*Journal of Organometallic Chemistry*
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

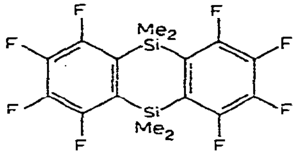
# POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL COMPOUNDS

# XI*. SOME ORGANOSILICON DERIVATIVES OF 1,2,3,4-TETRAFLUOROBENZENE

IONEL HAIDUC** AND HENRY GILMAN
*Iowa State University, Department of Chemistry, Ames, Iowa 50010 (U.S.A.)*

(Received July 4th 1967)

The metalation of 1,2,3,4-tetrafluorobenzene with n-butyllithium in tetrahydrofuran (THF) has been recently reported by Tamborski *et al.*[3] to give mono- and dilithio-tetrafluorobenzene derivatives. Within our program of investigation of polyhaloaromatic organosilicon compounds, we attempted to use this reaction for the synthesis of 1,2,3,4,5,6,7,8-octafluoro-9,9,10,10-tetramethyldisilanthrene (I):



I

The product of lithiation of 1,2,3,4-tetrafluorobenzene in tetrahydrofuran at low temperature, was treated with dimethyldichlorosilane (molar ratio 1:1). By subsequent work-up (see *Experimental Part*) only a very small amount of the desired product was isolated and the vapor phase chromatography showed that the reaction product was rather complex and contained four major components. By vacuum distillation on a spinning band column, four compounds were isolated and identified by $^1H$ nuclear magnetic resonance, mass spectroscopy and elemental analysis. Additional evidence was obtained in some cases by preparing authentic samples by alternative routes.

The compounds isolated in this work are the following: (*a*) 1-(butyldimethylsilyl)-2,3,4,5-tetrafluorobenzene (II), b.p. 55–56°/0.6 mm, $n_D^{20}$ 1.4500, as the major reaction product; (*b*) bis(2,3,4,5-tetrafluorophenyl)dimethylsilane (III), b.p. 53°/0.2 mm, $n_D^{20}$ 1.4770; (*c*) (butyldimethylsilyl)butyltrifluorobenzene, b.p. 74°/0.2 mm, $n_D^{20}$ 1.4695, which is apparently a mixture of isomers, *e.g.*, (IVa) or (IVb); and (*d*) 1,2,3,4,5,6,7,8-octafluoro-9,9,10,10-tetramethyldisilanthrene (I), m.p. 228–230°.

---

[*] For Part X, see ref. 1; for Part IX, see ref. 2.

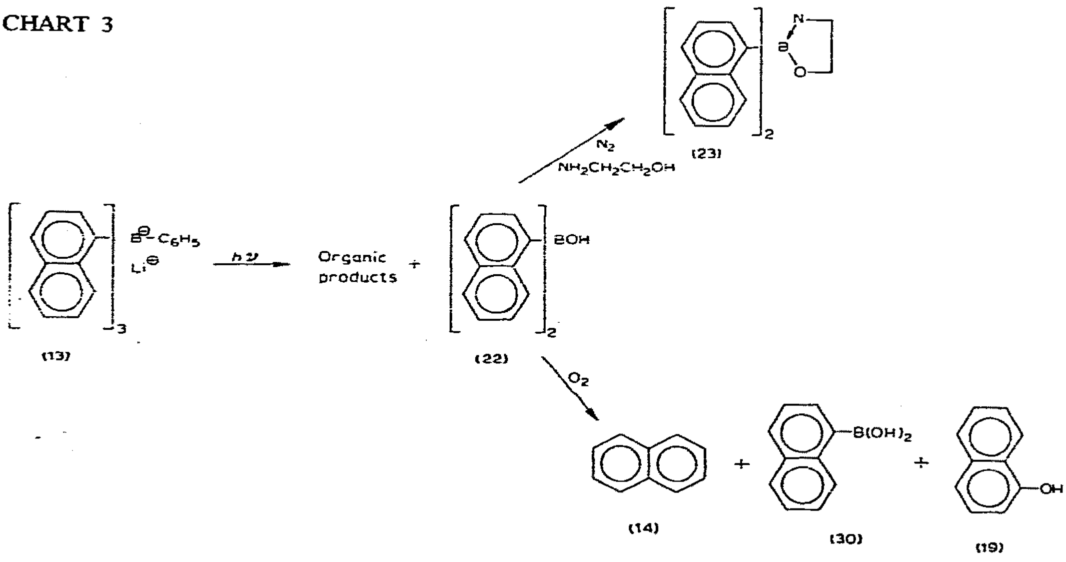
[**] Post-doctoral visiting scholar, 1966–1967. Present address: Babes-Bolyai University, Chemistry Department, Cluj (Romania).

which would result when four 1-naphthyl groups are attached to a central boron atom. As a result of this difficulty, we have instead irradiated lithium phenyltri-1-naphthylborate **(13)**[4].

