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Abstract

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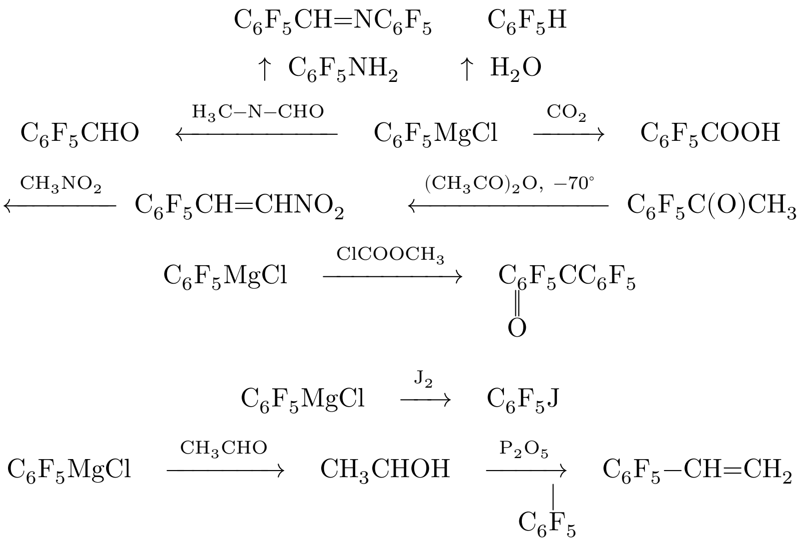
PREPARATION AND REACTIONS OF PENTAFLUOROPHENY AND HEPTAFLUORONAPHTHYLMAGNESIUM CHLORIDES

The use of the Grignard reagent makes it possible readily to synthesize various compounds containing a pentafluorophenyl residue. The literature describes various examples of such syntheses using pentafluorophenylmagnesium bromide and pentafluorophenylmagnesium iodide ([1], [2]). However, the starting compounds—pentafluorobromo- and pentafluoroiodobenzenes—are comparatively difficult to obtain.

We succeeded in obtaining pentafluorophenylmagnesium chloride by means of the "entrainment reaction" with ethylene bromide in ether. An attempt to obtain the organomagnesium compound in tetrahydrofuran (under these conditions pentachlorophenylmagnesium chloride is formed in 77.5% yield ([4])) led to the formation of a polymer that did not melt up to 360°. On the basis of the IR spectrum and elemental analysis, we propose the following structure for it:

$$\mathrm{C_6F_5-(C_6F_4)_n-C_6F_4Cl}, \quad \text{where } n = 6, 7.$$

We carried out the following syntheses on the basis of pentafluorophenylmagnesium chloride:



$$\begin{tikzcd}
C_6F_5CH{=}NC_6F_5 & C_6F_5H & \\
C_6F_5CHO \arrow[u, "C_6F_5NH_2"'] & C_6F_5MgCl \arrow[l, "H_3C-N-CHO"'] \arrow[u, "H_2O"'] \arrow[r, "CO_2"] & C_6F_5COOH
\end{tikzcd}$$

$$\xleftarrow{CH_3NO_2} C_6F_5CH{=}CHNO_2 \qquad \xleftarrow{(CH_3CO)_2O,\ -70^\circ} C_6F_5C(O)CH_3$$

$$C_6F_5MgCl \xrightarrow{ClCOOCH_3} C_6F_5\underset{\underset{O}{\|}}{C}C_6F_5$$

$$C_6F_5MgCl \xrightarrow{J_2} C_6F_5J$$

$$C_6F_5MgCl \xrightarrow{CH_3CHO} CH_3\underset{\underset{C_6F_5}{|}}{C}HOH \xrightarrow{P_2O_5} C_6F_5{-}CH{=}CH_2$$

