123. Fluoro(phenylsulfinyl)methyllithium. Note on the ^{13}C-NMR Spectrum of a Fluorocarbenoid

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(12.I.84)

Summary

The title compound is synthesized with ^{13}C- and ^{6}Li-labelling on the fluorinated carbon atom. H/Li-Exchange in fluoromethyl phenyl sulfoxide (**1**→**2**) causes a $\Delta\delta(^{13}C) = +11.4$ ppm, a $\Delta J(^{13}C,^{1}H) \approx 0$ Hz, and a $\Delta J(^{19}F,^{13}C) = +80.4$ Hz. Tentative conclusions about the structure of the title compound are drawn from these changes.

In the course of our ^{13}C-NMR investigations of α-halogeno-lithium compounds, the so-called carbenoids[2], we were able to generate and measure derivatives of the halogens chlorine, bromine, and iodine [1–4][2]. Also, an extensive NMR study of α-N-[3], α-O-[4], α-S- and α-Se-substituted organolithium derivatives was undertaken by us [9] [10]. The heteroatom which so far defied all our attempts was fluorine. Thus, Br/Li exchange in geminal bromo fluoro derivatives either produced highly unstable[5] or highly insoluble[6] Li-compounds of which no NMR spectra could be obtained.

The recent report by *Reutrakul & Rukachaisirikul* [12] about the generation and synthetic applications of fluoro(phenylsulfinyl)methyllithium and their statement that this 'sulfinyl carbanion seems to be stable at 0° for at least one hour' prompted us to

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[2] See also the references cited in [5].

[3] For instance, *N*-methyl-*N*-(methoxymethyl)carbamoyllithium [6] ^{13}C-labelled at the carbonyl C-atom gave rise to a *t* ^{13}C-NMR signal ($\delta = 252$ ppm ($\Delta\delta = 90$ ppm), $^{1}J(^{13}C,^{6}Li) = 13$ Hz) at −110° (for the nomenclature of $\Delta\delta$ see [4]).

[4] The α-ROCLi derivatives gave disappointingly broad signals even at the lowest possible observation temperatures (−130°); they were generated [7] [8] by Sn/^{6}Li exchange from ^{13}C-labelled precursors. $^{6}Li^{13}CH_2O^{6}Li$: $\delta \approx 50$ ppm (*very* broad). $^{6}Li^{13}CH_2OCH_2OCH_3$: $\delta = 74$ ppm, $\Delta\delta = 19$ ppm, $^{1}J(C,H) \approx 125$ Hz, $\Delta J(C,H) = 17$ Hz, signal visible up to room temperature, THF solution (for the nomenclature of $\Delta\delta$ see [4]). $C_6H_{13}{}^{13}CH^{6}Li(OCH_2OCH_2C_6H_5)$: $\delta = 74.5$ ppm, $\Delta\delta = 6.8$ ppm, $^{1}J(C,H) = 125$ Hz, $\Delta J(C,H) = -16$ Hz. None of these α-ROCLi derivatives showed a $^{13}C,^{6}Li$-coupling.

[5] From [11-^{13}C]-11-bromo-11-fluorotricyclo[4.4.1.0]undecane, a [4.4.1]propellane, no detectable organolithium species could be generated.

[6] Unlabelled bromotrifluoroethylene was converted to trifluorovinyllithium according to the procedure of *Normant et al.* [11]. The reaction mixture contained a heavy, colorless precipitate, showed no signals in the ^{19}F-NMR spectrum, but was cleanly quenched with H_2O to give trifluoroethylene.

