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THE ACID CATALYZED ISOMERIZATION OF 2-(1-NAPHTHYL)-2,4,4-TRIMETHYL-2,4-DISILAPENTANE

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Summary

The product of the acid catalyzed rearrangement of 2-(1-naphthyl)-2,4,4-trimethyl-2,4-disilapentane is 2-(2-naphthyl)-2,4,4-trimethyl-2,4-disilapentane. This result completes the revision of a previous report in which 1,8-bis(trimethylsilyl)naphthalene was claimed to undergo acid catalyzed rearrangement to the 1,7-isomer.

It was recently reported [1] that the reaction of 1,8-dilithionaphthalene (I) with trimethylchlorosilane yields 1,8-bis(trimethylsilyl)naphthalene (II), and that the latter undergoes acid catalyzed rearrangement to the 1,7-isomer (III). In subsequent work it was shown [2] that reaction of I with trimethylchlorosilane in fact yields 2-(1-naphthyl)-2,4,4-trimethyl-2,4-disilapentane (IV) (Scheme 1(a)). We now report that the acid catalyzed rearrangement of IV in fact yields 2-(2-naphthyl)-2,4,4-trimethyl-2,4-disilapentane (V) (Scheme 1(b)).

Under the conditions described in [1], the trifluoroacetic acid catalyzed rearrangement of IV leads to a single rearrangement product, along with some decomposition byproducts and unreacted starting material. The rearrangement product was unambiguously identified as V by ^{1}H and ^{13}C NMR, and by comparison with authentic material. The ^{1}H NMR spectrum features three singlets at δ -0.01 (9H), 0.07 (2H) and 0.37 (6H) ppm, and a complex multiplet at 7.31-7.98 (7H) ppm.

The $^{13}C\{^1H\}$ NMR confirms that the product is a monosubstituted naphthalene: three of the ten signals in the aromatic region are due to quaternary carbons and seven to protonated carbons. In addition, there are three signals in the aliphatic region at δ 0.02, 1.43 and 3.16 ppm. The off-resonance decoupled ^{13}C NMR spectrum shows quartets (CH_3) at 0.02 and 1.43 ppm and a triplet (CH_2) at 3.16 ppm. The product of rearrangement was indistinguishable (^1H and ^{13}C NMR) from material prepared by lithiation of 2-bromonaphthalene (VI) followed by reaction with $(CH_3)_3SiCH_2Si(CH_3)_2Cl$ [2] (Scheme 1(c)).

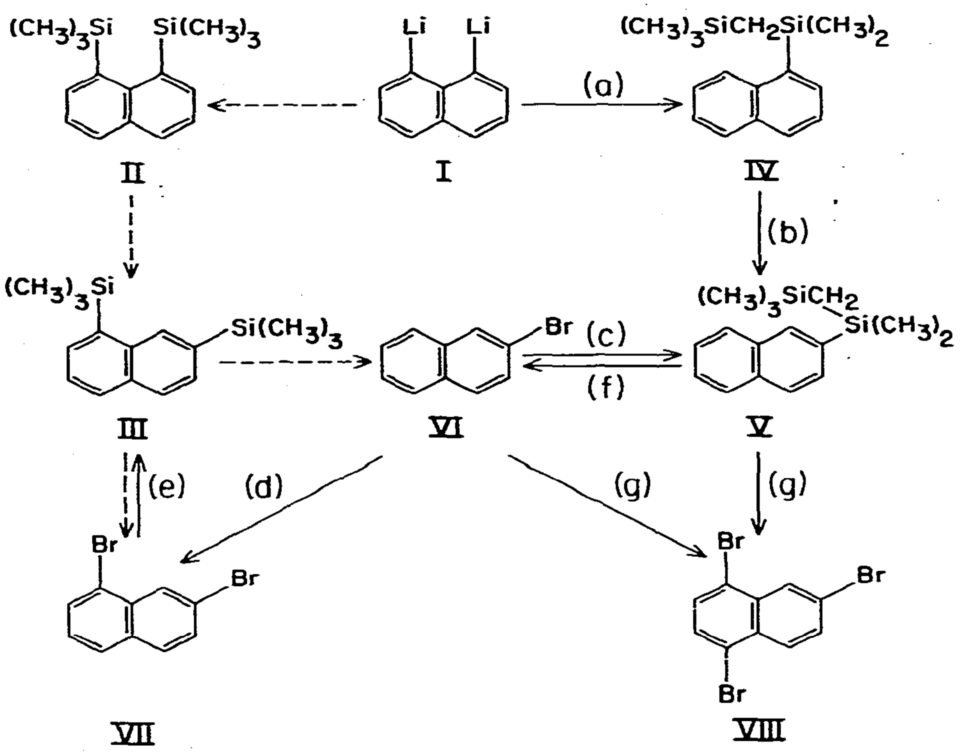
The rearrangement of IV to V follows the familiar pattern of acid catalyzed $\alpha \rightarrow \beta$ migrations in the naphthalene series. That the rate of migration is slow in comparison to the acid catalyzed isomerization of 1,2- to 1,3-bis(trimethylsilyl)-benzene [1] is attributable to the relief of strain accompanying the latter rearrangement [3]. No additional hypothesis is required to explain the results.

