Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

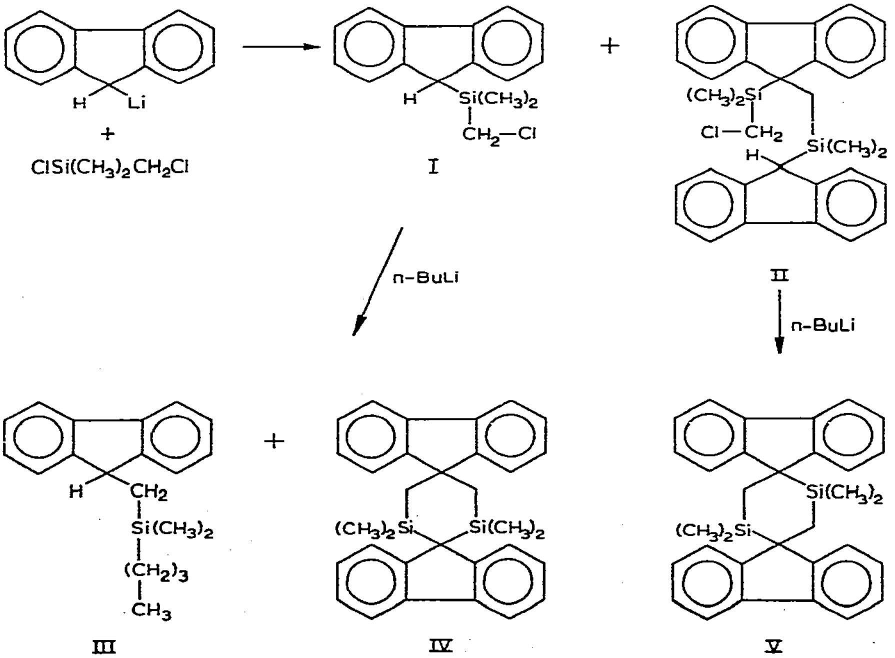
SHORT COMMUNICATION

The reaction of 9-[(chloromethyl)dimethylsilyl]fluorene with n-butyllithium

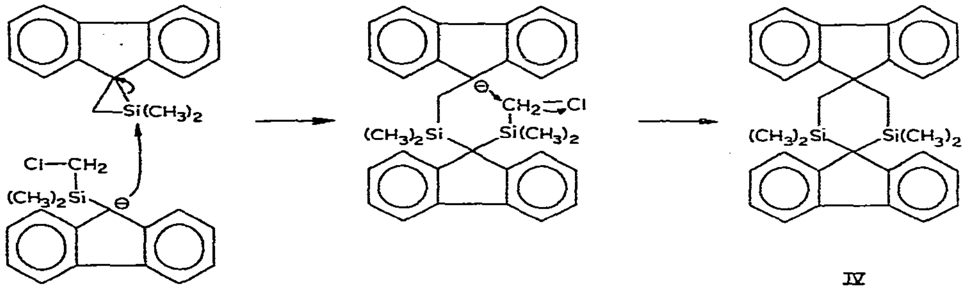
Greenhow and McNeil[1] have shown that 9-(2-chloroethyl)fluorene and related compounds on treatment with strong base react to give excellent yields of spirocyclopropylfluorenes. It seemed of interest to investigate the behaviour of an analogous silicon containing compound.

9-[(Chloromethyl)dimethyl]silylfluorene, (I), was prepared by the addition of 9-fluorenyllithium to (chloromethyl)dimethylchlorosilane. A second product obtained in low yield was assigned structure (II).

Treatment of (I) at room temperature with n-butyllithium gave (III) as the major product (70%) and a small amount of (IV) (17%). The structure of (III) was confirmed by an independent synthesis from 9-fluorenyllithium and n-butyl(chloromethyl)dimethylsilane, (VI). The structure of (IV) was assigned on the basis that it differed from the other possible isomer, (V), prepared by the treatment of (II) with n-butyllithium.