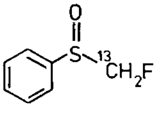
Scheme 1

$$C_6H_5SH + {}^{13}CH_3I \xrightarrow{[9]} C_6H_5{-}S{-}{}^{13}CH_3 \qquad (1)$$

$$C_6H_5{-}S{-}{}^{13}CH_3 + SO_2Cl_2 \xrightarrow{[13]} C_6H_5{-}S{-}{}^{13}CH_2{-}Cl \qquad (2)$$

$$C_6H_5{-}S{-}{}^{13}CH_2Cl + KF/[18]\text{-crown-6} \xrightarrow{[14]} C_6H_5{-}S{-}{}^{13}CH_2{-}F \qquad (3)$$

$$C_6H_5{-}S{-}{}^{13}CH_2F + NBS/H_2O/CH_3OH \xrightarrow{[14]} C_6H_5{-}SO{-}{}^{13}CH_2{-}F \qquad (4)$$



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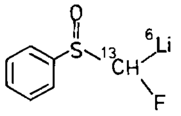

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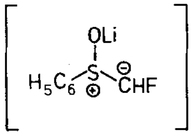

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$\delta({}^{13}C)$[a]):	100.5 ± 0.1 ppm	111.9 ± 0.1 ppm	($\Delta\delta$ = +11.5 ppm)
${}^1J({}^{13}C,{}^1H)$:	168.0 ± 1.3 Hz	169.0 ± 1.3 Hz	($\Delta J \approx 0$ Hz)
${}^1J({}^{13}C,{}^{19}F)$:	212.4 ± 1.3 Hz	292.8 ± 1.3 Hz	(ΔJ = +80.4 Hz)

[a]) The ${}^{13}C$-NMR spectra (THF) were measured with a sweep width of 5000 Hz and 1.25 Hz or 0.05 ppm/point; as a reference, the ${}^{13}C$-signal of THF at 1709.8 Hz or 67.96 ppm was used.

take another chance. Following known methods which were adapted to small scale preparation, we synthesized fluoromethyl phenyl sulfoxide (**1**), ${}^{13}C$-labelled at the fluorinated C-atom, see *Scheme 1*. The source of the label was (${}^{13}C$)iodomethane which was used to obtain thioanisol (*Eqn. 1*). Chlorination with SO_2Cl_2 (*Eqn. 2*), nucleophilic substitution with KF (*Eqn. 3*), and oxidation by treatment with *N*-bromosuccinimide in H_2O (*Eqn. 4*), produced the desired precursor **1** for metallation with (${}^6Li$)lithiumdiisopropylamide. The lithiation was achieved in a NMR tube in THF/(D_8)THF as described previously [4] [10] [15], and the subsequent measurement of the ${}^{13}C$-NMR spectrum (−100°; 0.13M **2**) furnished the parameters given in *Scheme 1* underneath the *Formulae* **1** and **2**[7]). The C-atom is deshielded upon lithiation, the C,H-coupling is hardly affected, while the C,F-coupling strongly increases. No C,^{6}Li-coupling could be detected. The ${}^{13}C$-NMR signal of the lithiated C-atom rapidly became smaller above −90° and had disappeared at −60°, indicating a much smaller stability than expected from the literature data [12].

Only speculative conclusions about the structure of **2** can be drawn from the ${}^{13}C$-NMR spectrum[8]). The small downfield shift $\Delta\delta$ is intermediate between the small upfield shifts observed upon α-lithiation of S-derivatives [10] and the large downfield shift occurring with halogeno derivatives [4]. While the direct C,H-coupling constants decrease considerable upon H/Li-exchange in hydrocarbons, and at C(α) of the S-, Se-

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[7]) The parameter for the starting material **1** were measured after quenching the NMR samples of the carbenoid **2** with moist THF at −100°.

[8]) For calculated structures of lithium fluorine carbenoids see [16] and [17].

and halogeno derivatives [3] [10], it is essentially unchanged on going from **1** to **2**. A comparison of the strong increase of the direct C,F-coupling with other halogens is not possible, the only direct coupling between heteroatoms and lithiated C-atoms so far reported is that with ^{77}Se and ^{31}P [10], which is also much larger than in the protonated precursors. However, from these increases of the coupling constants a change of hybridization, with increase of s-character of the bonds of the fluorinated C-atom seems reasonable and would lead to a structure, as shown in *Formula* **3**, in which the lithium is bound to oxygen. This would also explain the lack of the C,^{6}Li-coupling. However, our previous experience warrants caution with such conclusions from NMR data. As in other cases [10] [18], an analysis of the crystal structure may provide information which can be relevant also for the solution structure.