The previous identification of the rearrangement product as III [1] rested primarily on the ^1H NMR spectrum of the product and on the results of bromodesilylation reactions. In the course of our work we discovered that both lines of evidence were seriously flawed.

An important feature of the reported [1] ^1H NMR spectrum (CCl_4/CH_2Cl_2) was the presence of two singlets at δ 0.10 (9H) and 0.52 (9H) ppm which were assigned to $SiCH_3$ protons. Discounting slight shifts in signal frequency due to solvent and/or concentration factors, the reported $\Delta\delta$ of 0.42 ppm was in good agreement with our observation of $\Delta\delta$ 0.38 ppm for the two $SiCH_3$ singlets in V. Furthermore, the only other reported physical characteristic, n_D^{25} 1.5527, agreed well with our observation of n_D^{24} 1.5534 for V. However, since the reported [1] 1:1 ratio of integrated intensities was grossly at variance with our observation of a 3:2 ratio for the $SiCH_3$ singlets in V, and since no mention was made of the signal for the $SiCH_2Si$ protons, significant discrepancies still remained between our observations and those of the previous authors. For this reason we felt impelled to synthesize authentic III by an independent route. Bromination of VI yielded 1,7-dibromonaphthalene (VII) (Scheme 1(d)). Conversion of VII to the dilithio derivative followed by reaction with trimethylchlorosilane yielded III (Scheme 1(e)). The product had mass, ^1H, and ^{13}C NMR spectra consistent with the assigned structure.

In particular, the $^{13}C\{^1H\}$ NMR spectrum confirmed that the product was a disubstituted naphthalene: four of the ten signals in the aromatic region are due to quaternary carbons and six to protonated carbons. In addition, there are two signals in the aliphatic region at δ -0.87 and 0.47 ppm. An analysis of the coupled ^{13}C NMR spectrum confirmed the proposed structure. The ^1H NMR spectrum (100 MHz, 2:1 CCl_4/CD_2Cl_2) featured two singlets at δ 0.42 (9H) and 0.53 (9H) ppm, and a complex multiplet at 7.36-8.30 (6H) ppm. The chemical shift of the upfield singlet and the Δδ of 0.11 ppm provide conclusive evidence that III was not the product of the observed [1] rearrangement.

