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PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS XVI*. SYNTHESIS OF POLYFLUOROAROMATIC HETEROCYCLICS VIA 2-BROMOTETRAFLUOROPHENYL DERIVATIVES OF SULPHUR, GERMANIUM AND MERCURY

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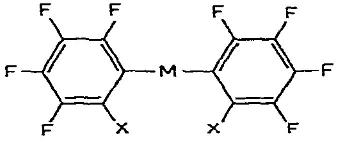
SUMMARY

1-Lithio-2-bromotetrafluorobenzene reacts with sulphur dichloride, diphenylgermanium dichloride and mercuric chloride to give bis(2-bromotetrafluorophenyl) derivatives. The reactions of these derivatives with n-butyllithium and the subsequent synthesis of several heterocyclic compounds are described.

INTRODUCTION

It has been shown[2,3] that 1,2-dibromotetrafluorobenzene resists dilithiation in ether/hexane, although the monolithio[4] derivative is formed virtually quantitatively. Chambers had shown[5] that both bromine atoms in bis(2-bromotetrafluorophenyl) sulphide[6] (Ia) will undergo exchange with lithium (from n-butyllithium) to form bis(2-lithiotetrafluorophenyl) sulphide which reacts with sulphur dichloride to give octafluorothianthrene[1,7]. The stepwise replacement of both bromine atoms of 1,2-dibromotetrafluorobenzene has been so far utilised only in reactions of the 2,2'-dihalooctafluorobiphenyls[3,7] and the preparation of (tetrafluoro-*o*-phenylene)bis(dimethylarsine)[8].

As a continuation of our studies[3,7] on polyfluoroaromatic heterocyclic derivatives of metal and non-metals, we have reacted 1-lithio-2-bromotetrafluorobenzene with sulphur dichloride, diphenylgermanium dichloride and mercuric chloride to give the bis(2-bromotetrafluorophenyl) derivatives, (Ia), (II) and (III)[2] respectively.



(Ia), M = S, X = Br   (II), M = $(C_6H_5)_2Ge$, X = Br
(Ib), M = S, X = I   (III), M = Hg, X = Br
(Ic), M = S, X = H

Bis(2-bromotetrafluorophenyl) sulphide, (Ia), can be dilithiated by n-butyllithium in ether/hexane; this dilithio compound reacts with iodine and water to give

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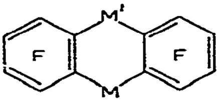
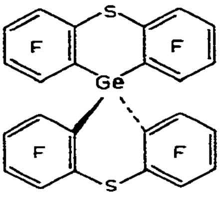
[*] For part XV see Ref. 1.

(Ib) and (Ic) respectively. With diphenylgermanium dichloride and germanium tetrachloride, the dilithio reagent of (Ia) forms the heterocyclic compounds (IV) and (V) respectively, each having a six-membered heterocyclic ring containing both a germanium and a sulphur atom. These two compounds show a marked difference in reactivity; when heated with sulphur at 230° *in vacuo*, (IV) is cleaved to give a mixture of octafluorothianthrene and a diphenylgermanium sulphide compound, whereas (V) does not react with sulphur at 360° *in vacuo*. Bis(2-lithiotetrafluorophenyl) sulphide reacts with selenium tetrachloride to give (VI) in 20% yield; the latter is obtained in 75% yield by heating bis(2-bromotetrafluorophenyl) sulphide and selenium *in vacuo* at 340°. (VI) demonstrates the relative ease of removal of selenium since on heating with copper at 350°, octafluorodibenzothiophene is formed in high yield but no octafluorodibenzoselenophene is observed. In similar experiments octafluoroselanthrene is completely converted to octafluorodibenzoselenophene at 320° whereas octafluorothianthrene undergoes only slight conversion to the five-membered ring system even at 380°. Both bis(2-bromotetrafluorophenyl) sulphide and bis(2-iodotetrafluorophenyl) sulphide react with sulphur at 230° *in vacuo* to give a quantitative yield of octafluorothianthrene.



(IV), $M = (C_6H_5)_2Ge, M' = S$
(VI), $M = Se$, $M' = S$
(VII), $M = M' = (C_6H_5)_2Ge$



(V)

(Spiro - compound)

Bis(2-bromotetrafluorophenyl)diphenylgermanium can also be dilithiated in ether/hexane and this dilithio compound reacts with diphenylgermanium dichloride to give (VII), which contains a six-membered ring containing two germanium atoms. Gilman[9] has prepared the corresponding (unfluorinated) aromatic silicon compound from the reaction of diphenylsilicon dichloride with 1,2-dilithiobenzene but the unfluorinated aromatic germanium derivative appears not to have been reported. Attempts to prepare (IV) from bis(2-lithiotetrafluorophenyl)diphenylgermanium and sulphur dichloride yielded mainly polymeric material with only a small proportion of (IV).

