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Preliminary communication

UNUSUAL LITHIUM TRANSFER REACTIONS IN LITHIUM-SUBSTITUTED ORGANOSILICON COMPOUNDS. REINVESTIGATION OF THE REACTION OF 1,8-DILITHIONAPHTHALENE WITH TRIMETHYLCHLOROSILANE

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Summary

The product of the reaction of 1,8-dilithionaphthalene with trimethylchlorosilane is 2-(1-naphthyl)-2,4,4-trimethyl-2,4-disilapentane rather than 1,8-bis(trimethylsilyl)naphthalene as previously reported. A novel, presumably intramolecular, metalation process transfers the organolithium function in 1-trimethylsilyl-8-lithionaphthalene to a methyl substituent on the trimethylsilyl group, and it is this new organolithium reagent which reacts with the second mole of trimethylchlorosilane. Ring-opening of 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silirene by methyllithium is followed by a similar transfer of the organolithium function from the vinylic carbon atom to a methyl group on silicon.

The recently reported [1] synthesis of 1,8-bis(trimethylsilyl) naphthalene (I) was of some interest in the context of the question of correlated rotation of alkyl groups [2] . Some features of the spectral properties of this compound were, however, difficult to explain. Notable was the observation of three singlets in its ^{1}H NMR spectrum at δ-0.07, 0.24, and 0.53

ppm which failed to coalesce even at 150°C. This observation, which was interpreted in terms of a high barrier to rotation about the silicon-naphthalene bonds in I, stood in marked contrast to the low barriers found for corresponding processes in 1,8-di-tert-butylnaphthalene [3] and in 1,8-bis(trimethylstannyl)naphthalene [1] . The reported [1] ratio of integrated intensities for the three singlets (9:3:6) also was puzzling. Reinvestigation now has shown that the compound obtained by the reaction of 1,8-dilithionaphthalene with trimethylchlorosilane is, in fact, an isomer of I, 2-(1-naphthyl)-2,4,4-trimethyl-2,4-disilapentane (II). The three signals observed in the aliphatic region of its ^{1}H NMR spectrum correspond to the trimethylsilyl, methylene and dimethylsilyl protons of II, with relative integrated intensities of 9:2:6, respectively.

Reaction of 1,8-dilithionaphthalene with trimethylchlorosilane for 120 hr as described [1] gave a product which, after GLC purification (5' x 0.25" 10% Carbowax 20M), was indistinguishable (bp, ^{1}H and ^{13}C NMR) from an authentic sample obtained in the original study [1] . The ^{1}H NMR spectrum (100 MHz, CD_2Cl_2)* featured signals at δ 0.00 (s, 9H, $SiCH_3$), 0.32 (s, 2H, $SiCH_2Si$), 0.58 (s, 6H, $SiCH_3$), and 7.36-8.48 ppm (complex m, 7H, aromatic H). The $^{13}C\{^{1}H\}$ NMR spectrum (25.2 MHz, CD_2Cl_2)* unambiguously confirmed that the product is a monosubstituted naphthalene: three of the ten signals in the aromatic region are due to non-protonated (quaternary) carbons (139.4, 137.3, 133.9 ppm) and seven to protonated carbons (133.5, 129.9, 129.4, 128.7, 125.8, 125.6, 125.4). In addition, there are three signals in the aliphatic region at 1.5, 1.63 and 4.71 ppm. The fully coupled ^{13}C NMR spectrum further confirmed the absence of one-bond C-H coupling for the three quaternary aromatic carbons and showed quartets (CH_3) at 1.5 and 1.63 ppm and a triplet (CH_2) at 4.71 ppm, as expected for II, but not for I. That the product has structure II was verified by independent synthesis: reaction of 1-lithionaphthalene with $(CH_3)_3SiCH_2Si(CH_3)_2Cl$ (prepared by addition of $(CH_3)_3SiCH_2Li$ to $(CH_3)_2SiCl_2$; properties in agreement with literature data [4,5]) gave a product which was indistinguishable (bp, GLC, ^{1}H and ^{13}C NMR) from that obtained by the alternate route described above.

The formation of II can be rationalized as shown in Scheme 1.

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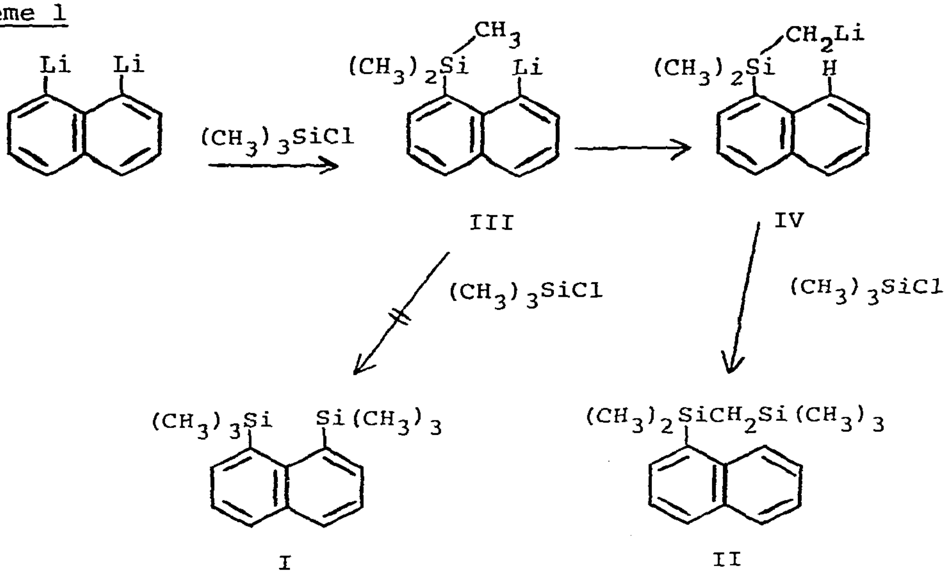
*Chemical shifts are expressed in ppm downfield from TMS using signals from CD_2Cl_2 (containing traces of $CHDCl_2$) as internal standard (δ(TMS) = 5.32 and 53.8 ppm for ^{1}H and ^{13}C, respectively).

