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UNEXPECTED CHEMISTRY IN AN ATTEMPTED GENERATION OF A STERICALLY HINDERED SILENE

THOMAS J. BARTON * and CHRISTOPHER R. TULLY

Department of Chemistry, Iowa State University, Ames, Iowa 50011 (U.S.A.)

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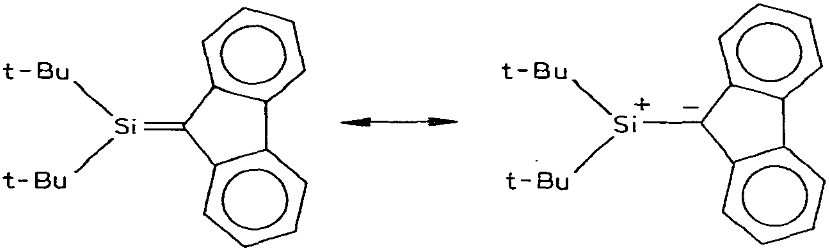
Summary

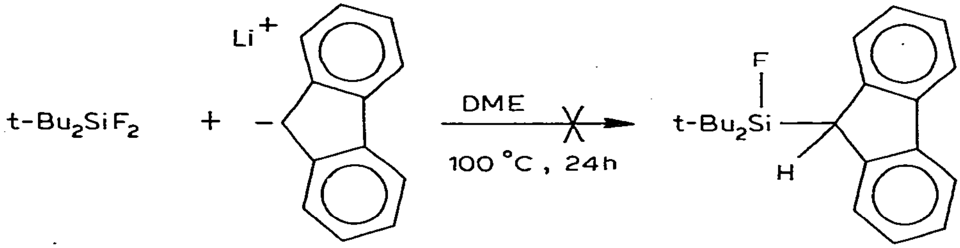
In an attempt to synthesize a silene, stabilized both electronically and by extreme steric bulk, two things of considerable interest were discovered: (1) perchlorate can function as a uniquely effective leaving group for alkylation on silicon, and (2) stable α-halosilyl carbanions can be generated through the aid of steric bulk.

Although molecules containing a silicon—carbon $(p-p)\pi$ double bond (silenes) have now been postulated in a wide variety of reactions [1] and three reports of matrix isolation and infrared observation have appeared [2], only the recent work of Brook [3] using extremely bulky substituents has provided any success in the search for a stable silene. This paper will report our attempts to prepare silene I, a molecule whose extreme steric bulk should impede dimerization. It was also possible that the undoubtedly polar silene [4] would be electronically stabilized by the fluorenyl moiety.



(I)

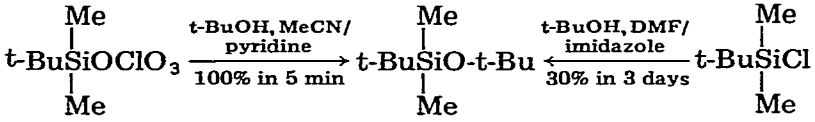
It is generally agreed that for alkylation of sterically hindered silanes, fluoride is the best leaving group [5]. Thus we thought to prepare silane II, a potential precursor of I, through alkylation of di-t-butyldifluorosilane. Quite surprisingly we found that heating a solution of di-t-butyldifluorosilane and fluorenyllithium at 100° C for 24 h afforded no detectable reaction.



(II)

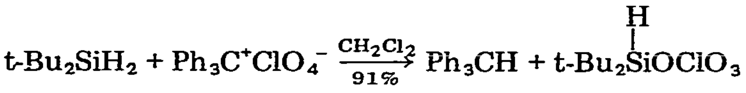
Recently we have discovered that perchlorate is a uniquely effective leaving group on silicon [6]. This is evidenced by the observations that triethylsilyl perchlorate is cleanly reduced to triethylsilane by sodium borohydride at temperatures well below ambient, and t-butyldimethylsilyl perchlorate reacts with tertiary alcohols much faster than does the traditional t-butyldimethylsilyl chloride [7].