The mercury compound, (III), has been described by Tamborski[2] but its properties have not been studied. It does not undergo lithium/bromine exchange with n-butyllithium in the same way as (Ia) and (II); instead the carbon–mercury bond is cleaved apparently even at −78° to give dibutylmercury and 1-lithio-2-bromotetrafluorobenzene. The formation of the latter is demonstrated by the addition of water, bromine or iodine when 1-hydro-2-bromo-[4], 1,2-dibromo- or 1-iodo-2-bromotetrafluorobenzene[10] is formed. Cleavage of a mercury–carbon bond by an alkyllithium derivative is well-known for mercury dialkyls[11] and, similar to Tatlow's[12] work with methyllithium at 0°, we have found that bis(pentafluorophenyl)mercury is cleaved by butyllithium at −78° to give (after hydrolysis) pentafluorobenzene and dibutylmercury.

(III) is of use in the preparation of heterocyclic compounds, since on heating at 230° *in vacuo* with either sulphur or selenium, it undergoes replacement of both mercury and bromine to give octafluorothianthrene or octafluoroselanthrene. For the formation of the latter, replacement of bromine by selenium has occurred at a lower temperature than previously encountered for direct substitution of selenium for halogen[7]. The mercury compound (III) is cleaved easily by bromine at 115° and by iodine at 230° *in vacuo* to give 1,2-dibromo- and 1-bromo-2-iodotetrafluorobenzene respectively.

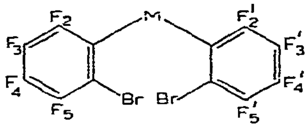
The ^{1}H NMR spectrum of bis(2-hydrotetrafluorophenyl) sulphide in deuterochloroform does not show the sixteen line pattern expected for a compound of the form 1-H-2-X-C_6F_4[4] since the two $H-F_m$ couplings are within 0.5 cps of each other and the $H-F_p$ coupling is unusually small, ~0.5 cps. The spectrum thus has the appearance of a pair of triplets with a certain amount of broadening.

The ^{19}F NMR spectra of (Ia), (II), (III) and (IV) were recorded at 94.1 MHz on a Varian HA 100 spectrometer and each spectrum shows four distinct groups of lines which can be assigned to four magnetically different fluorine atoms of the tetrafluorophenyl ring. As a first approximation each spectrum can be considered as an AMPX system and the observed coupling constants and chemical shifts are shown in Tables 1 and 2.

TABLE 1

CHEMICAL SHIFTS AND COUPLING CONSTANTS OF THE FLUORINE ATOMS IN $(2BrC_6F_4)_2M$

	M=S	M=$(C_6H_5)_2$Ge	M=Hg
Chemical shifts (ppm)			
F_2	126.8	119.7	119.4
F_3	153.9	154.1	155.1
F_4	150.7	150.1	153.2
F_5	125.7	125.0	127.1
Coupling constants (cps)			
F_2–F_3	22.15	23.35	26.4
F_2–F_4	5.0	5.05	2.55
F_2–F_5	9.3	10.7	11.55
F_3–F_4	19.55	19.2	18.85
F_3–F_5	3.1	3.65	2.65
F_4–F_5	21.3	20.90	20.15
F_2–Hg			462.0
F_5–Hg			112.0



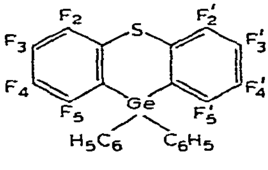
$F_2 \equiv F_2'$ etc.

TABLE 2

CHEMICAL SHIFTS AND COUPLING CONSTANTS OF THE FLUORINE ATOMS IN (IV)

Chemical shifts (ppm)	
F_2	133.1
F_3	151.3
F_4	155.6
F_5	120.9

Coupling constants (cps)	
F_2–F_3	20.5
F_2–F_4	3.4
F_2–F_5	12.3
F_3–F_4	19.6
F_3–F_5	5.35
F_4–F_5	23.6



$F_2 \equiv F_2'$ etc.