A number of peculiarities of the chemical behavior of pentafluorophenylmagnesium chloride should be noted. Thus, it does not form the acid upon carbonation with dry ice, nor upon passing CO_2 through an ethereal solution; C_6F_5COOH was obtained in good yield by passing CO_2 into a solution of the organomagnesium compound in tetrahydrofuran. The reaction with chloroformic ester stops at the stage of decafluorobenzophenone. Pentafluorophenylmagnesium chloride does not react with monochloroacetic acid or ethyl benzoate even upon heating to 100°. The best yield of pentafluorophenyl methyl ketone (the reactions with $(CH_3CO)_2O$, CH_3CN, and CH_3COCl were studied) was obtained by carrying out the reaction with $(CH_3CO)_2O$ at -70°; this ketone, in contrast to octafluoroacetophenone, readily gives derivatives at the carbonyl group. We also obtained the organomagnesium compound from a mixture of isomeric chloroheptafluoronaphthalenes ([5]); after hydrolysis, a mixture of α-H- and β-H-heptafluoronaphthalenes is formed.

When the principal part of the work had been completed, an article by Masgreiv et al. ([6]) became known, in which the preparation of the Grignard reagent from pentafluorochlorobenzene and its conversion into pentafluorobenzene and pentafluorobenzoic acid (in lower yields) were reported.

Experimental Part

Pentafluorophenylmagnesium chloride. Into a four-necked flask equipped with a stirrer, a reflux condenser with a calcium chloride tube, a dropping funnel, and a tube for introducing nitrogen were placed 1-2 crystals of iodine and 2.79 g (0.114 g-atom) of Mg, and the mixture was heated on an air bath until the iodine sublimed. After cooling, 45 ml of absolute ether was added, and, in a stream of dry N_2, 2-3 ml of a previously prepared mixture of 10.58 g (6.40 ml, 0.052 g-mol) of pentafluorochlorobenzene, 9.8 g (4.48 ml, 0.052 g-mol) of dry ethyl bromide, and 10 ml of absolute ether was added. The mixture was heated on a water bath until an intense reaction began, and then, with vigorous stirring and cooling with ice water, the remaining amount of the mixture of halogen derivatives was added; to complete the reaction, the contents of the flask were boiled for 30 min. After cooling, the mixture was decomposed with 10% HCl, extracted with ether, and dried over $MgSO_4$. The yield of pentafluorobenzene according to gas-liquid chromatography was 87%; by distillation on a column, pentafluorobenzene was isolated in 49.4% yield, b.p. 83-85°, $n_D^{19.5}$ 1.3913. Lit.: b.p. 88-89°, n_D^{18} 1.3931 (^{7}).

Pentafluorobenzoic acid. C_6F_5MgCl was prepared from 10.58 g of C_6F_5Cl and 2.79 g of Mg, as described above. The ether was distilled off as completely as possible, 30 ml of dry tetrahydrofuran was added, and a stream of dry CO_2 was passed through for 12 hr. The reaction mixture was decomposed with 10% HCl, continuously extracted from the aqueous layer with ether (12 hr), and the extract was dried over $MgSO_4$. After removal of the ether, the dry residue was recrystallized from a 1:1 mixture of toluene and petroleum ether; yield 7.34 g (66%), m.p. 105-105.5°. Lit.: m.p. 103-104° (^{7}).

Found, %: C 39.6; 39.8; H 0.58; 0.61; F 45.1; 45.2
$C_7HO_2F_5$. Calculated, %: C 39.6; H 0.4; F 44.8
Acid number found 263.8; calculated 264.0

UV spectrum (in C_2H_5OH): $\lambda_{\max}$ 218 and 261 mμ ($\lg\varepsilon$ 4.575 and 2.81). IR spectrum (in CCl_4, 0.2%): 1515 (s) and 1665 (m) (aromatic ring); 1010 (s) and 1020 (s) (C–F), 3510 (w) (free OH), 3100 broad (associated OH), 1775 (w) (free C=O), 1735 cm^{-1} (associated C=O). S-Benzylthiuronium salt, m.p. 182-182.5° (from 50% alcohol).