$$\text{Et}_3\text{SiOClO}_3 \xrightarrow[-40^\circ\text{C}]{\text{NaBH}_4} \text{Et}_3\text{SiH (quantitative)}$$



$$\text{t-Bu}\overset{\text{Me}}{\underset{\text{Me}}{\text{Si}}}\text{OClO}_3 \xrightarrow[\text{100\% in 5 min}]{\text{t-BuOH, MeCN/ pyridine}} \text{t-Bu}\overset{\text{Me}}{\underset{\text{Me}}{\text{Si}}}\text{O-t-Bu} \xleftarrow[\text{30\% in 3 days}]{\text{t-BuOH, DMF/ imidazole}} \text{t-Bu}\overset{\text{Me}}{\underset{\text{Me}}{\text{Si}}}\text{Cl}$$

Thus it was felt that perchlorate might function more effectively than even fluoride for alkylation on silicon. With this in mind di-t-butylsilyl perchlorate (III) was prepared from di-t-butylsilane in 91% yield using trityl perchlorate [7] in an exchange reaction.

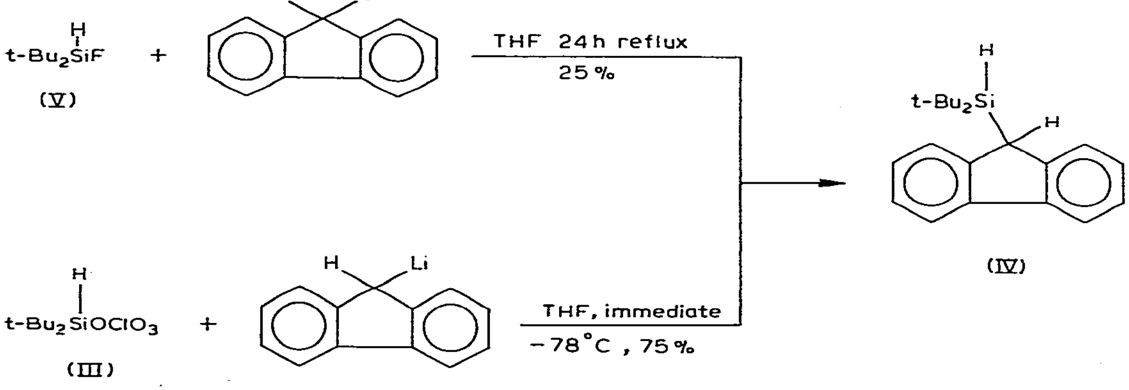


$$\text{t-Bu}_2\text{SiH}_2 + \text{Ph}_3\text{C}^+\text{ClO}_4^- \xrightarrow[91\%]{\text{CH}_2\text{Cl}_2} \text{Ph}_3\text{CH} + \text{t-Bu}_2\overset{\text{H}}{\text{Si}}\text{OClO}_3$$

(III)

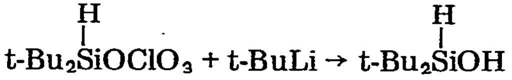
In dramatic contrast to the attempted reaction of di-t-butylfluorosilane,

SCHEME 1



fluorenyllithium can be titrated with perchlorate III at —78° C to give silane IV in 75% isolated yield. To provide a strict comparison of the reactivity of a silyl fluoride to a silyl perchlorate, a sample of di-t-butylfluorosilane (V) was prepared and treated with fluorenyllithium. After 24 h in refluxing THF only 25% conversion to IV had occured (Scheme 1).

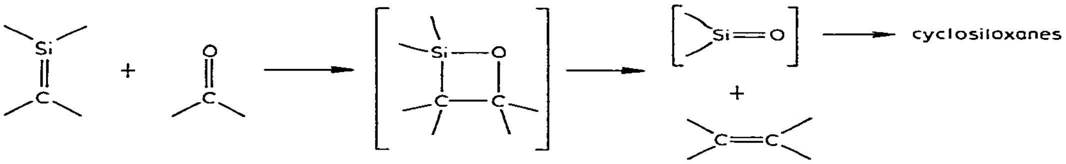
Unfortunately, before one accepts perchlorate as the most effective leaving group on silicon, we must report an important limitation. If perchlorate III is treated with t-butyllithium, reduction of the perchlorate group takes place rather than alkylation on silicon. This reaction is also very rapid at —78° C and gives a high yield of silanol VI. The reduction apparently hinges upon the availability of β-hydrogens, which are absent in fluorenyllithium.