The UV spectra of the isolated gas chromatograph zones were compared with those of authentic samples of all products, with the exception of **(15a)**–**(15c)** and **(17)**. The structures of **(15a)**–**(15c)** are assigned to be 1-cyclohexadienylnaphthalenes on the basis of their mass spectra (which show heaviest molecular ions at m/e 208 for $C_{16}H_{12}$) and their UV spectra which are essentially the same as that of naphthalene. The mass spectrum of compound **(17)** likewise, was found to have a molecular ion at m/e 256 corresponding to that of a dihydrobinaphthyl. The UV absorption spectrum of **(17)** was the same as that of naphthalene in the region of 270–340 m$\mu$ and did in no way resemble that of 1-phenylnaphthyl **(16)** or 1,1'-binaphthyl **(18)**. Thus, the two additional hydrogens are located in one of the rings joining the two naphthalene nuclei. It is most significant that neither biphenyl **(2)** nor the phenylcyclohexadienes **(3–5)** were found. This result is in full agreement with our earlier results which showed that the reactions occurring on the photolysis of tetraarylborates are intramolecular.

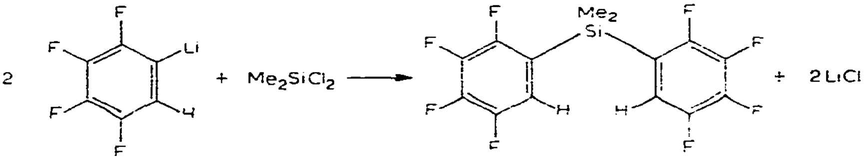
In our preliminary irradiation experiments of **(13)** under a nitrogen atmosphere, amounts of naphthalene **(14)** as great as 12% were isolated from the reaction mixtures. Later we found that **(14)** was not produced by a photochemical reaction but during the product-isolation steps in the presence of air. During the photochemical conversion of **(1)** in the absence of oxygen to yield **(2)**–**(5)**, diphenylborinic acid **(21)** is simultaneously produced[1]. In the case of **(13)**, the photolysis results in the formation of a di-1-naphthylborinic acid **(22)**. If oxygen is not carefully excluded during the isolation of the products from the photolysis of **(13)**, naphthalene **(14)** results. Formation of naphthalene **(14)** can be avoided if ethanolamine is added to the photolysis mixture before the work-up steps are begun. Formation of the oxygen-stable ethanolamine complex **(23)** of di-1-naphthylborinic acid **(22)** results.

CHART 3



except the region containing the peaks due to aromatic protons, where a multiplet consisting of nine lines, centered at $\tau$ 2.98 was observed. Peaks due to alkyl (n-butyl) protons were centered at $\tau$ 8.60 and $\tau$ 9.03 (triplet). The mass spectrum of (V) confirmed the molecular weight (calculated: 264; found 264).

The $^1$H NMR spectrum of compound (III) shows only the presence of aromatic protons (multiplet centered at $\tau$ 2.96) and methyl groups attached to silicon ($\tau$ 9.22) in the ratio $H_{arom}/H_{methyl} = 1:3$ (or $2:6$), confirming the presence of two aromatic protons and two Si–CH$_3$ groups in the molecule. A mass spectrum of (III) indicates a molecular weight of 356 [calculated for (III): 356]. An authentic sample was prepared in 37.0% yield by treating 1-lithio-2,3,4,5-tetrafluorobenzene[3] in diethyl ether with dimethyldichlorosilane (2:1 molar ratio) and the $^1$H NMR spectra were identical.