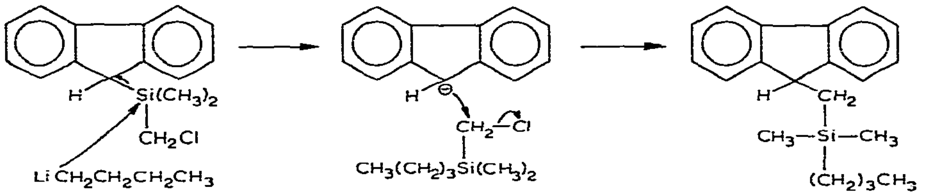


Products (III) and (IV) could have arisen by a reaction sequence involving the formation of a silacyclopropane followed by its subsequent cleavage. Such a mechanism would be similar to that proposed by Connolly and Urry[2] to explain the products observed during the Wurtz reaction of (chloromethyl)trimethylsilane. However, when the reaction was repeated at −80°, followed by carbonation, the major product isolated was 9-fluorenecarboxylic acid. Since it had already been shown that 9-fluorenyllithium reacts with (VI) at room temperature to give (III), it appears



IV

that the major pathway involves an initial displacement of fluorene by n-butyllithium followed by recoupling.



VI III

Therefore it seems that the ease of cleavage of the silicon fluorene bond[3] prevents either the preparation or the isolation of a silacyclopropane by this route.

Experimental

General. All reactions were carried out under an atmosphere of prepurified nitrogen. Melting points are uncorrected. Elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tennessee. Mass spectra and NMR data were determined on Metropolitan-Vickers MS-9 and Varian Associates A-60 spectrometers, respectively.

Reaction of 9-fluorenyllithium with (chloromethyl)dimethylchlorosilane. A solution of n-butyllithium in hexane (70 ml, 0.1 mole) was slowly added to 16.6 g (0.1 mole) of fluorene in 100 ml of THF. The resultant orange brown solution was added over 3 h to 14.3 g (0.1 mole) of rapidly stirred (chloromethyl)dimethylchlorosilane in 100 ml of THF cooled in an ice-bath. Following stirring for 4 h at room temperature, the reaction mixture was added to dilute hydrochloric acid and ethyl ether. The ether layer was washed with water, dried over sodium sulfate and concentrated under reduced pressure. The resultant pasty yellow solid was recrystallized a number of times from ethanol to obtain a total of 18.4 g (68%) of (I), m.p. 63–65°. (Found: C, 70.5; H, 6.15; parent mass, 272. $C_{16}H_{17}ClSi$ calcd.: C, 70.4; H, 6.28%; parent mass, 272.)

The NMR spectrum (CCl_4) consisted of singlets at τ 10.21, 7.42 and 6.18 ppm and a multiplet at 2.2–2.9 ppm with relative areas of 6:2:1:8 respectively.

In addition 0.8 g (8%) of a second product, (II), m.p. 145–148°, was isolated by recrystallization from methanol/chloroform mixtures. (Found: C, 75.3; H, 6.68; parent mass, 508. $C_{32}H_{33}ClSi_2$ calcd.: C, 75.5; H, 6.53%; parent mass, 508.)

The NMR spectrum of (II) consisted of singlets at τ 10.63, 10.30, 9.11, 7.94, 6.40 and a multiplet at 2.0–3.3 ppm with relative areas of 6 : 6 : 2 : 2 : 1 : 16 respectively.

Reaction of n-butyllithium with (I). (*a*) To a solution of 0.38 g (0.0014 mole) of (I) in 200 ml of ethyl ether 2 ml (0.0028 mole) of a solution of n-butyllithium in hexane were slowly added. The resultant red reaction mixture was stirred for 1 h at room temperature and then worked up as above with aqueous acid. The oil obtained from evaporation of the ether layer was chromatographed on alumina. Elution with heptane gave 0.29 g (70%) of (III), m.p. 26–28°, following recrystallization from 95% ethanol. (Found: C, 81.7; H, 9.02; parent mass, 294. $C_{20}H_{26}Si$ calcd.: C, 81.6; H, 8.90%; parent mass, 294.)