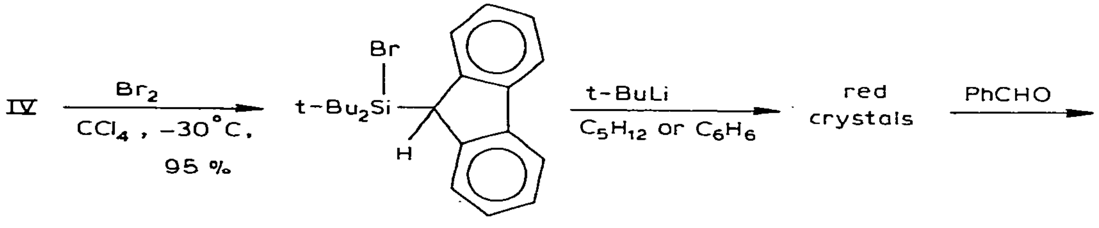
$$t\text{-}Bu_2\overset{H}{\overset{|}{Si}}OClO_3 + t\text{-}BuLi \rightarrow t\text{-}Bu_2\overset{H}{\overset{|}{Si}}OH$$

(III) (VI)

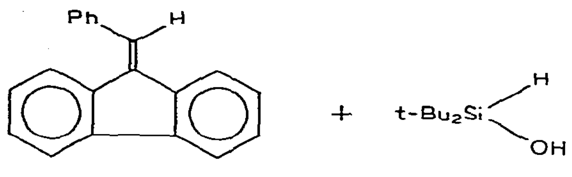
Now that a convenient method for the synthesis of silane IV was available, work was begun to attempt the transformation of IV to silene I. Bromination of IV at —30° C occurred cleanly to afford the desired silyl bromide (VII) in 95% yield. Dehydrobromination of VII was attempted with t-butyllithium as the steric bulk of the two reactants was considered sufficient to prevent any reaction by substitution. Treatment of VII with t-butyllithium in either pentane or benzene at ambient temperature produced a red solution from which well-formed, red crystals grew over a period of two days. In order to determine whether this crystalline material was indeed silene I, it was dissolved in dimethoxyethane and the solution treated with benzaldehyde. The rationale for this reaction is that it is rather well-established that silenes react with aldehydes and ketones to form the silaoxetane ring system, which in turn decomposes to silanone and olefin [1].



Thus when treatment of these red crystals with benzaldehyde afforded 9-benzylidenefluorene (VIII), the expected product from I and benzaldehyde, the intermediacy of the silene was strongly implicated. However, examination of the product mixture revealed that the silicon-containing product was not an oligomeric silanone, but rather the silanol IX.

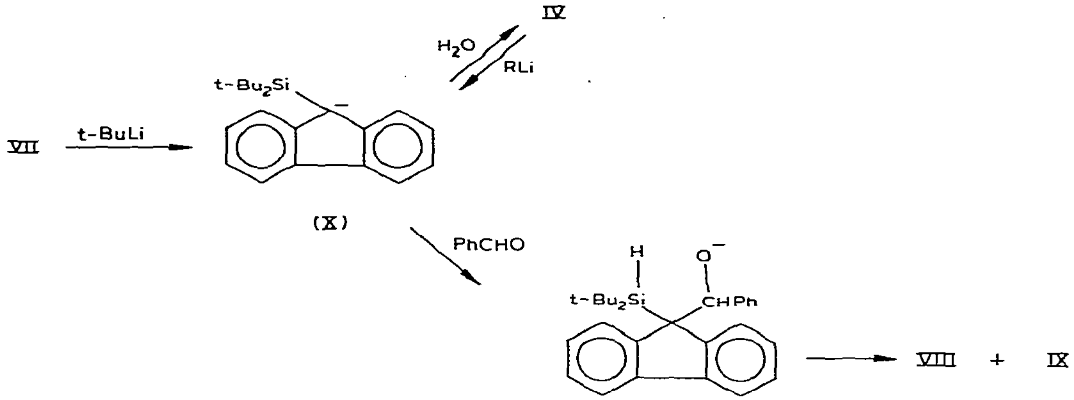


(VII)



(VIII) (IX)

