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Preliminary communication

UNEXPECTED BEHAVIOR OF SILOLES TOWARD ORGANOLITHIUM REAGENTS

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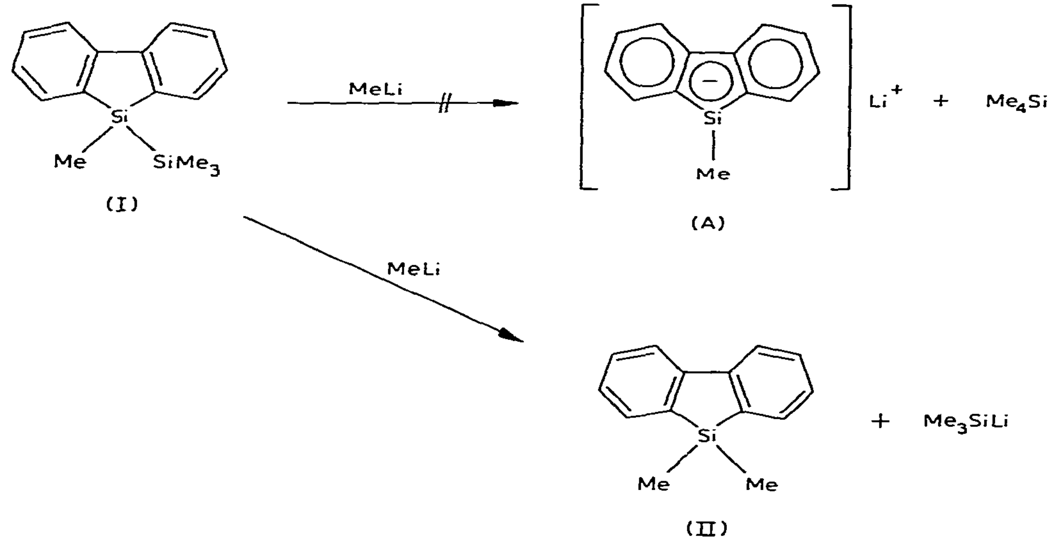
Summary

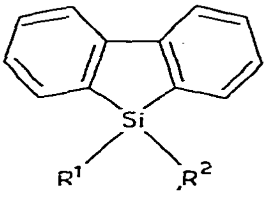
The reaction of 5-trimethylsilyl-5-methyldibenzosilole (I) with an excess of methyllithium in THF afforded 5,5-dimethyldibenzosilole (II) in quantitative yield. Treatment of I with an excess of butyllithium gave 5,5-dibutyldibenzosilole (III) quantitatively. Similar treatment of II with butyllithium in THF at room temperature gave III in almost quantitative yield, while treatment of III with methyllithium at reflux temperature gave II and 5-butyl-5-methyldibenzosilole in 10 and 40% yield, in addition to 37% of the starting III. 1,2,5-Tris(trimethylsilyl)-1-methyl-3,4-diphenylsilole also reacted with methyllithium to give 1,1-dimethyl-2,2,5-tris(trimethylsilyl)-3,4-diphenyl-1-silacyclopent-3-ene and 1,1-dimethyl-2,5-bis(trimethylsilyl)-3,4-diphenylsilole in 70 and 7% yield. A five-coordinate silicon compound is proposed as an intermediate.

In an attempt to prepare a stable silacyclopentadienide anion from certain siloles, we have found unexpected behavior of the siloles toward organolithium compounds. We treated 5-trimethylsilyl-5-methyldibenzosilole (I) (^{1}H NMR δ (ppm) 0.05 (Me_3Si, s, 9H), 0.45 (MeSi, s, 3H), 7.1—8.0 (ring protons, m, 8H); M^+ 268) with a 2.5-fold excess of methyllithium, expecting to observe stable anion A. No change was observed in ethyl ether at room temperature. However, when a methyllithium/ethyl ether mixture was added to dibenzosilole I in tetrahydrofuran (THF) at −78°C, a light green solution was formed. When the mixture was warmed to room temperature, the color of the solution became deep green. Hydrolysis of the mixture afforded an unexpected compound, 5,5-dimethyldibenzosilole (II) [1,2] quantitatively, but not 5-hydro-5-methyldibenzosilole, indicating that substitution of the trimethylsilyl group by methyllithium took place (Scheme 1).

SCHEME 1



Treatment of I with an excess of butyllithium in THF again afforded a deep green solution. Surprisingly, 5,5-dibutyldibenzosilole (III) was obtained in quantitative yield. This result indicates that both trimethylsilyl and methyl groups can be replaced by butyllithium. Such replacement of the substituents on the silicon atom in the dibenzosilole ring by organolithium compounds was found to be a remarkably general reaction. Thus, treatment of 5,5-dimethyldibenzosilole (II) with an excess of butyllithium at room temperature gave III quantitatively, while treatment of compound III with methyllithium at reflux temperature gave II and 5-butyl-5-methyldibenzosilole (IV) in 10 and 40% yield, in addition to 37% of the starting compound III. The reaction of I with 1 equiv. of butyllithium in THF, however, produced III and IV in 15 and 63% yield, respectively, in addition to 14% of the unchanged I.