We were able to confirm the previous report [1] that reaction of the rearrangement product in acetic acid with bromine for 30 min affords VI (Scheme 1(f)), identified by comparison with authentic material (m.p., GLC, IR). This regiospecific bromodesilylation of V had previously been rationalized [1] by invoking protodesilylation at the 1-position of the putative III, followed by regiospecific bromodesilylation of 2-trimethylsilylnaphthalene. Also in accord with the previous report [1], treatment of a benzene solution of the rearrangement product first with bromine and then with acetic acid led to a mixture of products, the major fraction of which was collected by GLC and had m.p. 75-76°C and IR bands at 620 and 599 cm^{-1}. On the basis of this evidence, the previous authors [1] had taken the product of bromination to be VII, and had thus been led to infer regiospecific bromodesilylation of the putative precursor, III. However, the same compound, also obtained more directly by bromination of VI under the same conditions, exhibits patterns in the mass and $^{13}C\{^1H\}$ NMR spectra which prove it to be a tribromonaphthalene. An analysis [5] of the decoupled and coupled ^{13}C NMR spectra, inspection of the ^1H NMR spectrum, and the m.p. of 82-83°C obtained after two recyrstallizations from ethanol all strongly suggest that this compound is 1,4-6-tribromonaphthalene (VIII) (lit [6] m.p. 86-87°C). Evidently, under the more vigorous conditions of bromination, V is first bromodesilylated to VI, which then suffers further bromination to VIII (Scheme 1(g)).



Scheme 1 (a) $(CH_3)_3SiCl$; (b) CF_3COOH; (c) n-BuLi followed by $(CH_3)_3SiCH_2Si(CH_3)_2Cl$; (d) HOAc followed by Br_2, 7 hr; (e) n-BuLi followed by $(CH_3)_3SiCl$; (f) HOAc followed by Br_2, 30 min; (g) Br_2 followed by HOAc.

Experimental

General Procedures

Nuclear magnetic resonance spectra were recorded on a Varian XL 100 or on a JEOL FX90Q instrument. Chemical shifts are reported in ppm downfield from TMS.

Gas liquid chromatography was performed using a 4 ft. 20% SE-30 silicone rubber gum column, or a 5 ft. 10% FFAP 60/80 Chromosorb W column.

Catalyzed rearrangement of 2-(1-naphthyl)-2,4,4-trimethyl-2,4-disilapentane (IV).

An NMR tube which had been oven dried and purged with nitrogen was charged with 0.5 mmol of IV, 0.0126 mmol of CCl_4, 0.0153 mmol of trifluoroacetic acid, and 0.6 ml of dry benzene. The tube was sealed under vacuum and kept in a thermostatted oven at 154°C. The tube was removed periodically, cooled to room temperature and an NMR spectrum recorded to monitor the rearrangement. After 165 h the ratio between the intensity of the peaks in the aliphatic region did not change noticeably. This experiment was repeated on a tenfold scale in a thick-walled tube, and the same mixture of products (^{1}H NMR, GLC) was obtained. GC-mass spectral analysis revealed the presence of two major high-boiling products, both with m/e^+ 272. The two compounds were collected as a mixture by preparative GLC and identified as IV and V by comparison (^{1}H and ^{13}C NMR) with a mixture of authentic samples.

Preparation of 2-(2-naphthyl)-2,4,4-trimethyl-2,4-disilapentane (V).

A solution of 2.3 N n-butyllithium in hexane (11.0 ml, 25 mmol) was added under argon at 0°C to a stirred solution of 2-bromonaphthalene (5.18 g, 25 mmol) in 50 ml of anhydrous diethyl ether. After 2 h, 2-chloro-2,4,4-trimethyl-2,4-disilapentane [2] (4.52 g, 25 mmol) was added and the mixture was stirred at room temperature for 15 h. The usual workup afforded a colorless oil which was distilled to give V (2.30 g, 33%), b.p. 100-102°C (0.025 mm Hg), n_D^{24} 1.5534. ^{1}H NMR (100 MHz, $CDCl_3$): δ -0.01 (s, 9H, $SiCH_3$), 0.07 (s, 2H, $SiCH_2Si$), 0.37 (s, 6H, $SiCH_3$), and 7.31-7.98 ppm (complex m, 7H, aromatic H). $^{13}C\{^1H\}$ NMR (22.5 MHz, $CDCl_3$): δ 137.7, 133.6, 133.0 ppm (quaternary carbons); δ 133.7, 129.9, 128.0, 127.7, 126.8, 126.1, 125.8 ppm (protonated aromatic carbons); δ 0.02, 1.43, 3.16 ppm (aliphatic carbons). Found: C, 70.52; H, 8.79; Si, 20.26. $C_{16}H_{24}Si_2$ calcd: C, 70.51; H, 8.88; Si, 20.61%.

