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Substitution of fluorine in C_6F_5X (X = COOMe, CF_3, CN, NO_2) and pentafluoropyridine by the triethylgermyl group

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Abstract

The perfluorinated arenes C_6F_5X (X = COOMe, CF_3, CN, NO_2) and pentafluoropyridine react with $P(NEt_2)_3$ and $ClGeEt_3$, giving $4\text{-}XC_6F_4GeEt_3$ (or $4\text{-}GeEt_3C_5F_4N$) and $P(NEt_2)_3FCl$.

1. Results and discussion

We have recently reported on the syntheses of trialkylsilyl-, germyl-, stannyl- and plumbylpolyfluoroarenes Ar_FMR_3 by the reaction of polyfluoroaryl bromides (iodides) Ar_FBr (Ar_FI) with halides R_3MX (X = Cl, Br) and $P(NAlk_2)_3$ [1]. Chloropentafluorobenzene did not react [1].

More recently, we have found that the fluorine atom in the 4-position of perfluorinated arenes C_6F_5X (X is an electron-accepting substituent) and pentafluoropyridine is easily substituted by the triethylgermyl group under the action of chlorotriethylgermane and tris(dialkylamino)phosphine.

Octafluorotoluene (1) reacted with $P(NEt_2)_3$ and chlorotriethylgermane in hexane to form 1-triethylgermyl-4-trifluoromethyltetrafluorobenzene (2) in 85–87% yield (^{19}F NMR). In addition, $P(NEt_2)_3FCl$ and some 4-diethylaminoheptafluorotoluene were formed. The perfluoro-4,4′-dimethyldiphenyl was not detected (^{19}F NMR). The fluorine-containing tolylgermane (2) is easily isolated by shaking the reaction mixture with conc. H_2SO_4 and subsequent vacuum distillation (yield 62%).

$$\underset{(1)}{C_6F_5CF_3} + ClGeEt_3 + P(NEt_2)_3 \xrightarrow[\text{temp.}]{\text{room}}$$

$$\underset{(2)}{4\text{-}CF_3C_6F_4GeEt_3} + 4\text{-}Et_2NC_6F_4CF_3 + P(NEt_2)_3FCl$$

Decreasing the reaction time from 26 to 5 h leads to reduced conversion of toluene (1) from 100 to 22% and reduced yield of compound 2. With hexane substituted by ether, the conversion of 1 and the yield of 2 remain the same, but in diglyme or benzonitrile, side processes occur which diminish the yield of 2 to 20–35% (^{19}F NMR).

The reaction of methyl pentafluorobenzoate with $P(NEt_2)_3$ and chlorotriethylgermane in hexane also leads to fluorine substitution in the pentafluorophenyl ring and formation of 1-triethylgermyl-4-methoxycarbonyltetrafluorobenzene.

$$C_6F_5COOMe + ClGeEt_3 + P(NEt_2)_3 \longrightarrow 4\text{-}MeOCOC_6F_4GeEt_3 + P(NEt_2)_3FCl$$

The triethylgermylation of pentafluorobenzonitrile and nitropentafluorobenzene with chlorotriethylgermane and $P(NEt_2)_3$ gave the compounds $4\text{-}CNC_6F_4GeEt_3$, $4\text{-}NO_2C_6F_4GeEt_3$ and traces of $4\text{-}Et_2NC_6F_4X$ (X = CN, NO_2).

$$C_6F_5CN + ClGeEt_3 + P(NEt_2)_3 \longrightarrow 4\text{-}CNC_6F_4GeEt_3 + P(NEt_2)_3FCl$$

$$C_6F_5NO_2 + ClGeEt_3 + P(NEt_2)_3 \longrightarrow 4\text{-}NO_2C_6F_4GeEt_3 + P(NEt_2)_3FCl$$

Treatment of the hexane solution of pentafluoropyridine and $ClGeEt_3$ with tris(diethylamino)phosphine led to the formation of 4-triethylgermyltetrafluoropyridine. The reaction time was less than 1 h. The changed order of mixing of the reagents (addition of

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the hexane solution of $ClGeEt_3$ and $P(NEt_2)_3$ to C_5F_5N) did not affect the yield of the germyldefluorination product.

$$C_5F_5N + ClGeEt_3 + P(NEt_2)_3 \longrightarrow 4\text{-}GeEt_3C_5F_4N + P(NEt_2)_3FCl$$

The less electrophilic hexafluorobenzene did not react with chlorotriethylgermane and $P(NEt_2)_3$ (hexane, 48 h).