III

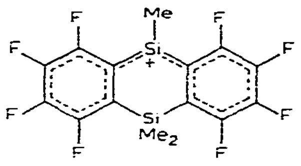
The simultaneous formation of compounds (II) and (III) in the reaction directed to the preparation of compound (I) can be understood if it be assumed that by adding two equivalents of n-butyllithium to one mole of 1,2,3,4-tetrafluorobenzene no complete substitution of the two aromatic hydrogens by lithium is achieved, and an excess of unconsumed n-butyllithium is always present in the reaction mixture. When dimethyldichlorosilane is added, a concurrent reaction of $Li_2C_6F_4$, $LiC_6F_4H$ and $LiC_4H_9$ with $Me_2SiCl_2$ takes place, resulting in the formation of (I), (II), and (III). The excess of butyllithium may also couple with the fluoroaromatic nucleus, as found for several organosilicon fluoroaromatic compounds*, resulting in elimination of LiF and formation of a n-butylsubstituted fluoroaromatic compound. This would explain the formation of (IV). A similar observation was reported in ref. 3, but no individual products were isolated. In this work compound (IV) was isolated as a constant boiling fraction with b.p. 74°/0.2 mm, and its $^1$H NMR spectrum indicates the presence of one aromatic hydrogen (sextet centered at $\tau$ 3.22), two methyl groups attached to silicon ($\tau$ 9.63) and two n-butyl groups (multiplets centered at $\tau$ 8.60 and $\tau$ 9.03). The proton ratio $H_{arom}/H_{methyl}/H_{butyl} = 1:6:18$ corresponds to a molecule with structure (IVa) or (IVb)(other isomers are also possible) and the mass spectrum indicates a molecular weight of 302 (calculated 302). The assumption that the compound (IV) isolated is a mixture of isomers is based on the fact that the vapor phase chromatogram of this compound has a marked shoulder, in spite of the constant boiling point, and NMR and mass spectral data which contain no indication about the possible presence of a contaminating foreign substance.

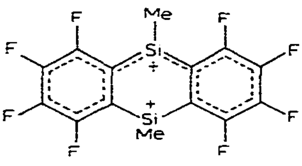
The desired compound (I) was deposited from the distillation residue after the separation of (II)–(IV), as colorless, needle-like crystals, in very low yield. After recrystallization from petroleum ether (b.p. 60–70°) its melting point was 228–230°. The mass spectrum of (I) shows a peak corresponding to the molecular mass 412

---

* See ref. 2; for other types of fluoroaromatic compounds see ref. 4.

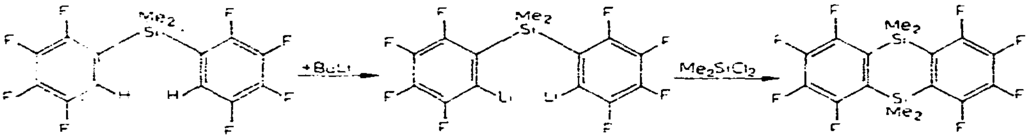
[molecular weight of (I), calculated 412]. The mass spectrum also shows the presence of molecular ions with $m/e = 397$ and 191, which correspond to molecular ions (Ia) and (Ib), respectively, formed by loss of one or two methyl groups. Probably such ions are stabilized through a delocalization of $\pi$-electrons, involving the silicon atoms:


Ia
$m/e = 397\ (e = 1)$


Ib
$m/e = 191\ (e = 2)$

Attempts were made to improve the yield of (I) by using the n-BuLi/tetramethylethylenediamine complex as metalating agent. This complex is known[5] to be more reactive than the uncomplexed butyllithium. However, only traces of (I) were obtained and extensive coupling of butyllithium with the fluoroaromatic group occurred with this reagent.

Compound (I) was also prepared by metalating compound (III), followed by treatment with dimethyldichlorosilane. The yield of (I) was however low (5.7 %).



EXPERIMENTAL

All the syntheses involving the use of organolithium reagents were performed in an atmosphere of dried, oxygen-free nitrogen. The glassware was dried in an oven at 120°, assembled while hot and flushed with a stream of dry nitrogen before introducing the reagents. The products obtained in this work are air-stable and can be purified without special precautions concerning the presence of oxygen or atmospheric moisture. Commercial reagents were used, except n-butyldimethylchlorosilane, which was prepared as described below. Mass spectra were recorded on an Atlas MAT-$CH_4$ type mass spectrograph, and $^1H$ NMR spectra on a Varian 60 NMR spectrograph. For distillations a Nester–Faust spinning band column was used. Vapor phase chromatograms were obtained on a F and M 500 apparatus.

