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Reactions of (chlorodifluoromethyl)benzene and (chlorodifluoromethoxy)benzene with nucleophilic reagents

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Dedicated to Professor Richard D. (Dick) Chambers on the occasion of his 70th birthday.

Abstract

Condensation reactions of (chlorodifluoromethyl)benzene and (chlorodifluoromethoxy)benzene with phenoxide and thiophenoxide ions have been performed in DMF or NMP with heating. In these conditions, the reaction between phenylselenide ion and (chlorodifluoromethyl)benzene did not occur. This latter reaction requires an additional visible light irradiation to proceed, as reported by Yoshida et al.
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Keywords: Fluoroalkyl halides; Substitution reaction; Nucleophilic reagents

1. Introduction

Few studies have been devoted to the condensation of nucleophilic reagents with (chlorodifluoromethyl)benzene **1**. Substitution of the chlorine atom by a phenylthio group occured in the reaction of halide **1** with sodium thiophenoxide in *N*-methylpyrrolidone at reflux in a yield limited to 15% [1]. A similar substitution reaction with sodium phenylselenide was performed in DMF at 100 °C under visible light irradiation in 89% yield [2]. Owing to the importance of *gem*-difluoro compounds [3], we proposed to revisit these condensation reactions ourselves. We extended our study to phenoxide ions and to another chloride, (chlorodifluoromethoxy)benzene **2**. To our knowledge, no reaction of this latter with nucleophiles has been reported until now.

$\underset{\mathbf{1}}{PhCF_2Cl}$ $\underset{\mathbf{2}}{PhOCF_2Cl}$

2. Results and discussion

2.1. Reactions with sodium thiophenoxide

We confirmed the results of the initial report of Yagupolskii and Korinko [1]: the condensation of chloride **1** with sodium thiophenoxide in refluxing DMF, or NMP, for 3 h led to [(difluorophenylmethyl)sulfanyl]benzene **3** in yields lower or equal to 15%. For these first experiments, sodium thiophenoxide was prepared from thiophenol and sodium hydroxide. Better results were obtained when dry sodium methoxide was used as a base. Moreover, the mixture was initially protected by an inert atmosphere in order to limit the possible oxidation of the thiophenate salt into diphenyl disulfide. In these conditions, the yield of **3** increased to 71%. A similar result was obtained with potassium thiophenoxide (Eq. (1)).

$$\mathbf{1} + \text{NasPh or KSPh} \xrightarrow[\text{reflux, 3 h}]{\text{NMP}} \underset{\mathbf{3}}{PhCF_2SPh} \quad (1)$$

In order to compare the behaviour of thiophenoxide ion with that of its selenide analogue, condensation of the thiolate with chloride **1** was attempted in DMF at 100 °C

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under visible light irradiation, as described by Yoshida et al. [2] for the selenide ion. However, no reaction occurred under these conditions.

Attempts to apply strict thermal conditions (Eq. (1)) for the reaction of chloride **2** with potassium thiophenoxide showed that the reactivity of **2** is lower than that of **1**. Substitution of the chlorine atom was not complete and [(difluorophenoxymethyl)sulfanyl]benzene **4** was obtained as a mixture with diphenyl disulfide. The latter was formed notwithstanding the precautions taken to avoid oxidation. Compound **4** was isolated by chromatography on a silica gel column in 14% yield (Eq. (2)).

$$\mathbf{2} + \mathrm{KSPh} \xrightarrow[\text{reflux, 3 h}]{\text{NMP}} \underset{\mathbf{4}}{\mathrm{PhOCF_2SPh}} + \mathrm{PhSSPh} \qquad (2)$$

2.2. Reactions with sodium phenylselenide

The selenide ion was prepared by action of sodium borohydride on diphenyl diselenide in ethanol [2] or by treatment of the diselenide with sodium metal in THF under ultrasonic irradiation [4]. Condensation of the selenide ion with chloride **1** was performed in DMF at 100 °C under visible light irradiation [2]. In our hands, [(difluorophenylmethyl)selanyl]benzene **5** was isolated by chromatography on silica gel in a 45% yield (Eq. (3)). Curiously enough, the reaction did not proceed without light as reported by Yoshida et al., though this selenide ion is considered an excellent nucleophilic reagent [4,5].

$$\mathbf{1} + \mathrm{NaSePh} \xrightarrow[\text{100 °C, 4 h}]{\text{DMF, } h\nu} \underset{\mathbf{5}}{\mathrm{PhCF_2SePh}} \qquad (3)$$

Simple thermal condensations were also attempted in NMP at reflux, as for the thiophenoxide ion reaction (Eq. (1)), but without success.