Products VIII and IX are easily explained if the red, crystalline product from VII and t-butyllithium is simply the lithium salt X. Such α-silyl carbanions are well known to condense with aldehydes to afford olefins, and VIII and IX would be our expected products [8]. Indeed, quenching of the red crystals with water produced starting silane IV. Also, the NMR spectra of these red crystals could be duplicated by treating IV with either n-butyl- or t-butyl-lithium in THF. While metallation on silicon followed by a prototropic shift is a possible explanation, we assume that this is simply another example of reduction of a sterically hindered halosilane [9]. Thus, the initially exciting red crystals are undoubtedly the substituted fluorenyl salt X.



When conducted in THF the reaction of bromide VII with either t-butyl- or n-butyl-lithium is quite different. Here the fluorenyl proton is cleanly abstracted (reaction followed by NMR) to give the desired carbanion XII. Addition of water to this solution regenerates bromide VII, thus no rearrangement has taken place. The amazing stability of this unique α-halosilyl carbanion is particularly distressing in view of the report by Jones and Lim [10] that in a hydrocarbon medium a less hindered α-chlorosilyl carbanion immediately eliminates chloride ion to form a silene. More recently Wiberg and Preiner have succeeded in generating a silene from several ester substituted α-silyl carbanions [11]. The stability of XII is probably a combination of the stabilizing solvation of lithium cation by THF and steric inhibition to silene formation *.

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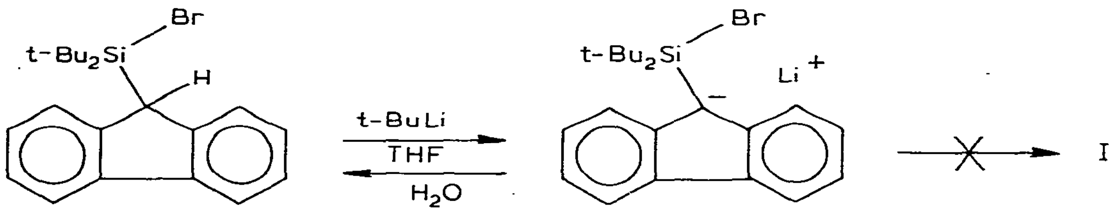
* Although we cannot totally exclude the possibility that XII is the radical anion of VII, the fact that this color is unchanged up to room temperature argues against it [cf. 12].



(VII) (XII)

Experimental

Reaction of di-t-butyldifluorosilane with fluorenyllithium

Fluorenyllithium was prepared by adding n-butyllithium (5 ml of 1.6 *M* solution in hexane, 8.0 mmol) to a solution of 1.33 g fluorene and 25 ml DME in a sealable pyrex tube with cooling. After 0.5 h at room temperature, 1.44 g (80 mmol) of di-t-butyldifluorosilane was added to the red solution and the tube was cooled, evacuated and sealed. After heating at 100° C for 24 h the tube was opened and the red solution was quenched with aqueous NH_4Cl and found to contain only starting materials (by GLC and NMR).

Preparation of di-t-butylsilane

Di-t-butyldifluorosilane (60 g, 0.33 mol) was added slowly to a slurry of $LiAlH_4$ (12 g, 0.33 mol) in 100 ml THF at reflux. After refluxing an additional 2 h the reaction mixture was slowly poured over a mixture of ice and aqueous NH_4Cl. Pentane (150 ml) was then added to the mixture and the pentane layer was extracted several times with water until the aqueous extract no longer smelled of THF. The pentane layer was then distilled (b.p. 126—128° C) to furnish 40.5 g (84%) of the title compound which had identical spectral properties to those reported by Doyle and West [13] though this preparation is a considerable improvement over their preparation.

Preparation of di-t-butylsilyl perchlorate (III)

Trityl perchlorate (15.8 g; 46 mmol) was placed in a flask equipped with a rubber septum and magnetic stirrer. The flask was cooled in an ice bath and 40 ml methylene chloride were added to obtain a yellow-orange slurry. Di-t-butylsilane (6.87 g; 47 mmol) was then added dropwise via syringe. After completion of addition the reaction mixture was homogeneous and colorless. Methylene chloride was removed at atmospheric pressure and di-t-butylsilyl perchlorate (III) was distilled directly from the reaction flask (10.2 g, 91%; b.p. 49° C/ 0.07 mmHg; 60 MHz ^1H NMR (CCl_4) δ 4.57 (s, 1 H), 1.15 (s, 18 H) ppm).