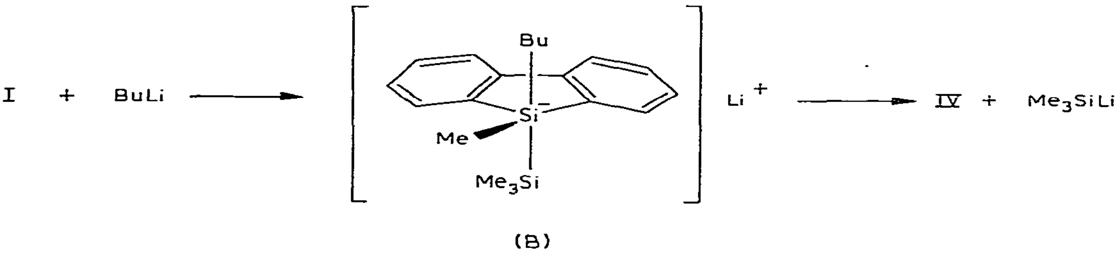
(III, $R^1 = R^2 = Bu$
IV, $R^1 = Bu, R^2 = Me$)

All spectral data of II were identical with those of an authentic sample prepared from the reaction of 2,2′-dilithiobiphenyl and dichlorodimethylsilane. The structures of III (^1H NMR δ (ppm) 0.70—1.05 (CH_3C and CH_2Si, m, 10H), 1.15—1.55 (CH_2CH_2, m, 8H), 7.1—7.9 (ring protons, m, 8H); M^+ 294) and IV (^1H NMR δ (ppm) 0.40 (MeSi, s, 3H), 0.70—1.05 (CH_3C and CH_2Si, m, 5H), 1.15—1.55 (CH_2CH_2, m, 4H), 7.0—7.8 (ring protons, m, 8H); M^+ 252) were identified by spectroscopic analyses. Combustion analyses of II, III and IV were also in agreement with these structures.

Gilman et al. [1] reported that the reaction of 2,2′-dilithiobiphenyl with 5-chloro-5-methyldibenzosilole gave II together with 5,5′-spirobi(dibenzosilole). They also found that the reaction of 2,2′-dilithiobiphenyl with methyltrichlorosilane afforded 5,5′-spirobi(dibenzosilole) in addition to 5-chloro-5-methyldibenzosilole [3]. Similar reactions have also been found in other systems: triphenylchlorosilane reacted with 1,4-dilithiobutane to give 1,1-diphenyl-1-silacyclopentane [4], and phenylethynylsilane derivatives reacted with butyllithium yielding butylsilane derivatives and phenylethynyllithium [5,6]. These reactions presumably belong to the same category as ours.

To explain the results obtained, we propose a five-coordinate silicon compound as a key intermediate, such as B for the reaction of I with butyllithium, in which the trimethylsilyl group and the lithium atom would leave simultaneously to give compound IV and trimethylsilyllithium (Scheme 2). The fact that many types of anionic five-coordinate silicon compounds have been prepared [7—10] supports the transient formation of intermediate B.