Found, %: N 7.19; 7.02; S 8.91; 8.48
$C_{15}H_{11}O_2F_5N_2S$. Calculated, %: N 7.39; S 8.47

Pentafluoroiodobenzene. To a solution of 13.25 g of J_2 in 125 ml of absolute ether, with vigorous stirring, a solution of the Grignard reagent (from 10.58 g of C_6F_5Cl and 2.79 g of Mg) was added dropwise. The mixture was decomposed with 5% HCl, extracted with ether, washed with 15% Na_2CO_3 solution, saturated $Na_2S_2O_5$ solution, and water, and dried over $MgSO_4$. The ether was distilled off on a column; on fractional distillation, 7.2 g (46.7%) of pentafluoroiodobenzene was isolated, b.p. 159-160°/760 mm, 60-60.5°/25 mm, $n_D^{19.5}$ 1.4965. Lit. (^{7}): b.p. 161-163°, n_D^{19} 1.4970.

Found, %: C 24.6; 24.5; F 31.85; 31.95
C_6F_5J. Calculated, %: C 24.5; F 32.3

IR spectrum (neat): 1510 (s) and 1520 (s) (aromatic ring), 1005 (s) (C–F), 490 (m) cm^{-1} (C–J). UV spectrum (in C_2H_5OH): $\lambda_{\max}$ 226 and 252 mμ ($\lg\varepsilon$ 4.02 and 2.94).

Pentafluorobenzaldehyde. To a solution of the organomagnesium compound from 10.58 g C_6F_5Cl and 2.79 g Mg was added 14.12 g of N-methylformanilide (40 min at 20°); the mixture was boiled for 4 hr, cooled, decomposed with 20% HCl, repeatedly extracted with ether, washed with 15% Na_2CO_3 solution and water, and dried over $MgSO_4$. After removal of the ether, distillation in vacuo gave 6.4 g (62.4%) of pentafluorobenzaldehyde, b.p. 59–59.5° (11 mm), n_D^{25} 1.4520. Lit. (^{1}): b.p. 67-70°/15 mm).

Found, %: C 42.7; 42.6; H 0.76; 0.61; F 48.0; 48.2
C_7HOF_5. Calculated, %: C 42.9; H 0.5; F 48.5
Oxime number found 282.1; 283.4; calculated 285.9

IR spectrum (neat): 1710 (s) (C(= O)H), 1509 (s) (arom. ring), 1010 (s) and 1020 (s) cm^{-1} (C–F). UV spectrum (in C_2H_5OH): λ_{max} 236, 242, and 286 mμ ($\lg\varepsilon$ 4.38; 4.35 and 3.4).

A mixture of 0.85 g of pentafluorobenzaldehyde and 0.79 g of pentafluoroaniline (m.p. 126–128°) was heated for 1 hr at 125°, then poured into ice water; the precipitated solid was filtered off and recrystallized from alcohol; yield 0.96 g, m.p. 66–67°.

Found, %: C 43.4; 43.5; H 0.35; 0.38; N 4.02; 4.05
$C_{13}HF_{10}N$. Calculated, %: C 43.2; H 0.27; N 3.88

IR spectrum (in KBr, C 0.5%): 1635 (m) and 1660 (s) ($C = NArCH = NAr$), 1501 (s) (arom. ring), 999 (s) cm^{-1} (C–F). UV spectrum (in C_2H_5OH): λ_{max} 254 mμ ($\lg\varepsilon$ 4.22).

2,3,4,5,6-Pentafluoro-β-nitrostyrene. A mixture of 2.84 g (0.014 mole) of pentafluorobenzaldehyde, 0.88 g (0.014 mole) of nitromethane, and 1 ml of CH_3OH was cooled to −5°, and a solution of 0.57 g of NaOH in 1 ml of water was slowly added to the cooled mixture (temperature not above +5°). The paste that formed was dissolved in 5 ml of ice water and carefully poured into 6 ml of 15% HCl (temperature not above +5°). The lower oily layer was separated, the aqueous layer was extracted repeatedly with ether, the ether extracts were combined with the main layer, washed with 5% Na_2CO_3 solution and with water, and dried over $MgSO_4$. The ether was removed in vacuo, and the solid residue was recrystallized from CCl_4; yield 1.61 g (46.5%), m.p. 72.5°.