Preparation of di-t-butylfluorenylsilane (IV)

Fluorenyllithium (20 mmol) was prepared by adding 15.5 ml of 1.6 *M* solution of n-butyllithium (24.8 mmol) to an ice cooled solution of 3.32 g (20 mmol) fluorene in 70 ml THF. The characteristic bright red-orange color of the fluorenyl anion was produced immediately. After stirring at room temperature for 1 h the solution was cooled to ca. —75° C with a Dry-Ice/ethanol bath.

Approximately 7 ml di-t-butylsilyl perchlorate was drawn into a 10 ml syringe and weighed. The perchlorate was added dropwise to the Dry-Ice-cooled, red-orange solution of fluorenyllithium. An immediate reaction was apparent and when the light yellow end-point was reached the syringe was weighed again and the difference was 5.97 g (24.7 mmol) of silyl perchlorate. The light yellow solution contained a white precipitate which appeared to dissolve as the mixture warmed to room temperature. The mixture was poured into 100 ml of hexane and extracted with water several times. The hexane solution was evaporated and after 10 h under high vacuum, 7.22 g of yellow, mushy crystals were obtained. The product mixture was determined (by GLC) to consist primarily of a single product and fluorene. The material was loaded on a silica gel column and eluted with Skelly B. The elution was followed by GLC; fluorene came off first and the product closely behind it. Evaporation of all the eluent containing substantial amounts of product afforded 4.81 g (78% yield) of a white crystalline material (m.p. 89—91°C) which contained small amounts (<5%) of fluorene. Recrystallization from CH_3CN afforded a total (2 crops) of 4.0 g (65% yield) of pure di-t-butylfluorenylsilane: m.p. 93—94°C. ^1H NMR (CCl_4) δ 7.61 (m, 4 H), 7.19 (m, 4 H), 4.01 (s, 1 H), 3.92 (s, 1 H), 0.87 (broad s, 18 H) ppm. IR (CCl_4): 3060m, 3038w, 3020w, 2970s, 2930s, 2883s, 2858s, 2100s, 1467s, 1441s, 1386m, 1361m, 1330w, 1303w, 1231w, 1178m, 1100w, 1072s, 1029w, 1010m, 932m, 869s, 848s. Mass spectrum: *m/e* (rel. intensity) 308(8), 251(6), 210(6), 196(5), 194(5), 181(3), 165(14), 101(10), 75(100); $C_{21}H_{28}Si$ calculated *m/e* 308.1960; found *m/e* 308.1914.

Preparation of di-t-butylfluorosilane (V)

A sample of the title compound was prepared from trityl fluoroborate and di-t-butylsilane in the same fashion as the preparation of III. All physical and spectral properties of the material were identical to those reported by Weidenbruch and Peter [14].

Reaction of di-t-butylfluorsilane (V) with fluorenyllithium

Fluorenyllithium (1.0 mmol) was prepared as before from fluorene (0.166 g, 1.0 mmol) and n-butyllithium (0.63 ml of 1.6 *M* hexane solution, 1.0 mmol) in 3 ml THF. After stirring 30 min at room temperature, di-t-butylfluorosilane (0.2 g, 1.2 mmol) was added, causing a darkening of the characteristic red-orange color of the fluorenyl anion. No further color change was noted after 1 h at room temperature so the solution was heated at 65°C for an additional 24 h. The color of the solution appeared darker so the mixture was quenched by adding pentane and extracting first with saturated NH_4Cl solution and then with water. The pentane solution was evaporated and NMR and GLC analysis indicated that the residue contained fluorene and di-t-butylfluorenylsilane in the approximate ratio of 3/1, in addition to minor amounts of unidentified materials. Thus indicating that only about 25% conversion occurred.

