

Preliminary communication

Organosilicon compounds

IX. Interaction of 2,5-bis(trimethylsilyl)thiophene with *n*-butyllithium

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As an extension of our previous investigation into the NMR spectra of various silylfurans¹, we have examined the NMR spectrum of 2,5-bis(trimethylsilyl)thiophene (I). As was the case with silylfurans², the introduction of silyl moieties causes a downfield shift of the thienyl protons as a result of (*p*-*d*) π bond formation³ between the π -electron density of thiophene and the empty *d*-orbitals of silicon. The 3- and 4-protons of I (7.23 δ)★★ are not only shifted further downfield than the corresponding protons in thiophene (6.97 δ) but also appear at a more deshielded position than the 2- and 5-protons of thiophene (7.17 δ). Since thiophene can be readily metalated⁴ in the 2-position by *n*-BuLi, it was initially hoped that *n*-BuLi would affect metalation in the 3-position of I as a result of the comparable "acidities" of H₃ of I and H₂ of thiophene. Shirley⁵ has given support to such a tenet by stressing the importance of the relative "acidity" of the ring proton in determining the position of the entering lithium atom.

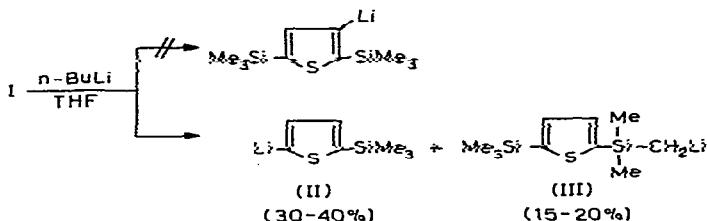
The reaction of I with one equivalent of *n*-BuLi in refluxing THF for 3–5 hours did not afford the 3-lithio derivative of I but rather produced two very interesting organolithium reagents. The first of these, 5-trimethylsilyl-2-lithiothiophene (II), was produced in 30–40% yield from the cleavage of a –SiMe₃ moiety from the thiophene ring. The second, 5-trimethylsilyl-2-lithiomethyl-dimethylsilylthiophene (III), was produced in 15–20% yield from the metalation of the Si–CH₃ group.

Even though the production of II by silicon–thiophene bond cleavage with *n*-BuLi has not, to our knowledge, been previously reported★★★, it was not altogether unexpected. For instance, a previous investigation⁶ in this laboratory has described the cleavage of the silicon–thiophene bond by another nucleophile, the aziridine anion, and has classified the thiophene moiety as an excellent leaving group from silicon. Furthermore, that *n*-BuLi has the capacity to affect silicon–aromatic bond cleavage has been documented

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★★NMR spectra in cyclohexane at infinite dilution and relative to TMS as internal standard.

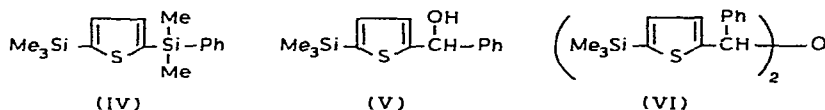
★★★The cleavage of the –SiMe₂H moiety from polyhalogenated thiophenes by *n*-BuLi has been investigated by Professor Henry Gilman and coworkers, Iowa State University, Ames, Iowa (U.S.A.)



by Gilman and coworkers in the case of pentachlorophenyldiphenylsilane⁷ and pentafluorophenyldiphenylsilane⁸.

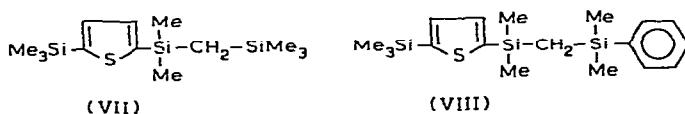
A precedent for the production of III, though a bit more surprising, is substantiated by several recent investigations dealing with Si-CH₃ metalations. Tetramethylsilane⁹, trimethylchlorosilane¹⁰ and hexamethyldisiloxane¹¹ have been metalated by such lithium reagents as *n*-BuLi, *t*-BuLi and the BuLi (TMEDA) complex. Our finding, however, represents the first report of such a metalation in silylthiophenes.

Verification for the production of II was obtained by employing two electrophilic reagents, phenyldimethylchlorosilane and benzaldehyde, to afford 5-trimethylsilyl-2-phenyldimethylsilylthiophene (IV) in 30% yield and 2-(5-trimethylsilyl)thienylphenylmethanol (V) in 30.2% yield, respectively. Structure proofs were accomplished by comparison of



physical constants, NMR and IR spectra with authentic samples of IV and V, synthesized from a known sample of II. In this case II was produced by the direct metalation of 2-trimethylsilylthiophene with *n*-BuLi⁴. V exhibited a remarkable tendency to dehydrate upon distillation to the corresponding ether (VI).

Confirmation of Si-CH₃ metalation (III) was obtained by utilizing trimethylchlorosilane and phenyldimethylchlorosilane to produce, respectively, VII (16.7%) and VIII (17.5%) whose NMR, IR and elemental analysis (Table 1) were consistent with the structure assignments.



In conclusion, the suggested "acidity" of the 3- and 4-protons of I was not the controlling factor in the reaction of I with *n*-BuLi. Rather, it appears that both the tendency for Si-CH₃ metalation and the labile nature of the silicon-thiophene bond control the reaction products. This study represents a preliminary report to a general investigation of the interaction of *n*-BuLi with silylheterocycles.

TABLE 1

Compound	B.p. (m.p.) (°C/mm)	n_D^{25}	Analysis found (calcd.) (%)		
			C	H	Si [S]
IV	85/0.05	1.5430	62.06 (61.99)	7.38 (7.65)	[10.96] [(11.04)]
V	125/0.05	1.5616	63.88 (64.06)	6.92 (6.93)	
VI	(102–104)	—	66.13 (66.34)	6.68 (6.77)	
VII	80/0.065	±.4900	51.85 (51.91)	9.43 (9.40)	28.16 (28.02)
VIII	125/0.01	1.5300	59.68 (59.58)	8.26 (8.35)	

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