Found, %: C 39.8; 39.9; H 1.06; 0.99; N 5.78; 5.81
$C_8H_2O_2F_5N_2$. Calculated, %: C 40.1; H 0.84; N 5.85

IR spectrum (in KBr, C 0.5%): 1310 (s) and 1379 (s) ($C - NO_2$), 1510 (s) (arom. ring), 1670 (m) (–CH=CH–), 1010 (s) cm^{-1} (C–F). UV spectrum (in C_2H_5OH): λ_{max} 264 mμ ($\lg\varepsilon$ 2.59).

Decafluorobenzophenone. To an ice-cooled solution of C_6F_5MgCl (from 30 g of C_6F_5Cl and 7.15 g of Mg) was slowly added a solution of 6.95 g of $ClCOOCH_3$ in 25 ml of absolute ether; the ether was distilled off, the same amount of benzene was added, and the mixture was boiled for 1 hr. It was decomposed with 10% HCl and extracted with ether; the ether extracts were washed with 15% Na_2CO_3 solution and with water, and dried over $MgSO_4$. The solvents were removed in vacuo, and the solid residue was recrystallized from petroleum ether (70-100°). Yield 8.9 g (33.2%), m.p. 89-90°. Lit. (^{1}): m.p. 91-92°.

Found, %: C 43.2; 43.0; F 51.9; 52.0
$C_{13}F_{10}O$. Calculated, %: C 43.1; F 52.5

IR spectrum (in KBr, C 0.5%): 1000 (s) (C–F), 1720 (s) (C=O), 1516 (s) cm^{-1} (arom. ring). UV spectrum (in C_2H_5OH): $\lambda_{\max}$ 250 mμ ($\lg \varepsilon$ 4.12).

α-(2,3,4,5,6-Pentafluorophenyl)ethyl alcohol. To a solution of C_6F_5MgCl (from 21.16 g of C_6F_5Cl and 5.08 g of Mg), cooled with a mixture of snow and salt, 16.7 g of acetaldehyde was rapidly added; the mixture was stirred while cooling for 1 hr and then for 2 hr at room temperature, decomposed, as usual, with 20% HCl, and extracted with ether. The ether extracts were washed with soda solution and with water, and dried over $MgSO_4$. The ether was distilled off, and by fractionation in vacuo 8.9 g of α-(2,3,4,5,6-pentafluorophenyl)ethyl alcohol (33.2%) was isolated; b.p. 102-103°/30 mm, n_D^{17} 1.4394. Lit. (^{2}): b.p. 80-82°/37 mm; n_D^{20} 1.4426.

Found, %: C 45.5; 45.4; H 2.41; 2.45; F 44.4; 44.5
$C_8H_5OF_5$. Calculated, %: C 45.4; H 2.36; F 45.0

IR spectrum (neat): 1530 (s) (arom. ring), 3400 (br) (OH), 982 (s) (C–F), 2981 (s) and 2940 (s) cm^{-1} (CH_3). UV spectrum (in C_2H_5OH): $\lambda_{\max}$ 259 mμ ($\lg \varepsilon$ 3.72).

2,3,4,5,6-Pentafluorophenylethylene. In a flask with a reflux condenser protected by a calcium chloride tube, 6.9 g (0.048 mole) of P_2O_5 and 0.4 g of hydroquinone were charged, and, with ice cooling, 16.07 g (0.076 mole) of α-(2,3,4,5,6-pentafluorophenyl)ethyl alcohol was added; the mixture was hea-

heated for 1 hour at 160° (in an oil bath), and the crude product was distilled from the flask at 40 mm. After fractional distillation, 9.47 g (62.5%) of 2,3,4,5,6-pentafluorophenylethylene was isolated, b.p. 62-63°/50 mm, n_D^{22} 1.4439. Lit. (^{2}): b.p. 140-141°, n_D^{20} 1.4414.