Reaction of di-t-butylsilyl perchlorate (III) with t-butyllithium

A solution of t-butyllithium (27 ml of 1 *M* pentane solution, 27 mmol) in 30 ml diethyl ether was cooled to ca. —75°C by a Dry-Ice/ethanol bath. The title perchlorate (5.0 g, 20 mmol) was added dropwise very slowly via syringe and an immediate reaction was observed as a white precipitate formed. After the addition was complete the Pyrex syringe exploded but the reaction flask was left intact. The colorless reaction mixture was warmed to room temperature and poured over ice. After extraction with aqueous NH_4Cl and finally water, evaporation of the pentane/ether layer afforded 2.96 g of mushy, white crystals which were determined to be di-t-butylsilanol: m.p. of sublimed material 64—66° C. ^{1}H NMR (CCl_4): δ 3.96 (2, 1 H), 1.56 (s, 1 H), 0.97 (s, 18 H) ppm. IR (CCl_4): 3700m, 2500w, 2985s, 2935s, 2895m, 2860s, 2092s, 1469s, 1442w, 1388w, 1363m, 1010m, 938w, 831s. Mass spectrum: $C_8H_{20}OSi$ calcd. *m/e* 160.1283; found *m/e* 160.1287.

Preparation of di-t-butylfluorenylsilyl bromide (VII)

Bromine (1.14 g, 7.1 mmol) in 4 ml CCl_4 was added to a solution of 2.0 g (6.5 mmol) di-t-butylfluorenylsilane in 20 ml CCl_4 at —30° C. After stirring ca. 15 min at this temperature the evolution of HBr ceased. The solution was stirred 15 min more then rotary evaporated to afford 3.23 g of a light brown solid residue. Sublimation of the residue under high vacuum afforded 2.41 g (95% yield) of the title compound: white crystals, m.p. 81—82° C. ^{1}H NMR (CCl_4): δ 7.78 (m, 4 H), 7.19 (m, 4 H), 4.24 (s, 1 H), 0.85 (s, 18 H) ppm. IR (CCl_4): 3062m, 3035w, 2960s, 2895s, 2861s, 1472s, 1444s, 1390m, 1365m, 1170w, 1072s, 1028w, 1008w, 935m, 871m. Mass spectrum: *m/e* (rel. intensity) 388(11), 386(11), 223(15), 221(15), 181(52), 179(52), 165(96), 139(81), 137(81), 58(100); $C_{21}H_{27}SiBr$ calcd. *m/e* 386.1065; found *m/e* 386.1028.

Reaction of di-t-butylfluorenylsilyl bromide with t-butyllithium

Silyl bromide VII (0.1 g, 0.26 mmol) was placed in an NMR tube equipped with a rubber septum and dissolved with 0.4 ml pentane. To this solution was added 0.30 mmol (150 μl of 2 *M* solution in pentane) of t-butyllithium. The solution turned a light red-orange color and the formation of tan precipitate was noted. The precipitation continued over a period of 2 days and it was noted that beautifully formed, red crystals had also appeared. The supernatant liquid was withdrawn via syringe and the solids were washed once with pentane. After withdrawal of the pentane wash, 0.5 ml DME was added and the solids dissolved to produce a red solution. The solution was divided in half and one portion was quenched with benzaldehyde (20 mg, 0.22 mmol). After 30 min at room temperature hexane (0.5 ml) and water (0.5 ml) were added to the product mixture. After vigorous shaking the hexane layer was removed and evaporated and the residue chromatographed on a silica-gel column. The column was eluted with CCl_4 first, followed by a 10% ether/CCl_4 solution. Evaporation of the CCl_4 eluent furnished a white solid which was found to be 9-benzylidenefluorene (VIII): ^{1}H NMR (CCl_4): δ 7.75—6.85 (m) ppm. m.p. 74—76° C (lit. [15] 76° C). UV (EtOH): λ_{max} 225, 249, 257, 325 nm (lit. [16] λ_{max} 227, 248, 256, 325 nm). $C_{20}H_{14}$ calcd. *m/e* 254.10956, found *m/e* 254.1104.

Evaporation of the 10% ether/CCl_4 eluent yielded a white solid whose NMR and IR spectra were identical to those obtained for di-t-butylsilanol (vide supra).

The other portion of the red DME solution was quenched with water (0.5

ml) and extracted with hexane. Evaporation of the hexane afforded a tan solid whose GC trace, and IR and NMR spectra were superimposable with authentic di-t-butylfluorenylsilane (IV).