The NMR spectrum of (III) consisted of a singlet at τ 10.52, a doublet at 8.55 ($J = 5$ cps), a triplet at 5.88 ($J = 5$ cps) and multiplets at 2.25–2.9, 8.65–9.4 and 9.8–10.2 ppm with relative areas of 6 : 2 : 1 : 8 : 7 : 2, respectively.

The second material eluted was 0.056 g (17%) of (IV), m.p. 228–230°, following recrystallization from ethanol. (Found: C, 81.0; H, 7.10; parent mass, 472. $C_{32}H_{32}Si_2$ calcd.: C, 81.3; H, 6.82%; parent mass, 472.)

The NMR spectrum of (IV) consisted of singlets at τ 10.08 and 8.38 and a multiplet at 2.0–2.8 ppm with relative areas of 3 : 1 : 4, respectively.

When a run was conducted at room temperature using only one equivalent of n-butyllithium, the same products were formed, but in lower yields and starting material, (I), was recovered.

(*b*). To a solution of 2.7 g (0.01 mole) of (I) in 200 ml of THF at −80°, 8 ml (0.011 mole) of n-butyllithium in hexane were slowly added. The red solution was stirred at −80° for 2.5 h and then pieces of dry ice were added. The brown solution was worked up as above. Recrystallization of the resultant yellowish solid from ethanol and carbon tetrachloride gave 1.55 g (74%) of 9-fluorenecarboxylic acid, m.p. 230–232°. In addition, 0.13 g (8%) of fluorene, m.p. 114–116° was distilled from the intensely yellow mother liquor.

Reaction of (II) with n-butyllithium. To a solution of 0.05 g (0.0001 mole) of (II) in 25 ml of THF, 2 ml (0.0028 mole) of n-butyllithium were slowly added. The resultant red solution was then stirred for 1 h. Following aqueous acid work-up as described above, the product was recrystallized from ethanol to obtain 0.026 g (55%) of (V), m.p. 322° (sublimes). (Found: C, 81.0; H, 7.00; parent mass, 472. $C_{32}H_{32}Si_2$ calcd.: C, 81.3; H, 6.82%; parent mass, 472.)

The NMR spectrum of (V) consisted of singlets at τ 10.20 and 8.25 and a multiplet at 2.2–2.8 ppm with relative areas of 3 : 1 : 4 respectively.

n-Butyl(chloromethyl)dimethylsilane. To a solution of 23.0 g (0.016 mole) of (chloromethyl)dimethylchlorosilane in 80 ml of THF cooled to 0°, 100 ml (0.016 mole) of n-butyllithium in hexane were slowly added. A white precipitate formed. It was removed by filtration and the filtrate was distilled to obtain 19.2 (73%) of n-butyl(chloromethyl)dimethylsilane, b.p. 68° (20 mm). (Found: C, 51.1; H, 10.43. $C_7H_{17}ClSi$ calcd.: C, 51.0; H, 10.40%.)

The NMR spectrum of n-butyl(chloromethyl)dimethylsilane consisted of singlets at τ 10.01 and 7.40 and a multiplet at 8.5–9.7 ppm with relative areas of 6 : 2 : 9 respectively.

Reaction of 9-fluorenyllithium with n-butyl(chloromethyl)dimethylsilane. To a solution of 1.7 g (0.01 mole) of fluorene in 20 ml of ethyl ether 7 ml (0.01 mole) of a solution of n-butyllithium in hexane were slowly added. The resultant red solution was stirred for 1 h and then added to a solution of 1.6 g (0.01 mole) of n-butyl(chloromethyl)dimethylsilane in 10 ml of ethyl ether. The mixture was stirred for 1 h and then worked-up with aqueous acid as described above. Vacuum sublimation of the resultant pasty yellow solid gave 0.53 g (31%) of fluorene, m.p. 112–114°. Recrystallization of the residue from ethanol gave 1.7 g (58%) of (III), m.p. 26–28°, identical in all respects to the material prepared by the treatment of (I) with n-butyllithium.

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Received November 30th, 1966