Found, %: C 48.9; 49.0; H 1.61; 1.59; F 49.2; 49.0
$C_8H_3F_5$. Calculated, %: C 49.5; H 1.54; F 49.0

IR spectrum (neat): 1625 (m) and 1670 (m) (–CH=CH–), 990 (s) (C–F), 1520 (s) cm^{-1} (aromatic ring). UV spectrum (in C_2H_5OH): $\lambda_{\max}$ 240 and 274 mμ ($\lg \varepsilon$ 4.12 and 2.76).

2,3,4,5,6-Pentafluorophenyl methyl ketone. To a solution of 31.2 g (0.3 mole) of $(CH_3CO)_2O$ in 80 ml of absolute ether, cooled with a dry ice-acetone mixture to −70°, a cooled solution of C_6F_5MgCl (from 30.08 g of C_6F_5Cl and 7.62 g of Mg) was slowly added with vigorous stirring. The mixture was stirred for 2 hours at −70°, brought to room temperature, and decomposed with saturated ammonium chloride solution; the aqueous layer was neutralized with solid sodium carbonate, extracted repeatedly with ether, washed with 15% sodium carbonate solution and with water, and dried over $MgSO_4$. The ether was distilled off, and distillation of the residue gave 15.45 g (48.5%) of 2,3,4,5,6-pentafluorophenyl methyl ketone, b.p. 48-50°/5 mm, $n_D^{17.5}$ 1.4330.

Found, %: C 46.0; 45.8; H 1.50; 1.57; F 45.4; 45.5
$C_8H_3OF_5$. Calculated, %: C 45.7; H 1.43; F 45.2

IR spectrum (neat): 1010 (s) (C–F), 1500 (s) and 1530 (s) (aromatic ring), 1720 (s) (C=O), 1412 (s), 1320 (s), 1370 (s), 2930 (m), and 3010 (w) cm^{-1} (CH_3). UV spectrum (in C_2H_5OH): λ_{max} 227 and 274 mμ ($\lg \varepsilon$ 4.31 and 3.46).

2,4-Dinitrophenylhydrazone, m.p. 159.5-160.5° (from a mixture of alcohol and ethyl acetate).

Found, %: N 14.55; 14.74.
$C_{14}H_7O_4F_5N_4$. Calculated, %: N 14.36.

Heptafluoronaphthylmagnesium chloride. To 0.184 g of Mg (0.0075 g-atom), activated with iodine, was added a solution of 1.09 g (0.0038 mole) of a mixture of α- and β-chloroheptafluoronaphthalenes in 4 ml of absolute ether; the mixture was heated under a stream of dry N_2 to boiling, and, with stirring, a solution of 0.71 g (0.0038 mole) of ethylene bromide in 5 ml of absolute ether was added over 30 minutes. The solution was boiled for 30 minutes, cooled, decomposed with 10% HCl, extracted with ether, and dried over $MgSO_4$. According to gas-liquid chromatography, the mixture contains 21.3% α-H- and 73% β-H-heptafluoronaphthalenes.

Polymer from pentafluorochlorobenzene. To 0.9 g of Mg (0.037 g-atom), activated with iodine, were added 5 ml of dry tetrahydrofuran and then, with cooling and stirring, 5.05 g of C_6F_5Cl (0.025 mole); spontaneous boiling occurs and a precipitate separates. The mixture was boiled for 1 hour, the tetrahydrofuran was distilled off, and 10% HCl was added until the unreacted Mg dissolved. The precipitate was filtered off, washed with warm dilute HNO_3, water, conc. NH_4OH, water, and methyl alcohol, and dried at 50° in vacuum over P_2O_5. The white powder does not melt and is insoluble in ordinary organic solvents.

Found, %: C 46.70; 46.92; Cl 2.75; 2.81; F 49.86; 49.98
$C_{48}F_{33}Cl$. Calculated, %: C 46.6; Cl 2.87; F 50.6

IR spectrum (in KBr, C 0.5%): 660 (m), 710 (s), 890 (w), 940 (w), 980 (s), 1000 (s) (C–F), 1245 (m), 1495 (s) (aromatic ring), 1650 (m) cm^{-1}.

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Note: Figure translations are in progress. See original paper for figures.