The red crystals were thus presumed to be the silylfluorenyllithium salt X. The NMR spectrum (Si—H singlet at δ 4.55 ppm) of these red crystals could be duplicated by treatment of di-t-butylfluorenylsilane with 1.1 equivalents of either n-butyl- or t-butyl-lithium. In fact, the red crystals themselves could be obtained in pentane or benzene by treatment of di-t-butylfluorenylsilane with 1.1 equivalents of t-butyllithium over a period of 1 or 2 days.

Reaction of di-t-butylfluorenylsilyl bromide (VII) with t-butyl- or n-butyllithium in THF

A sample of silyl bromide (53 mg, 0.14 mmol) was placed in an NMR tube along with 0.5 ml THF and the solution cooled to —75° C. n-Butyllithium (0.115 ml 1.6 *M* in hexane, 0.18 mmol) was injected and an immediate reaction took place and with mixing the solution turned a bright yellow-green color which appeared to have a fluorescent character. Similar treatment with t-butyllithium (0.09 ml 2 *M* in pentane, 0.18 mmol) afforded a dark green solution with an essentially identical NMR: ^{1}H NMR (THF) δ 8.07 (broad hump-seemed to vary somewhat in relative intensity from one run to the next), 7.84 ((d, J 7 Hz, these protons appeared to be weakly coupled (J 1 Hz) to another proton)), 6.83 ((t, J 7 Hz, also weakly coupled to another proton (J 1 Hz)), 6.50 ppm ((t, J 7 Hz, also weakly coupled to another proton (J 1 Hz)), the integration of these four absorptions is approximately equal, there is also a superious peak at δ 5.35 ppm present in all reactions but varying greatly in intensity, and in the t-butyllithium reaction there is a heptet (J 1 Hz) which was ascribed to isobutene (the aliphatic region was obscured by THF). Quenching of these solutions from either n-butyl- or t-butyl-lithium with water furnishes a single product whose GLC, NMR and IR spectra were identical to starting silyl bromide.

Acknowledgement

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References

1 L.E. Gusel'nikov, N.S. Nametkin and V.M. Vodovin, Accounts Chem. Res., 8 (1975) 18.
2 O.L. Chapman et al., J. Amer. Chem. Soc., 98 (1976) 7844; M.R. Chedekel, M. Skoglund, R.L. Kreeger and H. Shechter, ibid., 98 (1976) 7846; A.K. Mal'tsev, V.N. Khabashesku and O.M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 493.
3 A.G. Brooke and J.W. Harris, J. Amer. Chem. Soc., 101 (1979) 83.
4 M.D. Curtis, J. Organometal. Chem., 60 (1973) 63; R.D. Bush, C.M. Golino and L.H. Sommer, J. Amer. Chem. Soc., 96 (1974) 7105.
5 A.D. Petrov, B.F. Mironov, V.A. Ponomarenko and E.A. Chernyshev, Synthesis of Organosilicon Monomers, Consultants Bureau, New York, N.Y., (1964) 272.
6 T.J. Barton, A.K. Hovland and C.R. Tully, J. Amer. Chem. Soc., 98 (1976) 5695.
7 T.J. Barton and C.R. Tully, J. Org. Chem., 43 (1978) 3649.
8 D.J. Peterson, J. Org. Chem., 33 (1968) 780.
9 M.P. Doyle and C.T. West, J. Amer. Chem. Soc., 97 (1975) 3777.

10 P.R. Jones and T.F.O. Lim, J. Amer. Chem. Soc., 99 (1977) 2013.
11 V.N. Wiberg and G. Preiner, Angew. Chem., 89 (1977) 343.
12 E.G. Janzen and J.L. Gerlock, J. Organometal. Chem., 8 (1967) 354.
13 M.P. Doyle and C.T. West, J. Amer. Chem. Soc., 97 (1975) 3777.
14 M. Weidenbruch and W. Peter, Angew. Chem. Internat. Edit., 14 (1975) 642.
15 J. Thiele, Chem. Ber., 33 (1900) 851.
16 A.W. Johnson, J. Org. Chem., 24 (1959) 282.