Experimental Part

For details of techniques, instrumentation, and purification of reagents and solvents, see [4] [10].

(^{13}C)Chloromethyl Phenyl Sulfide. A modified literature procedure [13] was used. A solution of (^{13}C)methyl phenyl sulfide (0.87 g, 7 mmol), in CH_2Cl_2 (10 ml) was heated at reflux and combined with a solution of SO_2Cl_2 (0.5 ml, 7 mmol) in CH_2Cl_2 (5 ml). After 1 h, the solution was evaporated to give *ca.* 1 g of crude product which was used directly for the following conversion. IR ($CHCl_3$): 3150, 3100, 3080, 3070, 2960, 2930, 2860, 1585, 1480, 1440, 1390. ^{1}H-NMR (CCl_4): 7.6–7.0 (*m*, 5H, arom. H); 4.85 (*d*, *J* = 165, 2H, $^*CH_2Cl$). ^{13}C-NMR ($CDCl_3$): 135.4, 130.8, 129.1, 127.9, 50.9. MS: 161 (15, $M^+ + 2$), 159 (42), 158 (12), 124 (100), 123 (10), 109 (26), 77 (18).

(^{13}C)Fluoromethyl Phenyl Sulfide (*cf.* [14]). To a solution [18]-crown-6 (0.16 g, 0.60 mmol) in CH_3CN (6 ml) was added KF (0.70 g, 12 mmol; dried for 20 h at 160°/0.01 Torr) and, after heating at reflux for 1 h, [^{13}C]chloromethyl phenyl sulfide (0.90 g, 6 mmol). The mixture was heated at reflux for 5 days and then poured into 10 ml of ice/H_2O. Three extractions with 20 ml CH_2Cl_2 each, drying the combined org. phases over $MgSO_4$, and removal of the solvents furnished 0.25 g (30%) of the fluorinated product, b.p. 28°/0.01 Torr. ^{1}H-NMR ($CDCl_3$): 7.6–7.0 (*m*, 5H, arom. H); 5.7 (*dd*, $J(^{13}C,^1H) = 171$, $J(^{19}F,^1H) = 54$). ^{13}C-NMR ($CDCl_3$): 134.9 (*s*); 130.7 (*d*); 129.2 (*d*); 127.8 (*d*); 88.5 (*dt*, $J(^{19}F,^{13}C) = 216.7$). The compound was oxidized right after distillation.

(^{13}C)Fluoromethyl Phenyl Sulfoxide (**1**) (*cf.* [14]). To a solution of (^{13}C)fluoromethyl phenyl sulfide (0.25 g, 1.7 mmol) in CH_3OH (5 ml), stirred at 0°, was added *N*-bromosucciniimide (0.35 g, 2 mmol) and H_2O (0.1 ml). After stirring for 1 h, the mixture was quenched with H_2O (20 ml). Extraction with CH_2Cl_2 (3 × 20 ml), drying over $MgSO_4$, removal of the solvents and distillation gave 0.25 g (92%) of **1**, b.p. 65°/0.01 Torr. ^{1}H-NMR ($CDCl_3$): 7.6 (*s*, arom. H); 5.1 (*dd*, $J(^{13}C,^1H) = 168$, $J(^{19}F,^1H) = 48$). ^{13}C-NMR ($CDCl_3$): 98.2 ($J(^{19}F,^{13}C) = 212$); 124.8; 129.3; 129.6; 132.1.

Preparation of the NMR. Probe of Fluoro(phenylsulfinyl)(^{13}C)methyl(^{6}Li)lithium (**2**). A solution of diisopropylamine (50 µl, 0.33 mmol) in THF (0.5 ml) and (D_8)THF (0.3 ml; both dry!) was treated in an NMR tube at −20° with (^{6}Li)BuLi (0.30 mmol; 0.18 ml of hexane solution). After 15 min at 0°, the mixture was cooled to −100°, and slowly combined with **1** (39.5 mg, 0.25 mmol), dissolved in THF (1 ml). The measurement was carried out with a *Varian-XL-100* spectrometer.

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