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PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS XV*. PERFLUOROAROMATIC DERIVATIVES OF SULPHUR, SELENIUM AND TELLURIUM

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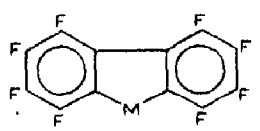
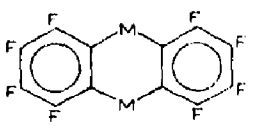
The study of polyfluoroaromatic derivatives of the chalcogens has, up to now, been rather limited. Bis(pentafluorophenyl)sulphide has been prepared by the reactions of sulphur on bis(pentafluorophenyl)mercury[2] (or C_6F_5HgCl)[2], cuprous pentafluorothiophenolate on bromopentafluorobenzene[3] and, more recently, by the reaction of pentafluorophenyllithium on sulphur dichloride[4]; by replacing pentafluorophenyllithium with 1-lithio-2-bromotetrafluorobenzene the corresponding 2-bromo compound has been synthesised, providing a route to octafluorodibenzthiophen[4]. The only selenium compound to be described is bis(pentafluorophenyl)-selenium[2] whereas no tellurium derivatives have been reported.

We have extended the range of pentafluorophenyl derivatives to all three elements by the use of either pentafluorophenyllithium on the respective halides or by the more simple method of heating the element with iodopentafluorobenzene[5] analogous to earlier work[6] on perfluoromethyl compounds of sulphur and selenium; see Charts 1 and 2. The ease of replacement of iodine as opposed to bromine in the direct syntheses was demonstrated in the preparations of bis(pentafluorophenyl)-sulphur and -selenium; when the elements were heated with bromopentafluorobenzene the yields obtained were less than 10% whereas iodopentafluorobenzene gave yields as high as 60–70%. The direct synthetic method was also employed in the preparation of the heterocycles (I) and (II) using 2,2'-diiodooctafluorobiphenyl and 1,2-diiodo-



(I)



(II)

tetrafluorobenzene respectively. The reaction of selenium with 1,2-diiodotetrafluorobenzene at 375° is interesting in that a mixture of (I, M = Se) and (II, M = Se) was obtained indicating a certain amount of ring coupling under these conditions. These heterocycles are thermally stable to above 400° and are rather stable toward cleavage reactions, for example, $SeC_{12}F_8$ resists the attack of chlorine (10 min) and of bromine (12 h) in refluxing carbon tetrachloride.

* For part XIV: see ref. 1.

