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Short Communication

The thiolate anion as a nucleophile
Part II*. Preparation and structures of the compounds $C_6F_2(SR^1)_2(SR^2)_2$

MICHAEL E. PEACH and ASHLEY M. SMITH
Department of Chemistry, Acadia University, Wolfville, Nova Scotia (Canada)
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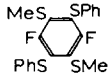
The compound $C_6F_2(SMe)_4$ has recently been assigned a structure, on the basis of the proton and fluorine NMR spectra, with the fluorine atoms *meta* to each another [1]. The work presented in this note shows that the correct structure of the compound $C_6F_2(SMe)_4$ is one with the fluorine atoms *para* to each another. The compound $C_6F_2(SPh)_4$ has been assigned a structure with the fluorine atoms *para* to each other on the basis of its oxidation and degradation with Raney nickel [2] but the fluorine NMR spectrum of this latter compound was not reported.

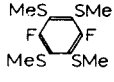
Further substitution of the compounds 1,4-$C_6F_4(SR)_2$ (R = Me, Ph) with the nucleophiles SPh^- or SMe^-, as shown below,

$$C_6F_4(SR^1)_2 + SR^{2-} \rightarrow C_6F_2(SR^1)_2(SR^2)_2 + 2F^-$$

where R^1 = Me, R^2 = Ph or R^1 = Ph, R^2 = Me, gives identical products. Assuming that no rearrangement occurs in these reactions, the structure of the product must be (I).



(I)



(II)

The NMR spectra of the compounds $C_6F_2(SR)_4$ (R = Me, Et, Ph) and $C_6F_2(SMe)_2(SPh)_2$ have been re-examined and details of the spectra are shown in Table 1. The fluorine chemical shift for $C_6F_2(SMe)_2(SPh)_2$ is intermediate in value between that for $C_6F_2(SPh)_4$ and $C_6F_2(SMe)_4$ hence it is probable that all these compounds have the same structure. The original reasoning concerning the structure was based on the relatively low chemical shift of $C_6F_2(SMe)_4$ and comparison with that of the difluorobenzenes (*o*-F_2, 139.0 Hz; *m*-F_2, 110.0 Hz; *p*-F_2, 119.5 Hz [3]). The ^{19}F NMR peak, although rather

*For Part I see ref. 1.

TABLE 1

Summary of NMR data (CCl_4 solution)

Compound	^{1}H NMR spectra		^{19}F NMR spectra [a]
	τ	J(H–F)/Hz	δ/ppm
$C_6F_2(SMe)_4$	7.509 T [b]	2.0	101.4 S (5)
$C_6F_2(SPh)_4$	2.887 S	—	91.04 S (4)
$C_6F_2(SMe)_2(SPh)_2$	7.607 T (Me)	2.8	96.91 S (5)
	2.769 S (Ph)	—	
$C_6F_2(SEt)_4$	7.033 Q (CH_2)	1.0	98.72 S (3)
	8.750 T (Me)	—	
$C_6F_4(SePh)_4$	2.613 M	—	126.81 S (4)

[a] Using CCl_3F as internal standard: approximate half-peak width (Hz) in brackets.
[b] T = triplet; S = singlet; Q = quartet; and M = multiplet.

broad in all spectra (half-peak width *ca.* 4∿5 Hz) cannot be resolved further.

In the ^{1}H NMR spectrum of $C_6F_2(SMe)_4$, which exhibits a triplet which is not temperature dependent, addition of lanthanide shift reagent does not affect the relative positions of the lines. It has been observed previously that the methyl protons in various fluoroaromatics containing a methylthio group can be split into a triplet due to coupling with *ortho*- and *meta*-fluorine atoms [4] and for this reason it may be assumed that in the symmetrical structure (II) the methyl protons are split into a triplet through averaged couplings to the *ortho*- and *meta*-fluorine atoms. The methyl protons in (I) are also split into a triplet by averaged couplings to the *ortho*- and *meta*-fluorine atoms: again, addition of a shift reagent did not affect the relative position of the lines.

The ^{1}H NMR spectrum of $C_6F_2(SEt)_4$ exhibits a quartet due to the methylene protons. In the high-resolution spectrum (100 MHz), each peak of the quartet is further resolved into a quartet, the coupling constant being equal to 1.02 Hz. This splitting can be attributed to coupling to fluorine, forming a triplet, which is further split by long-range proton coupling. No indication of further coupling occurs in the ^{1}H NMR spectrum of $C_6F_2(SMe)_4$ even at 220 MHz.