### *The reaction of* 1,2,3,4-*tetrafluorobenzene with n-butyllithium and dimethyldichlorosilane*

A solution of 15.0 g (0.1 mole) of 1,2,3,4-tetrafluorobenzene in 200 ml anhydrous THF (dried over sodium and distilled over sodium benzophenone ketyl before use) was treated with 128 ml solution of n-butyllithium in n-hexane (15 %), containing 0.2 mole of active compound, at −70°. The addition took 1 hour and the temperature was not allowed to rise over −65°. After the addition was complete the mixture was stirred at low temperature for an additional 45 min and then 12.9 g (0.1 mole) of dimethyldichlorosilane, dissolved in 50 ml THF, was added dropwise during 30 min. The mixture was allowed to reach gradually the room temperature, the solvent was removed in a rotary evaporator and the soluble components were extracted with petroleum ether (b.p. 60–70°). After the filtration of lithium chloride the solvent was evaporated again and the oil obtained was subjected to vapor phase chromatography. The presence of four major components was thus established. The synthesis was repeated with the same quantities, the product showed the same VPC and the mixtures were combined and distilled on a spinning band column. The following fractions were collected:

(1) b.p. 24–55°/0.6 mm, 0.7 g
(2) b.p. 55–56°/0.6 mm, 8.8 g [pure compound (II), $n_D^{20}$ 1.4500]
(3) b.p. 56–90°/0.6 mm, 1.2 g
(4) b.p. 90–96°/0.6 mm, 16.0 g
(5) b.p. 97°/0.6 mm, 2.3 g [pure compound (IV), $n_D^{20}$ 1.4696]

From the distillation residue a crystalline substance was isolated. After recrystallization from petroleum ether (b.p. 60–70°), 0.2 g crystals of (I), m.p. 220–230°, were obtained.

The purity of the liquid fractions was checked by VPC and the fractions (2) and (5) were found to be individual compounds. Fraction (4) was redistilled and the following new fractions were collected:

(6) b.p. 31–53°/0.2 mm, 0.9 g
(7) b.p. 53°/0.2 mm, 2.3 g [pure compound (III), $n_D^{20}$ 1.4770]
(8) b.p. 54–73°/0.2 mm, 9.3 g [mixture of (III) + (IV)]
(9) b.p. 74°/0.2 mm, 2.6 g [pure compound (IV), $n_D^{20}$ 1.4695]

### *Preparation of n-butyldimethylchlorosilane*

This compound was prepared by adding a solution of n-butyllithium in n-hexane (320 ml containing 32.02 g n-BuLi or 0.5 mole) to 300 ml dimethyldichlorosilane (excess) at 0°. The solvent (n-hexane) and the unreacted dimethyldichlorosilane were distilled off and 58.3 g of n-butyldimethylchlorosilane, were collected (yield 77.8%), b.p. 138–139° (lit.[6] 138°, yield 47.5%).

### *Preparation of* 1-(*butyldimethylsilyl*)-2,3,4,5-*tetrafluorobenzene*, (*II*)

A solution of 15.0 g (0.1 mole) of 1,2,3,4-tetrafluorobenzene in 200 ml anhydrous ether was treated with 64 ml solution of n-butyllithium in n-hexane (15%), containing 0.1 mole n-BuLi, at −65° and was stirred for 1 h until Color Test II[7] was negative. Then, 15.0 g (0.1 mole) of n-butyldimethylchlorosilane dissolved in 50 ml diethyl ether was added dropwise and after 1.5 h of stirring the mixture was allowed to reach room temperature. The reaction mixture was concentrated and then was distilled on a spinning band column. A fraction of 12.4 g (yield 56.8%), boiling at 46°/0.2 mm, $n_D^{20}$ 1.4502, was the desired 1-(butyldimethylsilyl)-2,3,4,5-tetrafluorobenzene. The purity of the product was established by VPC and the $^1$H NMR spectrum was identical with that of the compound (II) isolated from the first reaction described. (Found: Si, 10.3; mol. wt. mass sp., 264. $C_{12}H_{16}F_4Si$ calcd.: Si 10.6%; mol. wt., 264.3.)