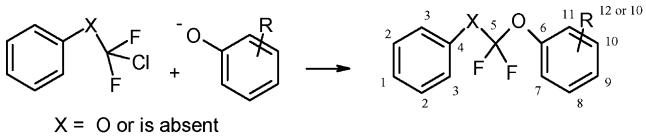
2.3. Reactions with sodium phenoxides

Reaction of sodium phenoxide with chloride **1** was performed in DMF at 100 °C for 24 h. (Difluorophenoxymethyl)benzene **6** was isolated by chromatography on silica gel in 75% yield (Eq. (4)).

$$\mathbf{1} + \mathrm{NaOPh} \xrightarrow[\text{100 °C, 24 h}]{\text{DMF}} \underset{\mathbf{6}}{\mathrm{PhCF_2OPh}} \qquad (4)$$

Compound **6** has already been prepared from sodium phenoxide and the analogous bromide $PhCF_2Br$ by heating the DMF solution at 80 °C for 24 h [6]. The higher yield (85%) obtained in milder conditions appears logical for a more reactive bromide.

Reaction of sodium phenoxide with chloride **2** was also examined. The condensation was performed in NMP at 150 °C for 24 h. 1,1′-[Difluoromethylene(bis)oxy]-dibenzene **7** [7] was obtained in 37% yield. The transformation of (chlorodifluoromethoxy)benzene **2** was not complete in stronger conditions than that used for the condensation of



Scheme 1. Reaction of substituted phenoxide ions with halides **1** and **2**.

(chlorodifluoromethyl)benzene **1**, showing again the lower reactivity of the halide **2** (Eq. (5)).

$$\mathbf{2} + \mathrm{NaOPh} \xrightarrow[\text{150 °C, 3 h}]{\text{NMP}} \underset{\mathbf{7}}{\mathrm{PhOCF_2OPh}} \qquad (5)$$

Similarly, other phenoxides have been condensed with halides **1** and **2** (see Scheme 1 and Table 1). In spite of the limited yields obtained, these condensations show that even the poorly reactive halide **2** is able to react with weak nucleophilic reagents.

2.4. Comparison of substrates and nucleophilic reagents

As pointed out by Yoshida et al., the carbon-chlorine bond in (chlorodifluoromethyl)benzene **1** is little polarized and therefore poorly reactive towards nucleophilic attack [2]. Owing to the inductive electron-withdrawing effect of the oxygen atom in (chlorodifluoromethoxy)benzene **2**, its reactivity is even lower than that of **1** [8–10].

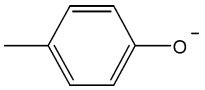
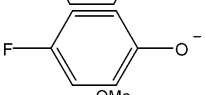
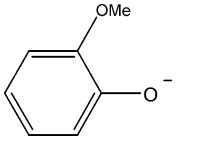
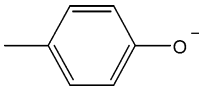
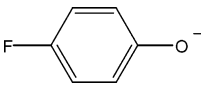
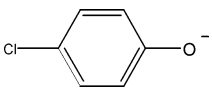
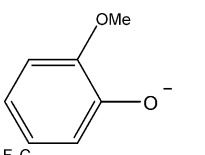
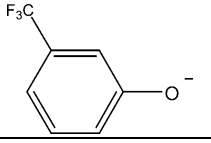
At first glance, comparison of the results obtained by condensation of (chlorodifluoromethyl)benzene **1** with different nucleophilic reagents appears rather puzzling (all the results are presented in Table 2).

Under strict thermal conditions, the selenide ion seems unable to perform the substitution of the chlorine atom, which occurs with the thiophenoxide analogue and even with the poorly nucleophilic phenoxide ion! Additional activation by visible light irradiation is necessary in the selenium series.

Concerning the simple thermal condensation of nucleophilic reagents with halides **1** and **2**, a S_N2 mechanism can be considered as proposed by Haas et al. [6] for the reaction of $PhCF_2Br$. Alternatively, a $S_{RN}1$ process could occur. In order to trap a possible radical intermediate, various unsaturated products (dec-1-ene, butyl vinyl ether, anisole) were introduced into the reaction medium (Eq. (4)) but no adduct was detected. A S_N1 mechanism seems unlikely owing to the low polarizability of the carbon-chlorine bond in halides **1** and **2**. The failure of the chlorine substitution by a phenylselanyl group is not easily explained by all these mechanisms.

Initiation of the selenide ion reaction has been interpreted as a photo-induced electron transfer from the nucleophile to the (chlorodifluoromethyl)benzene **1** [2]. A similar process could be involved in the reaction of the thiophenoxide ion [11], but it does not seem to occur. Obviously, the mechanisms involved in these condensations need more study [12].