When $P(NEt_2)_3$ was substituted by tris(dibutylamino)phosphine, the reaction slowed down but the pathway remained the same. For example, the reaction of octafluorotoluene, chlorotriethylgermane and $P(NBu_2)_3$ gave the arylgermane (**2**), 4-dibutylaminoheptafluorotoluene and $P(NBu_2)_3FCl$, but 72 h later the conversion of the starting toluene was only 57%. A similar picture is observed for pentafluoropyridine.

The analysis of the ^{19}F NMR spectra of the reaction mixtures obtained from compounds C_6F_5X (X = COOMe, CF_3, CN, NO_2) and C_5F_5N shows that fluorine is substituted only in the 4-position of perfluoroarenes. No isomers were formed in any appreciable amounts. This result is distinct from radical triethylgermylations of perfluoroarenes $C_6F_5CF_3$ and C_5F_5N by bis(triethylgermyl)mercury which gave isomer mixtures of 3- and $4\text{-}CF_3C_6F_4GeEt_3$, and 3- and $4\text{-}GeEt_3C_5F_4N$ [2]. Moreover, the rate of conversion of perfluoroarenes increases in the series

$$C_6F_6 \ll C_6F_5COOMe < C_6F_5CF_3 < C_6F_5CN < C_6F_5NO_2 \sim C_5F_5N$$

This order is in agreement with kinetic results for the reactions of perfluoroarenes with nucleophiles [3]. The following scheme for the transformations is suggested:

$$C_6F_5X + P(NEt_2)_3 \longrightarrow [4\text{-}X\text{-}C_6F_4PF(NEt_2)_3 \rightleftharpoons 4\text{-}X\text{-}C_6F_4^{-}\,{}^{+}PF(NEt_2)_3 \rightleftharpoons 4\text{-}X\text{-}C_6F_4{}^{+}P(NEt_2)_3F^{-} \rightleftharpoons 4\text{-}X\text{-}C_6F_4{}^{+}PF(NEt_2)_2{}^{-}NEt_2]$$

$$4\text{-}X\text{-}C_6F_4^{-}\,{}^{+}PF(NEt_2)_3 + ClGeEt_3 \longrightarrow 4\text{-}X\text{-}C_6F_4GeEt_3 + P(NEt_2)_3FCl$$

$$4\text{-}X\text{-}C_6F_4{}^{+}PF(NEt_2)_2{}^{-}NEt_2 + C_6F_5X \longrightarrow 4\text{-}Et_2NC_6F_4X + 4\text{-}X\text{-}C_6F_4PF_2(NEt_2)_2$$

This scheme accounts both for the high regioselectivity of fluorine substitution and the increased reactivity of perfluoroarenes C_6F_5X with the growth of the inductive effect of substituent X.

The transformations of octafluorotoluene, ethyl pentafluorobenzoate and pentafluoropyridine to the derivatives of diphenyl $4\text{-}XC_6F_4C_6F_4X\text{-}4'$ (X = CF_3, COOEt) and 4,4'-octafluorodipyridyl in the presence of $P(NEt_2)_3$ [4], apparently follow the same pathway. In these reactions, the role of the electrophile is played by an excess of perfluoroarene. However, we do not exclude that the mechanism of fluorine substitution in perfluoroarenes Ar_FF by the triethylgermyl group is more complex than the above scheme and may include other stages with participation of triethylchlorogermane.

