h 2 (4.7 g, 0.02 mol) and p-chloranil (5 g, 0.02 mol), in benzene (60 ml). After cooling, benzene was removed and the residue filtered on a silica column with cyclohexane (250 ml) as eluent, giving 7 (3.2 g, 90 %).

Complete aromatization of 1 was carried out by refluxing for 52 h 1 (5.6 g, 0.01 mol) and o.chloranil (7.6 g, 0.031 mol) in toluene (150 ml). Usual extraction finally gave 5.

Partial aromatization of 1 was carried out by refluxing for 30 h 1 (5.5 g, ∿ 0.095 mol) and p.chloranil (5 g, 0.02 mol) in toluene (50 ml). Toluene was removed and the residue, filtered on a silica column using pentane as eluent, gave 4 g of a colourless oil having a strong blue fluorescence (mixture of 3 and 4). These products were separated using HPLC : RP 8 column, 10 bars, injection in pure Me_2CO using $MeOH/H_2O$: 9/1 vol. as eluent, 10 ml/mn flow, UV detector at 300 nm). Under these conditions 3 was eluted first. Subsequent treatment of the mixture 3 + 4 with o.chloranil in boiling toluene afforded the naphthalene derivative 5 among other products.

Aknowledgements

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References and Notes

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