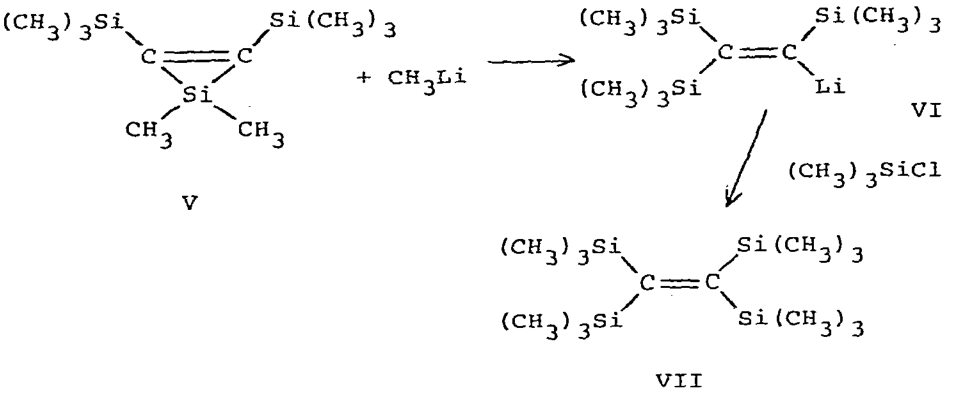
Scheme 1



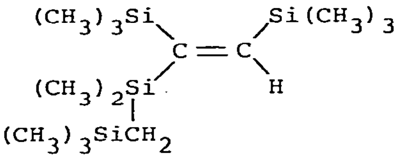
This proposed intramolecular proton abstraction from a methyl substituent on silicon evidently is facilitated by the close proximity of the reaction sites and by the obvious difficulty involved in reacting the sterically encumbered peri carbanion with an external substrate. Subsequent reaction with a second molecule of trimethylchlorosilane therefore takes place at the lithiated methylene carbon in IV.

That metalation competes with displacement in reactions of trimethylsilyl compounds with hindered organolithium reagents is known from studies of other workers [5,6,7] . (See also [8] for a related reaction).

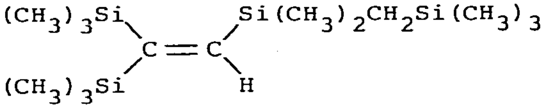
Scheme 2



A similar transfer of reaction site in a lithiated organosilicon compound was encountered during the course of studies on the reactions of 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silirene (V) [9]. This highly strained, hyper-reactive silacyclene had been found to be very susceptible to cleavage of the Si-C bond of the ring by nucleophilic reagents. This suggested a possible rational synthesis of the potentially interesting tetrakis(trimethylsilyl)ethylene (Scheme 2).
The dropwise addition of V to a solution containing a ninefold excess of methyllithium in diethyl ether was followed by addition of trimethylchlorosilane (all operations under nitrogen). Hydrolytic work-up gave not the expected VII but rather an isomer of VII whose structure is consistent with VIII or IX. [Found: C, 53.33; H, 11.38. $C_{14}H_{36}Si_4$ calcd.: C, 53.08; H, 11.46 ; ^1H NMR (CCl_4): δ - 0.29 (s, 2H, $SiCH_2Si$), - 0.11 (s, 9H, $CH_2Si(C\underline{H}_3)_3$), 0.01 (s, 6H, $Si(CH_3)_2$), 0.07 (s, 18H, $C{=}CSi(CH_3)_3$; accidental equivalence) and 7.20 ppm (s, 1H, C=CH)].



VIII



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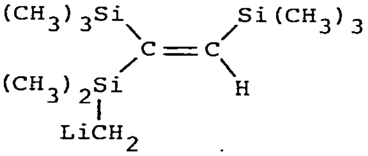
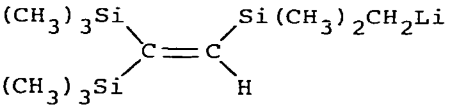
In this case also one may rationalize the formation of the observed product in terms of lithium transfer to a methyl substituent on silicon to give X or XI, respectively, whose subsequent reaction with trimethylchlorosilane produces VIII or IX. Support for this process was provided by an experiment in



X



XI

which the V/CH_3Li reaction product was treated with D_2O. The mass spectrum of the product, which was isolated in 31% yield, indicated that one deuterium atom had been incorporated and the ^1H NMR spectrum showed the vinyl proton as a singlet at δ 7.25 ppm.*

Studies are underway to test the mechanistic proposal in Scheme 1, to explore the generality of the lithium transfer reaction in other 1-trimethylelement-8-lithionaphthalenes, and to reinvestigate the course and mechanism of the rearrangement reaction previously ascribed to I [1].

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*A related process may be involved in the lithium-induced trimethylchlorosilylation of trans-$(CH_3)_3SiCH{=}CHSi(CH_3)_3$, a reaction which, after hydrolytic work-up, gave $[(CH_3)_3Si]_2CHCH_2Si(CH_3)_2CH_2Si(CH_3)_3$ [10].