Preparation of 1,7-dibromonaphthalene (VII)

Bromine (2.8 ml , 50 mmol) was added to a stirred solution of 2-bromonaphthalene (10.36 g, 50 mmol) in 60 ml of glacial acetic acid. The reaction mixture was kept for 7 h at room temperature in the dark, then poured into 200 ml of saturated aqueous sodium carbonate solution and extracted twice with 100 ml of diethyl ether. The organic layer was washed twice with water, dried over $MgSO_4$ and evaporated to give a white solid. Three recyrstallizations from methanol afforded VII (1.95 g, 13.6%), m.p. 73-75°C (lit [4] m.p. 74°C).

Preparation of 1,7-bis(trimethylsilyl)naphthalene (III)

A solution of 2.3 N n-butyllithium in hexane (4.4 ml, 10 mmol) was added under argon at 0°C to a stirred solution of 1,7-dibromonaphthalene (1.43 g, 5 mmol) in 50 ml of anhydrous diethyl ether. After 2 h, trimethylchlorosilane (1.4 ml, 11 mmol) was added and the mixture was stirred at room temperature for 15 h. The usual workup afforded 1.40 g of product which was chromatographed on silica gel (n-pentane) to give 1.04 g of a colorless oil. GC-mass spectral analysis revealed the presence of two major high boiling products: bromotrimethylsilylnaphthalene (m/e^+ 278, 280) and bis(trimethylsilyl)naphthalene (m/e^+ 272). The latter was collected (GLC) and identified as III. ^1H NMR (100 MHz, 2:1 CCl_4/CD_2Cl_2): δ 0.42 (s, 9H, $SiCH_3$), 0.53 (s, 9H, $SiCH_3$) and 7.36-8.30 ppm (complex m, 6H, aromatic H). $^{13}C\{^1H\}$ NMR (25.2 MHz, $CDCl_3$): δ 138.2, 137.4, 136.3, 133.6 ppm (quaternary aromatic carbons); δ 134.2, 133.2, 129.5, 129.2, 128.1, 125.5 ppm (protonated aromatic carbons); δ 0.47, -0.87 ppm (aliphatic carbons).

Bromination of 2-(2-naphthyl)-2,4,4-trimethyl-2,4-disilapentane

Bromine (1 ml, 20 mmol) was added to a stirred solution of V (0.296 g, 1.1 mmol) in 5 ml of dry benzene. After 15 min, 0.75 ml of glacial acetic acid was added, and the mixture was allowed to stand at room temperature overnight. The usual workup gave a mixture of products, the major fraction of which was collected by GLC and had m.p. 75-76°C. The mass spectrum had the expected four peaks centered at m/e^+ 365. The same product (by GLC, MS, and IR) was obtained under the same conditions from 2-bromonaphthalene, but two recrystallizations from absolute ethanol raised the m.p. to 82-83°C. This compound was tentatively identified as 1,4,6-tribromonaphthalene (VIII) (lit [6] m.p. 86-87°C); ^1H NMR (100 MHz, $CDCl_3$): δ 7.53 (s, H_2 + H_3), 7.60 (dd, H_7, ^3J 9.0 Hz, ^4J 1.9 Hz), 8.00 (dd, H_8, ^3J 9.0 Hz, ^5J 0.5 Hz), and 8.33 ppm (dd, H_5, ^4J 1.9 Hz, ^5J 0.5 Hz). $^{13}C\{^1H\}$ NMR (22.5 MHz, $CDCl_3$): δ 133.7 and 131.4 ppm (quaternary carbons); δ 122.9, 122.4, and 121.1 ppm (brominated carbons); δ 131.5, 131.0, 130.3, 129.8 and 129.4 ppm (protonated carbons).

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