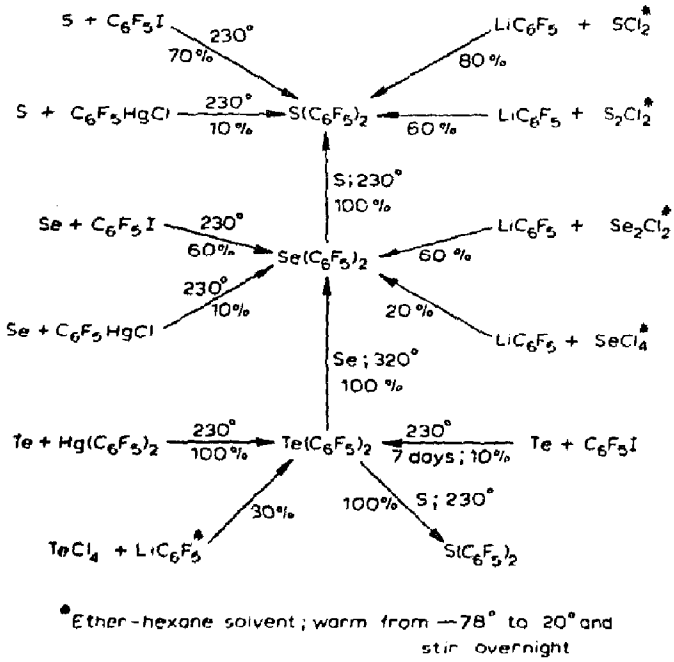


Chart 1

Bis(pentafluorophenyl)disulphide[7] and -diselenide formed during the direct syntheses have also been prepared, in combination with the $M(C_6F_5)_2$ compounds, by reacting pentafluorophenyllithium with the element "monohalide", M_2Cl_2, or in the case of the disulphide by treating sulphur dichloride with C_6F_5SLi. In the latter experiment and in the direct syntheses we have had evidence for the formation of $(C_6F_5)_2S_3$ m.p. 35–36°, but we have yet to obtain sufficient quantities for analysis. Pentafluorophenyllithium and tellurium tetrachloride give a mixture of $Te(C_6F_5)_2$,