TABLE 1. Reactions of perfluoroarenes with $ClGeEt_3$ and $P(NR_2)_3$

Perfluoroarene (mmol)	$ClGeEt_3$ (mmol)	$P(NR_2)_3$ (mmol)	Time (h)	Yield of Ar_FGeEt_3 (%)	
				By ^{19}F NMR	Isolated
$C_6F_5CF_3$[a](5)	6	$P(NEt_2)_3$(17.5)	26	87	62
$C_6F_5CF_3$[b](5)	6	$P(NBu_2)_3$(17.5)	72	56	
C_6F_5COOMe(4.4)	5.3	$P(NEt_2)_3$(15.5)	120	77	19
C_6F_5CN(2.5)	3	$P(NEt_2)_3$(8.75)	1	82	42
$C_6F_5NO_2$[c](5)	6	$P(NEt_2)_3$(17.5)	1	60	45
C_5F_5N[c](5)	6	$P(NEt_2)_3$(17.5)	1	75	60
C_5F_5N[d](2.96)	3.55	$P(NEt_2)_3$(10.4)	0.5	71	
C_5F_5N[c,e](5)	6	$P(NBu_2)_3$(10)	6	32	

[a] By-product 7% of $4\text{-}Et_2NC_6F_4CF_3$ (^{19}F NMR).

[b] Conversion 57%.

[c] Reagents mixed at 0–5°C.

[d] Hexane solution of $ClGeEt_3$ and $P(NEt_2)_3$ was added to C_5F_5N. By-product $4\text{-}NEt_2C_5F_4N$ (14%).

[e] Conversion 58%.

2. Experimental details

The NMR spectra were recorded on a Bruker WP 200SY (^1H at 200 MHz, ^{19}F at 188.3 MHz) spectrometer (TMS and C_6F_6 as internal references). The IR spectra were recorded on a Specord M 80 instrument in a thin layer. The reaction conditions and yields of products are given in Table 1.

2.1. Reactions of perfluoroarenes with $ClGeEt_3$ and $P(NEt_2)_3$

To a stirred solution of perfluoroarene and chlorotriethylgermane in hexane (1 ml of hexane per 1 mmol of Ar_FF), a $P(NEt_2)_3$ solution in an equal volume of hexane was added dropwise and the mixture was stirred for the time indicated in Table 1. The ^{19}F NMR spectrum was recorded (benzotrifluoride as an internal quantitative standard). The precipitate $P(NEt_2)_3FCl$ was filtered off, the filtrate was shaken with conc. H_2SO_4, dried over $CaCl_2$, the solvent was distilled off and the residue distilled in vacuum. The IR, ^1H and ^{19}F NMR spectra of the compounds 4-$CF_3C_6F_4GeEt_3$ [2], 4-$CNC_6F_4GeEt_3$ [1] and 4-$GeEt_3C_5F_4N$ [2] are identical to those of known products.

2.1.1. 1-Triethylgermyl-4-nitrotetrafluorobenzene

B.p. 114–116°C (6 mmHg). ^1H NMR ($CDCl_3$): δ 1.05–1.22 ($GeEt_3$). ^{19}F NMR ($CDCl_3$): δ 38.7 (F-2,6); 15.3 (F-3,5). IR spectrum: 2961, 2910, 2879, 1612, 1546, 1454, 1357, 1350, 1257, 1215, 1126, 1010, 977, 806, 780, 746 cm^{-1}. Anal. Found: C, 41.2; H, 4.34; F, 20.7; N, 4.37. $C_{12}H_{15}F_4GeNO_2$ calc.: C, 40.7, H, 4.24; F, 21.5; N, 3.96%.

2.1.2. 1-Triethylgermyl-4-methoxycarbonyltetrafluorobenzene

B.p. 116–118°C (9 mmHg). 1H NMR ($CDCl_3$): δ 3.96 ($COOCH_3$); 1.11–1.23 ($GeEt_3$). ^{19}F NMR ($CDCL_3$): δ 37.4 (F-2,6); 23.5 (F-3,5). IR spectrum: 2960, 2910, 2873, 1747, 1640, 1503, 1447, 1380, 1300, 1211, 1177, 1075, 1009, 955, 909, 802, 790, 740 cm^{-1}. Anal. Found: C, 45.5; H, 5.00; F, 21.1. $C_{14}H_{18}F_4GeO_2$ calc.: C, 45.8; H, 4.91; F, 20.7%.

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