EXPERIMENTAL

The reactions involving lithium reagents were carried out under an atmosphere of dry, oxygen-free nitrogen. Sealed-tube experiments were carried out in pyrex tubes. Molecular weights were recorded in benzene or chloroform at 30° by Miss Sylvia Park of this laboratory, using a Mechrolab vapour phase osmometer (model 301A) calibrated with benzil. Dr. A. Bernhardt, Max-Planck-Institut, Mülheim, Germany, performed the analyses. We acknowledge gifts of polyfluorobenzenes from the Imperial Smelting Corporation and germanium compounds from the Organisch Chemisch Instituut TNO, Utrecht.

Preparation of bis(2-bromotetrafluorophenyl) sulphide

n-Butyllithium (27 ml of a 1.56 *M* solution in hexane) was added to 1,2-dibromotetrafluorobenzene (12.32 g) in ether (130 ml) at −78° and stirred for 0.5 h. Sulphur dichloride (1.3 ml) was added and the mixture stirred at room temperature for 2 h. The yellow ether solution was filtered off from the white precipitate of lithium chloride formed during the reaction and solvent removed. The yellow crystalline solid so obtained was recrystallised from ethanol and then sublimed at 60–80° *in vacuo* (10^{-3} mm) to give a colourless crystalline solid, m.p. 98–100°; yield 6.2 g (63%). (Found: C, 29.95; H, 0.0; Br, 33.6; F, 31.75; mol. wt., 464. $C_{12}F_8Br_2S$ calcd.: C, 29.5; H, 0.0; Br, 32.8; F, 31.2%; mol. wt., 488.)

Reaction of bis(2-lithiotetrafluorophenyl) sulphide with iodine

n-Butyllithium (17 ml) was added to bis(2-bromotetrafluorophenyl) sulphide (6.28 g) in ether (100 ml) at −78° and stirred for 0.5 h. Iodine (13 g) was added and the mixture stirred at room temperature for 15 h. The ether solution was shaken with sodium thiosulphate solution to remove unreacted iodine, separated, dried ($MgSO_4$), filtered and solvent removed. The resultant light-brown solid was sublimed at 90–115° *in vacuo* (10^{-3} mm) to give a white crystalline solid, m.p. 133.5–136.5°; yield 5.7 g (77%). (Found: C, 25.4; H, 0.0; F, 26.6; I, 44.6; mol. wt., 558. $C_{12}F_8I_2S$ calcd.: C, 24.8; H, 0.0; F, 26.1; I, 43.6%; mol. wt., 582.)

Reaction of bis(2-lithiotetrafluorophenyl) sulphide with water

Bis(2-lithiotetrafluorophenyl) sulphide was prepared as above from n-butyllithium (7.5 ml) and bis(2-bromotetrafluorophenyl) sulphide (2.727 g) in ether (80 ml). Water (75 ml) was added at −78° and the mixture stirred at room temperature for 1.5 h. The ether solution was separated, dried ($MgSO_4$), filtered, and solvent removed to yield a light-brown liquid; vacuum distillation at 110–130° (10^{-3} mm) gave a colourless liquid; yield 1.9 g. (Found: C, 44.75; H, 0.8; F, 45.6. $C_{12}H_2F_8S$ calcd.: C, 43.65; H, 0.6; F, 46.0%.)

Reaction of bis(2-lithiotetrafluorophenyl) sulphide with germanium halides

(*a*) *Diphenylgermanium dichloride.* Bis(2-lithiotetrafluorophenyl) sulphide was prepared by the addition of n-butyllithium (5.5 ml) to bis(2-bromotetrafluorophenyl) sulphide (2.085 g) in ether (80 ml) at −78°. Diphenylgermanium dichloride (1.8 ml) was added and the mixture stirred at room temperature for 16 h. Filtration, followed by solvent removal and addition of ethanol gave a colourless crystalline solid which was sublimed at 130–140° *in vacuo* (10^{-3} mm) to give an analytically pure sample, m.p. 140–143°; yield 1.1 g (46%). (Found: C, 51.8; H, 1.8; F, 27.6; mol.wt., 534. $C_{24}H_{10}F_8GeS$ calcd.: C, 51.9; H, 1.8; F, 27.4%; mol.wt., 555.)

(*b*) *Germanium tetrachloride.* The above procedure was repeated, adding germanium tetrachloride (0.56 ml) to bis(2-lithiotetrafluorophenyl) sulphide (4.62 g). The product obtained was recrystallised from ether to give colourless crystals, m.p. 229.5–231.5°; yield 1.7 g (49%). (Found: C, 39.5; H,0.2; F, 42.4; mol.wt., 778. $C_{24}F_{16}GeS_2$ calcd.: C, 39.6; H, 0.0; F, 41.7%; mol.wt., 729.)