Table 1
Reaction of substituted phenoxide ions with halides **1** or **2**

1 or **2**	Phenoxide	Yield (%)	δ_F (ppm)	δ_C (ppm) (*J*: Hz)	*m/z* (%)
1		67[a]	−65.7 (CF_2; s)	20.8 (C_{10}) 121.9 (C_7) 125.6 (C_3, t, $^4J_{CF}$ = 4 Hz) 128.3 (C_8) 129.8 130.7 (C_1) 135.2 (C_4, t, $^2J_{CF}$ = 33 Hz) 148.3 (C_6)	CI methane 239 ($M + 1^{+\bullet}$, 36) 219 ($M - HF^+$, 100)
1		54[b]	−66.3 (CF_2; s) −117.5 (CF; m)	115.9 (C_8, d, J_{CF} = 23) 123.7 (C_7, d, $^3J_{CF}$ = 8) 125.5 (C_3, t, $^4J_{CF}$ = 4 Hz) 128.5 (C_2) 130.9 (C_1) 146.2 (C_6) 160.3 (C_{10}, d, J_{CF} = 244)	CI methane 235 ($M + 1^{+\bullet}$, 43) 215 ($M - HF^+$, 100)
1		31[c]	−66.0 (CF_2; s)	55.9 (C_{12}) 112.6 120.5 122.4 (C_5, t, $^1J_{CF}$ = 263) 124.5 125.8 (C_3, t, $^4J_{CF}$ = 4 Hz) 126.6 128.3 (C_8) 130.7 (C_1) 133.9 (C_4, t, $^2J_{CF}$ = 32 Hz) 152.6	CI methane 231 ($M + 1^{+\bullet}$, 100)
2		45[d]	−56.0 (CF_2; s)	21.2 (C_{10}) 120.5 120.6 (C_5, t, $^1J_{CF}$ = 255) 121.0 (C_3) 125.4 (C_7) 125.9 (C_1) 129.7 (C_2) 130.3 (C_8) 135.2 147.7 (C_6, t, J_{CF} = 2) 150.3 (C_4, t, J_{CF} = 2)	143 (6 $PhOCF_2^+$) 77 (28)
2		25	−56.4 (CF_2; s) −117.0 (CF; m)	116.1 (C_8 d, J_{CF} = 23) 120.8 (C_5, t, $^1J_{CF}$ = 252) 121.0 (C_3) 122.9 (C_7, d, $^3J_{CF}$ = 9) 126.0 (C_1) 129.5 (C_2) 146.2 (C_6. t, $^4J_{CF}$ = 2) 150.3 (C_4, t, J_{CF} = 2) 160.4 (C_{10}, d, J_{CF} = 254)	254 ($M^{+\bullet}$, 100) 235 (27) 159 (50) 143 (39) 77 (92)
2		20	−56.1 (CF_2; s)	120.8 (C_5, t, $^1J_{CF}$ = 254) 120.9 (C_3, t, $^4J_{CF}$ = 1) 122.4 (C_7, t, $^4J_{CF}$ = 1) 126.0 (C_1) 129.6 (C_2, C_8) 131.4 (C_9) 148.8 (C_6, t, $^3J_{CF}$ = 2) 150.2 (C_4, t, $^3J_{CF}$ = 2)	272 ($M^{+\bullet}$, 26) 270 ($M^{+\bullet}$, 85) 251 (14) 143 (41) 77 (100)
2		29[e]	−55.9 (CF_2; s)	55.7 (C_{12}) 112.8(C_{10}) 120.4 (C_8) 120.85(C_3) 121.1 (C_5, t, $^1J_{CF}$ = 254) 122.7(C_7) 125.6(C_1) 126.9 (C_9) 129.3 (C_2) 139.2 (C_{11}) 150.5 (C_4–C_6, t, $^3J_{CF}$ = 2) 152.0 (C_6–C_4, t, $^3J_{CF}$ = 2)	254 ($M^{+\bullet}$, 100) 235 (27), 159 (50) 143 (39) 77 (92.)
2		28	−55.9 (CF_2; s) −63.3 (CF_3; s)	118.2 (C_{11} q, $^3J_{CF}$ = 4) 120.8 (C_5, t, $^1J_{CF}$ = 255) 121.0 (C_3) 122.7 (C_9 q, $^3J_{CF}$ = 9) 123.5 (C_{12} q, $^1J_{CF}$ = 263) 124.3 (C_7) 126.17 (C_1) 129.6 (C_2) 130.20 (C_6) 132.2 (C_{10} q, $^2J_{CF}$ = 33) 150.1 (C_4–C_6, t, $^3J_{CF}$ = 2) 150.5 (C_6–C_4, t, $^3J_{CF}$ = 2)	304 (68, $M^{+\bullet}$) 285 (26) 143 (38) 77 (100)

δ_H ppm: [a]2.23 (3H, CH_3, s) 7.12, 7.70 (9H, H_{arom}, m). [b]7.02–7.78 (9H, H_{arom}, m). [c]3.92 (3H, CH_3, s) 6.92–7.78 (9H, H_{arom}, m). [d]2.23 (3H, CH_3, s) 7.09–7.44 (9H, H_{arom}, m). [e]3.75 (3H, CH_3, s) 6.88–7.31 (9H, H_{arom}, m).