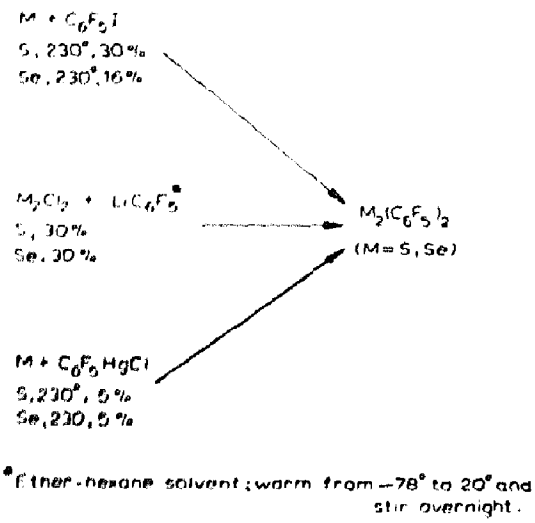


Chart 2

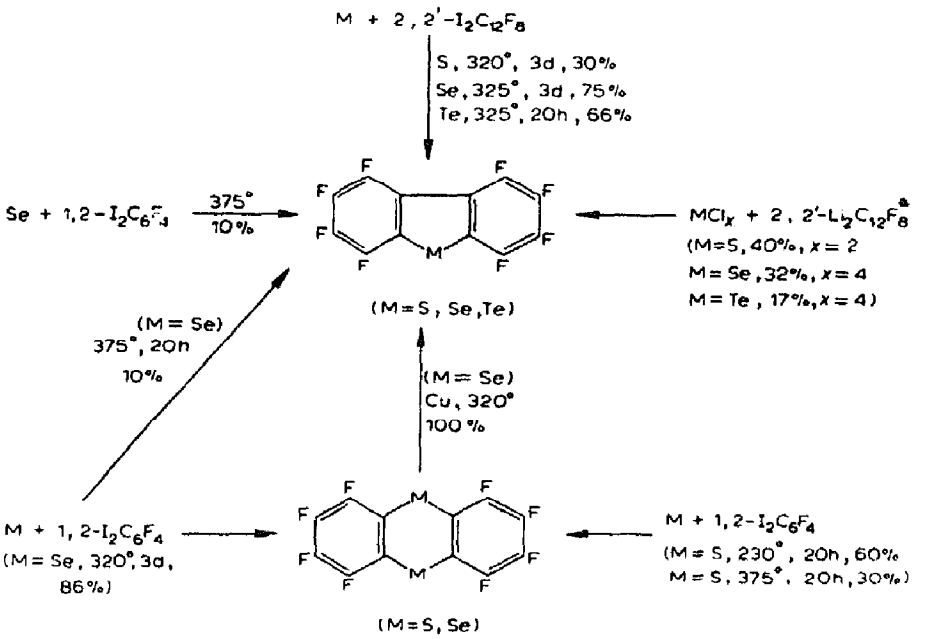


Chart 3 *Ether-hexane solvent; warm from −78° to 20° and stir overnight

TABLE 1

PERFLUOROAROMATIC DERIVATIVES OF SULPHUR, SELENIUM AND TELLURIUM: MELTING POINTS AND ANALYTICAL DATA

Compound	*M.p.* (°C)	*Analysis found (calcd.)*			
		C(%)	*H*(%)	*F*(%)	*Mol.wt.*
$S(C_6F_5)_2$	84–85°	39.3	0.00	52.1	333
		(39.3)	(0.00)	(51.9)	(366)
$Se(C_6F_5)_2$	71–72°	34.69	0.15	46.02	397, 417
		(34.8)	(0.00)	(46.01)	(413)
$Te(C_6F_5)_2$	50–51°	30.9; 31.1	0.00	41.80	451
		(31.1)	(0.00)	(41.20)	(462)
$S_2(C_6F_5)_2$	50–51°	36.4	0.17	47.90	383
		(36.1)	(0.00)	(47.70)	(398)
$Se_2(C_6F_5)_2$	46–48°	29.4	0.25	38.8	
		(29.3)	(0.00)	(38.6)	
$(SC_6F_4)_2$	102.5–104°	39.8	0.20	42.20	
		(40.0)	(0.00)	(42.20)	
$(SeC_6F_4)_2$	117–120°	32.7	0.00	32.95	429
		(31.75)	(0.00)	(33.50)	(454)
$S(C_{12}F_8)$	108.5–109.5°[a]	44.0	0.00	46.50	
		(43.9)	(0.00)	(46.30)	
$Se(C_{12}F_8)$	118.5–120.5°	38.5	0.10	40.70	356
		(38.4)	(0.00)	(40.50)	(375)
$Te(C_{12}F_8)$	116–119°	33.95	0.00	36.10	
		(34.00)	(0.00)	(35.90)	
$Te(C_6F_5)_4$	*ca.* 210°[b]	35.75	0.00	48.05	
		(36.10)	(0.00)	(47.90)	

[a] Reported[4]: 99–100°. [b] Decomposes without melting.

$Te(C_6F_5)_4$ and perfluorobiphenyl; tetrakis(pentafluorophenyl)tellurium decomposes into perfluorobiphenyl and bis(pentafluorophenyl)tellurium on heating in a sealed tube to about 200–220°.

EXPERIMENTAL

We are grateful to the Imperial Smelting Corp. Ltd. for gifts of iodopentafluorobenzene, 1,2-diiodotetrafluorobenzene and 1,2-dibromotetrafluorobenzene. The syntheses of 2,2'-dibromo- and 2,2'-diiodooctafluorobiphenyl have been described previously by us[8]. Dr. A. Bernhardt, Mülheim, Ruhr performed the analyses and the molecular weights were determined by Miss Sylvia Park of this department using a Mechrolab osmometer.

Direct syntheses were carried out by sealing the element and the respective iodopolyfluoroarene into pyrex vessels (*ca.* 20 cm long × 2.0 cm diameter) under vacuum; after heating in an oven the vessels were cut open and the contents separated by crystallisation, vacuum sublimation or vapour phase chromatography.

Reaction of 2,2'-dilithiooctafluorobiphenyl with sulphur dichloride

n-Butyllithium (9 ml of *ca.* 2.7 *M* solution) was added to 2,2'-dibromooctafluorobiphenyl (4.56 g) in 100 ml of ether at −78° and stirred for 1 h. Sulphur dichloride (0.1 mole) was added and the stirred mixture allowed to slowly reach room temperature; stirring was then continued overnight. The mixture was filtered, the solvent removed under vacuum and the yellowish crystalline solid purified by vacuum sublimation (10^{-4} mm) at 40–60° to give a white solid, m.p. 108.5–109.5°; yield 1.3 g.

All the experiments employing lithium reagents were carried out in a similar manner.

SUMMARY

The syntheses of several pentafluorophenyl derivatives of sulphur, selenium and tellurium and of four heterocycles containing sulphur and selenium are described.

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