### *Preparation of bis*(2,3,4,5-*tetrafluorophenyl*)*dimethylsilane*, (*III*)

A solution of 1-lithium-2,3,4,5-tetrafluorobenzene, prepared as for the compound (II), from 0.1 mole 1,2,3,4-tetrafluorobenzene, was treated with 6.5 g (0.05 mole) dimethyldichlorosilane dissolved in 50 ml diethyl ether, at −65°, added dropwise during 1 h. The precipitate of LiCl was filtered after the mixture reached room temperature, the ether was removed in a rotary evaporator and the liquid residue was distilled on a spinning band column. The fraction boiling at 93–95°/1.2 mm, $n_D^{20}$ 1.4785, was found pure by VPC and consisted of bis(2,3,4,5-tetrafluorophenyl)dimethylsilane (III). The yield was 6.6 g (37.0 %). (Found: Si, 7.53; mol. wt. mass sp., 356. $C_{14}H_8F_8Si$ calcd.: Si, 7.88 %; mol. wt., 356.3.)

*Preparation of* 1-(*butyldimethylsilyl*)-2,3,5,6-*tetrafluorobenzene*, (*V*)

A solution of 7.5 g (0.05 mole) of 1,2,4,5-tetrafluorobenzene in 200 ml diethyl ether was treated with 32 ml of a solution of n-butyllithium in n-hexane (15 %) containing 0.05 mole n-BuLi, at −65° and after 1.5 h of stirring at low temperature, 7.5 g (0.05 mole) n-butyldimethylchlorosilane in 120 ml diethyl ether was added dropwise. After the reaction mixture reached room temperature the ether was removed in a rotary evaporator and the liquid residue was distilled on a spinning band column. The fraction boiling at 83–85°/2.2 mm, $n_D^{20}$ 1.4545, was pure 1-(butyldimethylsilyl)-2,3,5,6-tetrafluorobenzene (V). The yield was 8.5 g (63.4 %). (Found: Si, 10.4; mol. wt. mass sp., 264. $C_{12}H_{16}F_4Si$ calcd.: Si, 10.6 %; mol. wt., 264.3.)

*Preparation of compound* (*I*) *via metalation of compound* (*III*)

A solution of 10.7 g (0.03 mole) of compound (III) in 150 ml THF was treated with 38.4 ml solution of n-BuLi in n-hexane (15 %) at −65° and then with 3.9 g (0.03 mole) of dimethyldichlorosilane, dissolved in 25 ml THF, added dropwise. Working up as above, yielded 0.7 g crystalline material, m.p. 229–230°, identified as (I) by mixed melting point. Yield 5.7 %. The major product was an unidentified oil (22.5 g), containing several components, according to VPC probably products of coupling of n-BuLi with the fluoroaromatic groups.

## ACKNOWLEDGEMENT

We are grateful to Mrs. Y. Vinson for recording the mass spectra and to Mr. R. Thrift for recording $^1H$ NMR spectra. One of us (I. H.) acknowledges receiving a U.S. Department of State Grant, within the scientific and cultural exchange program between U.S.A. and Romania (under the sponsorship of the Committee on International Exchange of Persons and National Academy of Sciences, Washington, D.C.) and is thankful to the Babes-Bolyai University, Cluj (Romania) for the selection as a participant in this program.

## SUMMARY

Details are provided for the lithiation of 1,2,3,4-tetrafluorobenzene with n-butyllithium, followed by treatment with dimethyldichlorosilane, to give octafluorotetramethyldisilanthrene (I), 1-(butyldimethylsilyl)-2,3,4,5-tetrafluorobenzene (II), bis(2,3,4,5-tetrafluorophenyl)dimethylsilane (III) and (butyldimethylsilyl)butyltrifluorobenzene (IVa or/and b). Alternative syntheses for compounds (II) and (III), and the preparation of 1-(butyldimethylsilyl)-2,3,5,6-tetrafluorobenzene are reported.

## REFERENCES

1 T. Brennan and H. Gilman, *J. Organometal. Chem.*, 11 (1967) 185.
2 H. Gilman and F. W. G. Fearon, *J. Organometal. Chem.*, 10 (1967) 535.
3 R. J. Harper, E. J. Soloski and C. Tamborski, *J. Org. Chem.*, 29 (1964) 2385.
4 M. R. Wiles and A. G. Massey, *Chem. Ind. (London)*, (1967) 663, and references cited herein.
5 A. W. Langer, *Trans. N.Y. Acad. Sci.*, 27 (1965) 741.
6 A. D. Petrov, V. F. Mironov and V. G. Glukhovtsev, *Zh. Obshch. Khim.*, 27 (1957) 1535; *Chem. Abstr.*, 52 (1958) 3668.
7 H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, 62 (1940) 1848.