Preparation of (VI)

(*a*). *From bis(2-bromotetrafluorophenyl) sulphide and selenium.* Bis(2-bromotetrafluorophenyl) sulphide (0.44 g) and selenium (0.5 g) were heated at 340° in a sealed evacuated tube for 16 h. The contents of the tube were extracted with ether and shaken with sodium thiosulphate solution to decompose any selenium–bromine compound and then to remove bromine. The ether layer was separated, dried ($MgSO_4$),filtered and solvent removed. The light brown solid obtained was sublimed at 50–70° under vacuum (10^{-3} mm) to give an off-white solid, m.p. 102–103°; yield 0.275 g (75%). (Found: C, 35.6; H, 0.0; F, 37.5; mol.wt., 447. $C_{12}F_8SSe$ calcd.: C, 35.4; H, 0.0; F, 37.3%; mol.wt., 407.)

(*b*). *From bis(2-lithiotetrafluorophenyl) sulphide and selenium tetrachloride.* Selenium tetrachloride (1.1 g) was added to bis(2-lithiotetrafluorophenyl) sulphide, prepared at −78° from n-butyllithium (6.5 ml) and bis(2-bromotetrafluorophenyl) sulphide (2.43 g). After stirring at room temperature for 16.5 h and filtering the resulting liquid, solvent removal, recrystallisation from ethanol and sublimation at 50–60° under vacuum yielded an off-white crystalline solid; the infrared spectrum and melting point of the sample were identical to that obtained in (*a*).

Preparation of bis(2-bromotetrafluorophenyl)diphenylgermanium

This was prepared using the above procedure from diphenylgermanium dichloride (4.2 ml) and 1-lithio-2-bromotetrafluorobenzene prepared from 1,2-dibromotetrafluorobenzene (6.16 g). Recrystallisation from ethanol followed by vacuum sublimation at 140–150° gave a white crystalline solid, m.p. 147–150°; yield 5.2 g (76%). (Found: C, 42.5; H, 1.6; mol.wt., 679. $C_{24}H_{10}Br_2F_8Ge$ calcd.: C, 42.2; H, 1.5%; mol.wt., 683.)

The reaction of bis(2-lithiotetrafluorophenyl)diphenylgermanium with diphenylgermanium dichloride

Diphenylgermanium dichloride (0.84 ml) was added to the dilithio reagent prepared at −78° from n-butyllithium (3 ml) and bis(2-bromotetrafluorophenyl)-diphenylgermanium (1.37 g) in ether (80 ml). The work-up procedure described above was followed by recrystallisation from ethanol and then ether to give colourless plates, m.p. 278.5–282.5°; yield 0.25 g (17%). (Found: C, 57.85; H, 2.8; F, 21.1; mol.wt., 786. $C_{36}H_{20}F_8Ge_2$ calcd.: C, 57.7; H, 2.7; F, 20.3; mol.wt., 750.)

Preparation of bis(2-bromotetrafluorophenyl)mercury

This was prepared from mercuric chloride (5.5 g) and 1-lithio-2-bromotetrafluorobenzene prepared from 1,2-dibromotetrafluorobenzene (9.24 g). Vacuum sublimation at 120–140° gave a colourless microcrystalline solid, m.p. 154–156° (lit.[3] 160–162°): yield 9.7 g (99%). (Found: C, 22.0; H, 0.0; Br, 24.3; F, 23.4; mol.wt., 713. $C_{12}Br_2F_8Hg$ calcd.: C, 21.95; H, 0.0; Br, 24.3; F, 23.15%; mol.wt., 657.) The observed deviation in melting point may be analogous to that observed for bis(pentafluorophenyl)mercury[13,14].

Reaction of bis(2-bromotetrafluorophenyl)mercury with n-butyllithium

(*a*). *Followed by addition of water.* n-Butyllithium (7 ml) was added to bis(2-bromotetrafluorophenyl)mercury (2.25 g) in ether (90 ml) at −78° and stirred for 1 h. Water (90 ml) was added and the mixture stirred at room temperature for 3 h. The ether layer was separated, dried ($MgSO_4$), filtered and solvent removed to give a brown liquid. Infrared spectra indicated that 1-hydro-2-bromotetrafluorobenzene was the only fluoroaromatic compound present. After removing all the latter by pumping on a vacuum line for 1 h, distillation at room temperature under vacuum gave a colourless liquid. (Found: C, 32.8; H, 5.9. $C_8H_{18}Hg$ calcd.: C, 30.5; H, 5.8%.)

(*b*). *Followed by addition of bromine.* The above was repeated but bromine was added in lieu of water. A similar work-up procedure, but using sodium thiosulphate solution to remove unreacted bromine, gave a brown liquid shown to contain, mainly, 1,2-dibromotetrafluorobenzene by infrared and vapour phase chromatography.

Reaction of bis(2-bromotetrafluorophenyl)mercury with halogens

(*a*). *Bromine.* Bis(2-bromotetrafluorophenyl)mercury (0.47 g) and bromine (0.15 ml) were heated at 115° in a sealed evacuated tube for 5 h. After extraction with ether, removal of unreacted bromine with sodium thiosulphate solution, separation of ether layer, solvent removal gave a colourless liquid which was identified by its infrared spectrum and VPC retention time as 1,2-dibromotetrafluorobenzene; yield 0.32 g (73%).

(*b*). *Iodine.* The above procedure was repeated using bis(2-bromotetrafluorophenyl)mercury (0.677 g) and iodine (1.25 g) at 230° for 23 h. The colourless liquid obtained was identified by infrared to be 1-bromo-2-iodotetrafluorobenzene; yield 0.43 g (59%).

Reaction of bis(2-bromotetrafluorophenyl)mercury with chalcogens

(*a*). *Sulphur.* Bis(2-bromotetrafluorophenyl)mercury (0.65 g) and sulphur (0.55 g) were heated at 230° in a sealed evacuated tube (previously dried at 230° and then flamed out) for 22 h. The contents of the tube were extracted with ether, filtered to remove mercuric sulphide and unreacted sulphur, solvent removed and the resultant yellow solid sublimed at 50–70° *in vacuo*. The off-white crystalline solid obtained had an identical infrared spectrum and melting point to octafluorothianthrene, m.p. 102.5–104°; yield 0.35 g.

In a similar experiment, in which the tube was not flamed out before use, a mixture of octafluorothianthrene and bis(2-hydrotetrafluorophenyl) sulphide, (Ib), was obtained.

(*b*). *Selenium.* The above procedure was repeated using bis(2-bromotetrafluorophenyl)mercury (0.47 g) and selenium (0.55 g); octafluoroselanthrene (0.21 g) was obtained.

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REFERENCES

1 S. C. COHEN, M. L. N. REDDY AND A. G. MASSEY, *J. Organometal. Chem.*, 11 (1968) 563.
2 C. TAMBORSKI AND E. J. SOLOSKI, *J. Organometal. Chem.*, 10 (1967) 385.
3 S. C. COHEN AND A. G. MASSEY, *J. Organometal. Chem.*, 10 (1967) 471.
4 D. E. FENTON, A. J. PARK, D. SHAW AND A. G. MASSEY, *J. Organometal. Chem.*, 2 (1964) 437.
5 R. D. CHAMBERS, J. A. CUNNINGHAM AND D. J. SPRING, *IVth Int. Symp. on Fluorine Chemistry*, Estes Park, Colorado, July 1967.
6 R. D. CHAMBERS AND J. A. CUNNINGHAM, *Chem. Commun.*, (1966) 469.
7 S. C. COHEN, M. L. N. REDDY AND A. G. MASSEY, *Chem. Commun.*, (1967) 451.
8 N. V. DUFFY, A. J. LAYTON, R. S. NYHOLM, D. POWELL AND M. L. TOBE, *Nature*, 212 (1966) 177.
9 H. GILMAN AND E. A. ZUECH, *J. Amer. Chem. Soc.*, 82 (1960) 3605.
10 D. D. CALLENDER, P. L. COE AND J. C. TATLOW, *Tetrahedron*, 22 (1966) 419.
11 G. E. COATES, *Organometallic Compounds*, Methuen, 1960.
12 J. BURDON, P. L. COE, M. FULTON AND J. C. TATLOW, *J. Chem. Soc.*, (1964) 2673.
13 P. L. COE, R. STEPHENS AND J. C. TATLOW, *J. Chem. Soc.*, (1962) 3227.
14 R. D. CHAMBERS, G. E. COATES, J. G. LIVINGSTONE AND W. K. R. MUSGRAVE, *J. Chem. Soc.*, (1962) 4367.