SCHEME 2

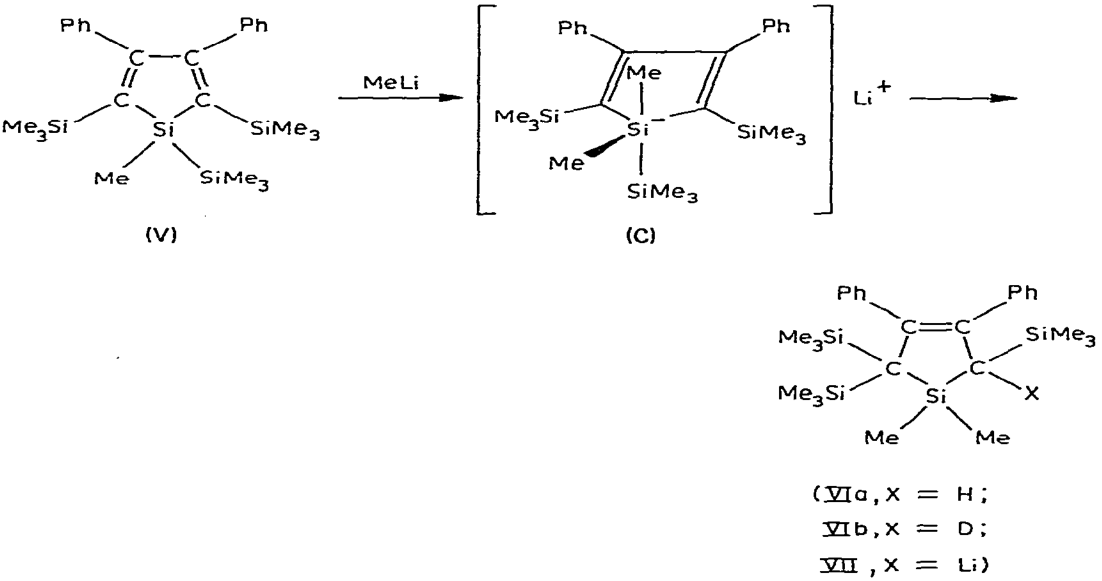


We could not succeed to trap the silyllithium in this reaction; however, methyllithium produced in the reaction of II with butyllithium could be trapped by phenyldimethylchlorosilane as phenyltrimethylsilane.

Similar treatment of 1,2,5-tris(trimethylsilyl)-1-methyl-3,4-diphenylsilole (V) [11] is of considerable interest, because rearrangement of the trimethylsilyl group attached to silicon to an adjacent unsaturated carbon atom occurs. Thus, 3 ml (3.6 mmol) of a 1.2 *M* methyllithium/ethyl ether solution was added to 0.434 g (0.93 mmol) of V in 5 ml of THF at –78°C. The mixture was warmed up to room temperature and stirred for 4 h. Hydrolysis of the resulting dark red solution afforded 1,1-dimethyl-2,2,5-tris(trimethylsilyl)-3,4-diphenyl-1-silacyclopent-3-ene (VIa) in 70% yield, in addition to 1,1-dimethyl-2,5-bis(trimethylsilyl)-3,4-diphenylsilole [11] (7% yield). Deuterolysis of the mixture gave a deuterio compound (VIb), indicating the presence of a carbon—lithium bond in the molecule. All spectral data for VIa and VIb were consistent with the proposed structure (For VIa: ^{1}H NMR δ (ppm) –0.24 (Me_3Si, s, 9H), 0.10 (Me_3Si, s, 9H), 0.21 (Me_3Si, s, 9H), 0.40 (MeSi, s, 3H), 0.51 (MeSi, s, 3H), 1.62 (CH, s, 1H), 6.5—7.0 (ring protons, m, 10H); ^{13}C NMR δ (ppm) 0.9 (Me_3Si), 2.8 (MeSi), 3.3 (MeSi), 3.6 (Me_3Si), 5.0 (Me_3Si), 26.4

(CH(SiMe$_3$)), 27.8 (C(SiMe$_3$)$_2$), 125.1, 125.6, 126.2, 126.9, 129.7, 131.6, 142.2, 142.4, 142.7, 143.6 (olefinic and phenyl ring carbons); Anal. Found: C, 67.27; H, 9.44. $C_{27}H_{44}Si_4$ calcd.: C, 67.42; H, 9.22%. For VIb: exact mass, Found 481.2573 (Calcd. 481.2583), isotopic purity (more than 99%)). In this reaction, no products arising from addition of methyllithium across the silacyclopentadiene ring could be detected. The production of VI may be understood in terms of the transient formation of intermediate C, followed by rearrangement to lithium compound (VII) which can be detected by ^{1}H NMR spectroscopic analysis (^{1}H NMR δ (ppm) -0.37 (Me$_3$Si, s, 9H), 0.12 (Me$_3$Si, s, 18H), 0.22 (Me$_2$Si, s, 6H)).

SCHEME 3



(V)

(C)

(VIa, X = H;
VIb, X = D;
VII, X = Li)

The reaction of a variety of the siloles with organolithium compounds is currently examined and will be reported elsewhere.

References

1 H. Gilman and R.D. Gorsich, J. Amer. Chem. Soc., 80 (1958) 3243.
2 R.W. Coutant and A. Levy, J. Organometal. Chem., 10 (1967) 175.
3 H. Gilman and R.D. Gorsich, J. Amer. Chem. Soc., 80 (1958) 1883.
4 D. Wittenberg and H. Gilman, J. Amer. Chem. Soc., 80 (1958) 2677.
5 H. Gilman and H. Hartzfeld, J. Amer. Chem. Soc., 75 (1953) 4531.
6 M. Ishikawa, H. Sugisawa, S. Katayama and M. Kumada, unpublished results.
7 H. Burger, Angew. Chem. Int. Edit., 12 (1973) 474.
8 C.L. Frye, J. Amer. Chem. Soc., 92 (1970) 1205.
9 R.K. Marat and A.F. Janzen, Can. J. Chem., 55 (1977) 1167.
10 E.F. Perozzi and J.C. Martin, J. Amer. Chem. Soc., 101 (1979) 1591.
11 M. Ishikawa, H. Sugisawa, O. Harata and M. Kumada, J. Organometal. Chem., 217 (1981) 43.