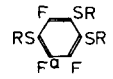
Molecular models show that there is considerably more steric hindrance in $C_6F_2(SEt)_4$ than in $C_6F_2(SMe)_4$, and rotation about the C–S–R bonds is somewhat restricted. It is noteworthy that substitution of pentafluorobenzonitrile and 4-trifluoromethyl-tetrafluorobenzonitrile with sodium pentafluorophenolate gave substitution *ortho* and *para* to the nitrile groups leaving two *meta*-fluorine atoms [5], the fluorine chemical shifts being 148.45 [3,5-C_6(CN)$F_2(OC_6F_5)_3$] and 131.85 ppm [2,6-bis(pentafluorophenoxy)-4-trifluoromethyldifluorobenzonitrile] respectively relative to $CFCl_3$ as an internal standard. Such values are relatively high in comparison with the results reported here. In these latter compounds the nitrile group is the predominant

orientating group for further substitution and not the added pentafluorophenoxy group, whereas in the current work the added SR group appears to provide the major influence in governing the position of further substitution.

In the conversion $C_6F_4(SR)_2 + 2SR^- \rightarrow C_6F_2(SR)_4 + 2F^-$, provided that no rearrangement occurs, the intermediate (III) with the orientation shown below must be formed. In any subsequent nucleophilic substitution the SR group will be *ortho/para* directing (predominantly *para*), and fluorine F^a [in structure (III)] will be the most favorable for substitution, being *ortho*, *meta* and *para* to the three different SR groups.

For this reason it may be concluded that the structures of the compounds $C_6F_2(SR)_4$ prepared by nucleophilic substitution of hexafluorobenzene are similar to that of (I) in which the fluorine atoms are *para*.

Attempts to prepare the selenium analog, *i.e.* $C_6F_2(SePh)_4$, from hexafluorobenzene and the benzeneselenolate anion led to the formation of $C_6F_4(SePh)_2$, together with considerable oxidation of the selenolate ion to the diselenide. The NMR data for this compound are also shown in Table 1.



(III)

Experimental

The general techniques have been described previously [1]. NMR spectra were recorded on a Varian HA 56/60, A60, HA100, or HR220 instrument, using CCl_4 solutions and TMS (^1H) or ($FCCl_3$)(^{19}F) as internal standards. Microanalyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, West Germany.

$C_6F_2(SPh)_4$, which was previously reported as impossible to prepare [1], was obtained by employing a lower reaction temperature, *viz.*, 50 - 60°C for 5 - 10 min, before pouring on to ice; m.p. 140 - 142°C (lit. value [2]: 142 - 144°C).

$C_6F_4(SePh)_2$, m.p. 122 - 124°C, was prepared together with copious quantities of $(PhSe)_2$ from C_6F_6 and $SePh^-$. Analysis: Found: C, 47.2; H, 2.17%. $C_{18}H_{10}F_4Se_2$ requires C, 47.0; H, 2.19%. No $C_6F_2(SePh)_4$ was obtained even when a nitrogen atmosphere was used in the glove box.

$C_6F_2(SMe)_2(SPh)_2$, m.p. 112 - 114 °C, was prepared either by the reaction $C_6F_4(SMe)_2 + SPh^-$ or from $C_6F_4(SPh)_2 + SMe^-$. In the former case, a cooled solution of SPh^- (in ethylene glycol) was added to refluxing pyridine, but in the latter case in order to obtain the desired product the reaction mixture was kept at a temperature of 10 - 15°C. Analysis: Found: C, 56.9; H, 3.83; S, 30.4; F, 8.86%. $C_{20}H_{16}S_4F_2$ requires C, 56.8; H, 3.82; S, 30.4; F, 8.99%.

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References

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Forthcoming Meetings

5th European Symposium on Fluorine Chemistry

This Symposium will take place at the Aviemore Centre, Aviemore, Inverness-shire, Scotland during the period 16-20th September, 1974.

Developments in the synthesis and physicochemical properties of fluorine compounds will be covered in three broadly based symposia dealing with

(a) organic,
(b) inorganic, and
(c) organometallic compounds.

The programme will also feature sessions on the following topics:

(d) chemistry and technology of fluoride melts,
(e) metabolism of fluorine compounds in animal and plant systems,
(f) fluorine-containing polymers.

For further information please contact: Dr. J. M. Winfield, Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland.