Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS

IX*. (PENTAFLUOROPHENYL)GERMANES

D. E. FENTON, A. G. MASSEY AND D. S. URCH
Chemistry Department, Queen Mary College, Mile End Road, London E.1 (England)

(Received February 14th, 1966)

Perfluoro-organo derivatives of germanium have been known for several years. However, other than the study of (trifluoromethyl)trihalogermanes by Clark and Willis[2], investigations have been limited to the preparation of compounds for infrared[3], and nuclear magnetic resonance spectral studies[4]. Studies regarding the pentafluorophenyl derivatives of Group IV elements have been reviewed by Tamborski[5].

We have prepared several (pentafluorophenyl)germanes as part of a study of the properties and NMR spectra of pentafluorophenyl derivatives of Main Group elements.

EXPERIMENTAL

Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen in oven-dried glass apparatus. The analyses were performed by A. BERNHARDT, Mülheim, Ruhr; molecular weights were recorded in benzene at 37° using a Mechrolab vapour phase osmometer calibrated with benzil. We wish to thank the Imperial Smelting Corporation and the Organisch Chemisch Instituut T.N.O., Utrecht for generous gifts of bromopentafluorobenzene and germanium compounds, respectively.

Tetrakis(pentafluorophenyl)germane

(*a*) Pentafluorophenyllithium[6] was prepared in ether/hexane solvent at −78° from bromopentafluorobenzene (9 g) and *n*-butyllithium; tetrachlorogermane (1.73 g) was added – mole ratio 1:4.5 – and the reaction mixture stirred at −78° for 3 h before being allowed to come to ambient temperature overnight. The ether/hexane layer was siphoned off and on evaporation gave white crystals (m.p. 246–248° in sealed tubes**); the residue in the reaction vessel was extracted with benzene to yield a further crop of crystals having the same m.p. Yield of tetrakis(pentafluorophenyl)germane, 2.8 g. (Found: C, 39.2, H, 0.05; F, 51.2; mol. wt., 708. $C_{24}F_{20}Ge$ calcd.: C, 38.95; H, 0.0; F, 51.35%; mol. wt., 740.) Tetrakis(pentafluorophenyl)germane is air-stable and moderately soluble in common organic solvents.

(*b*) Pentafluorophenylmagnesium bromide[7] was prepared from bromopentafluorobenzene (10 g) and magnesium (1 g) in ether. Tetrachlorogermane (1.2 g) was

---

[*] For Part VIII see ref. 1.

[**] On the hot-stage microscope the compound sublimes at atmospheric pressure without melting from 224–230°.

added – mole ratio 1:7.25 – and the reaction mixture stirred for 20 h before hydrolysis with distilled water. Evaporation of the ether layer gave a viscous liquid which on extraction with more ether gave a viscous liquid (of unknown constitution) and a white amorphous solid; sublimation of this solid at 170° (10^{-3} mm) gave pure tetrakis(pentafluorophenyl)germane. Yield 1.02 g.

Tris(pentafluorophenyl)chlorogermane

Pentafluorophenyllithium was prepared at —78° in pentane and tetrachlorogermane (2.2 g) added – mole ratio 3.5:1 – the mixture being stirred and allowed to warm up slowly to room temperature overnight. The supernatant liquid was siphoned off and evaporated to leave colourless crystals. The solid residue remaining in the reaction flask was extracted three times with pentane, each extract being evaporated to leave further crops of the same crystals. Recrystallisation from pentane gave 4.4 g of pure tris(pentafluorophenyl)chlorogermane, m.p. 103–104°. (Found: C, 35.5; H, 0.2; Cl, 5.9; F, 47.1; mol. wt., 631. $C_{18}ClF_{15}Ge$ calcd.: C, 35.5; H, 0.0; Cl, 5.8; F, 46.8 %; mol. wt., 609.) Tris(pentafluorophenyl)chlorogermane is soluble in ether, benzene, pentane, chloroform and acetone.

Tris(pentafluorophenyl)bromogermane

This was prepared in the same manner as the chloro derivative except that tetrabromogermane (4.1 g) was used. Yield, 3.0 g of white crystals, m.p. 105–107°. (Found: C, 35.5; H, 0.1; Br, 12.0; F, 42.3; mol. wt., 638. $C_{18}BrF_{15}Ge$ calcd.: C, 33.1; H, 0.0; Br, 12.2; F, 43.6 %; mol. wt., 653.)

Bis(pentafluorophenyl)dibromogermane

Pentafluorophenylmagnesium bromide was prepared in ether from bromopentafluorobenzene (5 g) and magnesium (0.5 g). Tetrachlorogermane (1.2 g) was added and the mixture stirred for 12 h at room temperature. The ether layer was removed, evaporated and the resulting viscous liquid distilled at 180–185° (12 mm) to give the colourless liquid, bis(pentafluorophenyl)dibromogermane, 0.68 g. (Found: C, 26.0; H, 0.1; F, 34.7; $C_{12}Br_2F_{10}Ge$ calcd.: C, 25.4; H, 0.0; F, 33.5 %.) The sensitivity of this compound towards atmospheric moisture probably accounts for rather poor analytical figures.

It was further characterised by careful hydrolysis using distilled water to bis(pentafluorophenyl)germanium oxide, $[(C_6F_5)_2GeO]n$, m.p. 238–248°. (Found: C, 34.3; H, 0.0; F, 45.1. $C_{12}F_{10}GeO$ calcd.: C, 34.1; H, 0.0; F, 45.0 %.) This white oxide can be sublimed under good vacuum at 220°. It is soluble in acetone but is insoluble in benzene, ether and pentane. A molecular weight determination using Rast's method showed the oxide to be polymeric but, due to poor solubility, no accurate value for the degree of polymerisation could be obtained*.

Bis(pentafluorophenyl)diphenylgermane

Diphenyldichlorogermane (5.43 g) was added to a slight excess of pentafluorophenyllithium in ether/hexane solvent at —78°. The mixture was stirred and allowed

---

* *Note added in proof.* Molecular weight determinations in acetone using a Mechrolab vapour phase osmometer suggest the oxide is tetrameric (Found: mol. wt. 1753. $[(C_6F_5)_2GeO]_4$calcd.: 1692).

to warm up slowly to room temperature overnight before the ether layer was removed and evaporated to leave white crystals of bis(pentafluorophenyl)diphenylgermane. The compound, when recrystallised from petroleum ether (30–40°), had a m.p. 125–127°; yield 5.2 g. (Found: C, 52.2; H, 1.6; mol. wt., 549. $C_{24}H_{10}F_{10}Ge$ calcd.: C, 51.4; H, 1.8 %; mol. wt., 561.) Bis(pentafluorophenyl)diphenylgermane is soluble in the common organic solvents.

(Pentafluorophenyl)triphenylgermane

Triphenylbromogermane (2.8 g) was added to pentafluorophenyllithium (prepared at −78° from bromopentafluorobenzene, 1.8 g, and n-butyllithium) and the mixture stirred whilst being allowed to warm slowly up to room temperature overnight. The ether layer was then siphoned off and the solvent removed under a vacuum to leave a crystalline solid; fractional crystallisation from petroleum ether (30–40°) followed by vacuum sublimation at 50–70° gave pure (pentafluorophenyl)triphenylgermane, 1.3 g, m.p. 114–116°. (Found: C, 61.1; H, 3.35; mol. wt., 462. $C_{24}H_{15}F_5Ge$ calcd.: C, 61.1; H, 3.2 %; mol. wt., 471.)

Reaction of tris(pentafluorophenyl)chlorogermane with:

(*a*) *Distilled water.* Tris(pentafluorophenyl)chlorogermane (0.5 g) was melted and poured slowly into vigorously stirred cold distilled water. Extraction of the water with pentane, followed by recrystallisation from the same solvent, gave white crystals (m.p. 115–117°) of tris(pentafluorophenyl)germanol. (Found: C, 36.8; H, 0.4; F, 48.15. $C_{18}HF_{15}GeO$ calcd.: C, 36.6; H, 0.2; F, 48.15 %.) The proton NMR spectrum of a solution of the germanol in carbon tetrachloride showed only a single weak absorption at 4.0 ± 0.05 ppm downfield from tetramethylsilane.

Heating crystals of tris(pentafluorophenyl)germanol at 130° for 12 h (atmospheric pressure) gave a virtually theoretical yield of the white, amorphous hexakis(pentafluorophenyl)digermoxane, m.p. 270–271°. (Found: C, 37.3; H, 0.0; F, 48.8. $C_{36}F_{30}Ge_2O$ calcd.: C, 37.1; H, 0.0; F, 49.0 %.)

(*b*) *Sodium hydroxide solution.* (*i*) Tris(pentafluorophenyl)chlorogermane (0.285 g) on treatment with 5 ml of 5 N sodium hydroxide for 16 h at room temperature gave 0.21 g of pentafluorobenzene, *ca.* 90 % cleavage. (*ii*) Tris(pentafluorophenyl)chlorogermane (0.288 g) after treatment with 5 ml of 0.1 N sodium hydroxide for 16 h at room temperature gave only 0.09 g of pentafluorobenzene, *i.e. ca.* 40 % cleavage.

(*c*) *Ammonia.* Damp ammonia was bubbled through an ethereal solution of tris(pentafluorophenyl)chlorogermane (0.5 g) to give an immediate precipitate (m.p. 269–271°) of hexakis(pentafluorophenyl)digermoxane (0.48 g). The infrared spectrum of this sample of digermoxane showed it to be identical to that obtained on heating tris(pentafluorophenyl)germanol.

(*d*) *Pentafluorophenyllithium.* When treated with pentafluorophenyllithium in an ether/hexane solvent, tris(pentafluorophenyl)chlorogermane gave good yields of tetrakis(pentafluorophenyl)germane.

(*e*) *n-Butyllithium.* Tris(pentafluorophenyl)chlorogermane (2 g) and n-butyllithium were stirred together in an ether/hexane solvent for 12 h at room temperature. Evaporation of the solvent gave a viscous, colourless liquid which on the addition of methanol gave 0.45 g of white crystals (m.p. 75–76°) of tris(pentafluorophenyl)-

n-butylgermane. (Found: C, 42.0; H, 1.3; F, 45.1. $C_{22}H_9F_{15}Ge$ calcd.: C, 41.9; H, 1.4; F, 45.2 %.) No Li–Cl exchange to give tris(pentafluorophenyl)germyllithium occurred.

Attempted preparation of (pentafluorophenyl)trichlorogermane

(*a*) The reaction between pentafluorophenyllithium and tetrachlorogermane in varying ratios close to the theoretical 1:1 consistently gave tris(pentafluorophenyl)-chlorogermane as the major product.

(*b*) Ethyl(pentafluorophenyl)mercury[8] (0.396 g) and tetrachlorogermane (0.214 g) after two days in a sealed tube at room temperature gave only 0.013 g of ethylmercuric chloride (m.p. 191–193°).

(*c*) Methyl(pentafluorophenyl)mercury[9] (1.05 g) and tetrachlorogermane (0.59 g) after seven days in a sealed tube at 40° gave only 0.04 g of methylmercuric chloride (m.p. 169–170°).

Infrared spectra

The infrared spectra were recorded on a Grubb-Parsons double beam grating spectrophotometer; the peaks are recorded in cms^{-1}.

$(C_6F_5)_4Ge$ (as mull in nujol and in hexachlorobutadiene): 1642 m, 1557 s, 1515 s, 1475 s, 1381 m, 1285 m, 1237 w, 1140 w, 1107 m, 1092 sh, 1087 s, 1033 w, 1018 w, 971 s, 819 m, 752 m, 725 m, 627 m.

$(C_6F_5)_3GeCl$ (as above): 1639 m, 1560 s, 1512 s, 1482 s, 1385 m, 1290 m, 1237 w, 1146 w, 1111 m, 1089 s, 1018 w, 971 s, 826 m, 752 m, 725 m, 621 m.

$(C_6F_5)_3GeBr$ (as above): 1648 m, 1566 s, 1515 s, 1471 s, 1389 m, 1294 m, 1242 w, 1149 w, 1111 w, 1087 s, 1041 w, 1038 w, 1019 w, 985 s, 826 m, 750 m, 730 m, 625 m.

$(C_6F_5)_3GeOH$ (as above): 3378 bd, 1650 m, 1565 s, 1515 s, 1486 s, 1471 sh, 1387 m, 1290 m, 1139 w, 1105 w, 1087 s, 1015 w, 971 s, 823 m, 750 w, 732 sh, 719 m, 704 m, 625 m.

$(C_6F_5)_6Ge_2O$ (as above): 1614 m, 1562 s, 1515 s, 1471 s, 1379 m, 1248 w, 1143 w, 1111 m, 1093 s, 1041 w, 1020 m, 995 s, 985 s, 896 bd, 828 m, 757 w, 751 w, 726 m, 623 m.

$(C_6F_5)_3GeC_4H_9$ (as above): 1639 m, 1560 s, 1515 s, 1470 s, 1374 m, 1285 m, 1139 w, 1085 s, 1051 w, 1020 w, 971 s, 888 w, 858 w, 819, 813 db, 754 w, 724 w, 704 w, 625 bd.

$(C_6F_5)_2Ge(C_6H_5)_2$ (as above): 1642 m, 1560 s, 1511 s, 1470 s, 1428 m, 1379 m, 1281 m, 1191 w, 1158 w, 1139 w, 1093 s, 1085 w, 1002 w, 971 s, 813 m, 735 s, 724 m, 694 s, 621 bd.

$(C_6F_5)Ge(C_6H_5)_3$ (as above): 1642 m, 1560 s, 1511 s, 1470 s, 1428 m, 1379 m, 1281 m, 1183 w, 1152 w, 1136 w, 1089 s, 1077 s, 1026 w, 1002 w, 971 s, 806 m, 735 s, 721 m, 694 s, 680 w, 617 bd.

$[(C_6F_5)_2GeO]_n$ (as above): 1639 m, 1557 s, 1515 s, 1470 bd, 1418 m, 1383 m, 1342 w, 1288 m, 1242 w, 1140 w, 1111 sh, 1089 s, 1030 w, 1015 w, 971 s, 902 s, 833 m, 819 m, 752 m, 622 w.

$(C_6F_5)_2GeBr_2$ (as neat liquid): 1724 wk, 1631 m, 1584 s, 1538 sh, 1508 s, 1468 s, 1412 w, 1381 m, 1337 w, 1287 m, 1235 w, 1143 m, 1098 m, 1082 s, 1029 m, 1001 m, 985 s, 819 m, 748 m, 719 m, 617 w.

DISCUSSION

Tetrakis(pentafluorophenyl)germane is readily prepared by the reaction of tetrachlorogermane with an excess of either pentafluorophenyllithium (1:4.5 ratio) or pentafluorophenylmagnesium bromide (1:7.25 ratio). It is a white solid, thermally stable in vacuum at its melting point (246–248°) for periods of up to one month. There is no evidence for cleavage of pentafluorophenyl groups by iodine, iodine monochloride, or bromine, under conditions which cause cleavage of phenyl groups from tetraphenylgermane. For example, after 40 days in a sealed tube at 250° there was no detectable reaction with iodine; also there was no reaction with bromine in boiling ethylene dibromide after five hours, whereas tetraphenylgermane reacted completely after two hours[10]. There was no cleavage by 5 *N* aqueous sodium hydroxide after sixteen hours at room temperature.

This relative inertness is a characteristic of the tetrakis(pentafluorophenyl) derivatives of Group IV elements and has been attributed to steric effects arising from the tetrahedrally coordinated pentafluorophenyl groups[11]. The electronegativity of the pentafluorophenyl group has been shown to be between those of chlorine and bromine[12], and so the inductive effect of this group may well inhibit electrophilic attack[15]. It is observed that tetrakis(pentafluorophenyl)stannane is less stable to nucleophilic attack (by base in a heterogeneous system) than the corresponding silane[5], or germane. This may be understood if it is assumed that the polarising ability of the atoms, Si, Ge, Sn increases in that order. If this is so, it is to be expected that the pentafluorophenyl group will be more effective in conferring bonding potential upon the *d*-orbitals of Sn, rather than those of Ge or Si. If, further, there is little d_π–p_π bonding (as has been suggested by Chambers and Chivers[16]) between the pentafluorophenyl rings and the central atoms then Sn will behave as the most electron deficient element in this series, and so tetrakis(pentafluorophenyl)stannane will be more susceptible to nucleophilic attack than either the germane or silane, as is observed. A loss of symmetry is accompanied by an increase in reactivity, and this is reflected in both the (pentafluorophenyl)halogermanes and the (pentafluorophenyl)-organogermanes.

The hydrolysis of tris(pentafluorophenyl) chlorogermane has been studied in some detail. When the molten chlorogermane is poured into cold distilled water, tris(pentafluorophenyl)germanol, $(C_6F_5)_3GeOH$, is formed as an air-stable white solid. Above 130° the germanol slowly loses water at atmospheric pressure to give hexakis(pentafluorophenyl)digermoxane in a virtually quantitative yield:

$$2\,(C_6F_5)_3GeOH \rightarrow (C_6F_5)_3GeOGe(C_6F_5)_3 + H_2O$$

The same digermoxane can be prepared in a single step by the reaction of tris(pentafluorophenyl)chlorogermane with alcoholic silver nitrate, or damp pyridine, ammonia or triethylamine. Stronger bases also cleave pentafluorophenyl groups from germanium as pentafluorobenzene to give polymeric oxides containing non-stoichiometric proportions of pentafluorophenyl groups; for example, 5 *N* aqueous sodium hydroxide and tris(pentafluorophenyl)chlorogermane during sixteen hours at room temperature gave about 90 % a yield of pentafluorobenzene whereas 0.1 *N* aqueous sodium hydroxide in the same period gave 40 % cleavage, together with a small quantity of hexakis(pentafluorophenyl)digermoxane. The polymers which result are believed to arise from inter- and intra-molecular condensation reactions and probably contain straight-chain, annular and cross-linked systems. The ready cleavage of perfluoro-organo groups from germanium by hydrolysis has been established previously in the case of CF_3GeI_3, which produced fluoroform[2].

Alkali metals react with triphenylhalogermanes to give either hexaphenyldigermanes or alkali metal derivatives[13]. The reaction of sodium in boiling xylene with tris(pentafluorophenyl)chlorogermane resulted in a direct attack of the C–F bonds without the formation of isolable compounds: the use of magnesium in refluxing ether led to the reclaimation of the starting material in high yield. Lithium clippings in tetrahydrofuran reacted with tris(pentafluorophenyl)chlorogermane to give a yellow solution but no definite compounds could be recovered on evaporation of the solvent.

A coupling reaction attempted between triphenylstannyllithium and tris(pentafluorophenyl)chlorogermane in tetrahydrofuran gave mainly hexaphenyldistannane and triphenylchlorostannane. This occurrence of unexpected product may be explained by exchange of halogen and alkali metal. We also attempted to prepare alkali metal derivatives, $MGe(C_6F_5)_3$, by the use of metal–halogen exchange reactions; however, tris(pentafluorophenyl)chlorogermane gave only substitution products when treated with, for example, pentafluorophenyllithium or butyllithium. In a related series of experiments we have shown that triphenylstannyllithium undergoes lithium–bromine exchange with bromopentafluorobenzene:

$$LiSn(C_6H_5)_3 + C_6F_5Br \rightarrow C_6F_5Li + BrSn(C_6H_5)_3$$

Like the tris(pentafluorophenyl)halogermanes the n-butyl, and phenyl derivatives are readily hydrolysed (*e.g.* by alcoholic base) to give pentafluorobenzene.

When tetrachlorogermane is treated with pentafluorophenylmagnesium bromide in ether, a halogen exchange occurs, and bis(pentafluorophenyl)dibromogermane is the product. The reaction of tetrachlorogermane and pentafluorophenyllithium in a 1:2 ratio in ether/hexane or pure hexane solvents gave only tris(pentafluorophenyl)chlorogermane; the use of a 1:1 ratio also gave this same compound, together with, after hydrolysis, an oxide of non-stoichiometric composition – $(C_6F_5)_{0.34}GeO_{1.8}H$. (Pentafluorophenyl)tribromogermane has been prepared by other workers[14] using the reaction between (pentafluorophenyl)methylmercury and tetrabromogermane. However, our experiments using tetrachlorogermane and both (pentafluorophenyl)methylmercury, and (pentafluorophenyl)ethylmercury, have given only small yields of the organomercury halide.

ACKNOWLEDGEMENT

One of us (D.E.F.) acknowledges a maintenance award from the Science Research Council.

SUMMARY

The preparation and some properties of (pentafluorophenyl)germanes [$(C_6F_5)_n GeX_{4-n}$; n = 4, 3 or 2 and X = Cl, Br, or C_6H_5] are described.

REFERENCES

1 S. C. Cohen, D. E. Fenton, A. J. Tomlinson and A. G. Massey, *J. Organometal. Chem.*, 301.
2 H. C. Clark and C. J. Willis, *J. Am. Chem. Soc.*, 84 (1962) 898.
3 S. L. Stafford and F. G. A. Stone, *Spectrochim. Acta*, 17 (1961) 412.
4 T. D. Coyle, S. L. Stafford and F. G. A. Stone, *Spectrochim. Acta*, 17 (1961) 968.
5 C. Tamborski, E. J. Soloski and S. M. Dec, *J. Organometal. Chem.*, 4 (1965) 446.
6 E. Nield, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, (1959) 166.
7 P. L. Coe, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, (1962) 3227.
8 D. E. Fenton and A. G. Massey, unpublished results.
9 R. D. Chambers, G. E. Coates, J. G. Livingstone and W. K. R. Musgrave, *J. Chem. Soc.*, (1962) 4367.
10 L. M. Dennis and W. I. Patnode, *J. Am. Chem. Soc.*, 52 (1930) 2779.
11 J. M. Holmes, R. D. Peacock and J. C. Tatlow, *Proc. Chem. Soc.*, (1963) 108.
12 A. G. Massey, E. W. Randall and D. Shaw, *Chem. Ind. (London)*, (1963) 1244.
13 D. Quane and R. S. Bottei, *Chem. Rev.*, 63 (1963) 403.
14 R. D. Chambers and J. Cunningham, *Tetrahedron Letters*, 28 (1965) 2389.
15 C. Eaborn and K. C. Pande, *J. Chem. Soc.*, (1961) 3715.
16 R. D. Chambers and T. Chivers, *J. Chem. Soc.*, (1964) 4782.