Table 2
Reaction of (chlorodifluoromethyl)benzene **1** with various nucleophiles

Nucleophile	Conditions	Product	Yield (%)
PhSNa	NMP, reflux 3 h	3	71
PhSeNa	NMP, reflux 3 h	5	–[a]
PhSNa	*hv*, DMF, 100 °C, 4 h	3	–[a]
PhSeNa	*hv*, DMF, 100 °C, 4 h	5	45
PhONa	DMF, 100 °C, 24 h	6	76

[a] Not detected by ^{19}F NMR analysis of the reaction mixture.

3. Conclusion

The starting chlorides **1** and **2** are formed as secondary products in the chlorine to fluorine exchange reaction by hydrogen fluoride used generally to produce trifluoromethylated compounds [15]. They can also be prepared on purpose when the halogen exchange is performed with pyridinium poly(hydrogen fluoride) [16]. In spite of the feeble reactivity of chlorides **1** and **2**, substitution of the chlorine atom by thermally stable nucleophilic reagents (phenoxides, thiophenoxides, arylselenides ions) occurs in dipolar aprotic solvents, either under simple thermal conditions or under additional visible light irradiation.

4. Experimental

THF (tetrahydrofuran) was distilled over sodium/benzophenone. DMF and NMP were distilled over calcium hydride. Solvents were kept under argon. Sodium phenates and thiophenates were prepared from equimolecular quantities of phenol (0.05 M) or thiophenol and sodium methoxide (0.05 M) in 100 ml of anhydrous methanol; the solvent was removed in vacuo and the salt was protected from moisture and oxygen. NMR spectra were recorded as $CDCl_3$ solutions on a Bruker AC-300 spectrometer. Reported coupling constants and chemicals shifts were based on a first order analysis. Internal reference was the residual peak of $CHCl_3$ (7.27 ppm) for ^1H (300 MHz),

central peak of $CDCl_3$ (77 ppm) for ^{13}C (75 MHz) spectra and internal $CFCl_3$ (0 ppm) for ^{19}F (282 MHz) NMR spectra. IR spectra were recorded as CCl_4 solutions on an Impact 400D Nicolet spectrophotometer. GCMS were performed with Chrompack CP Sil 19 CB chromatography column, length 30 m, diameter 0.25 mm, film thickness 0.25 μm, initial temperature 50 °C over 2 min, gradient 10 °C/min, final temperature 250 °C on a HP 5989B quadrupolar mass spectrometer. High resolution mass spectra were performed with a Finnigan MAT 95S spectrometer. Boiling points were determined by the Siwoloboff method on a Buchi melting point apparatus.

4.1. General procedure

The chloride **1** or **2** (Rhodia) (7.5 mmol) and the nucleophilic reagent (7.5 mmol) in NMP (3 mL) were stirred under argon in the conditions given for each compound described. The reaction was monitored by ^{19}F NMR. After hydrolysis and extraction with diethyl ether (3 mL × 15 mL) at room temperature, the organic layers were combined, washed with water, dried over magnesium sulfate, concentrated in vacuo and purified by chromatography on a silica gel column.

4.1.1. [(Difluorophenylmethyl)sulfanyl]benzene **3**

The reaction temperature and time were respectively 180 °C and 3 h [1]. White crystals (m.p. 88 °C, yield 74%) were isolated after chromatography (elution with pentane). ^{19}F NMR: −72.3 ($C\underline{F}_2$, s). ^{1}H NMR: 7.45–7.60 (6H, M) 7.70–7.85 (4H, M). ^{13}C NMR: 125.5 (C_3, t, $^{3}J_{CF}$ = 5 Hz) 127.6 (C_6) 127.8 (C_5, t, $^{1}J_{CF}$ = 279 Hz) 128.4 (C_8) 129.1 (C_2) 130.0 (C_9) 130.7 (C_1) 136.1 (C_4, t, $^{2}J_{CF}$ = 25 Hz) 136.4 (C_7). MS (CI NH_3): *m/z* = 236 (6%, $M^{+\bullet}$) 217 (4%, M^+−F). 127 (100%, $PhCF_2$) 77 (7%, Ph). Elemental analysis calc. for $C_{13}H_{10}F_2S$: C (66.1%) H (4.2%); found: C (65.9%) H (4.2%).

4.1.2. [(Difluorophenoxymethyl)sulfanyl]benzene **4**

The reaction temperature and time were, respectively, 180 °C and 3 h. The elution was performed with pentane/ethyl acetate (98/2) (colourless oil, yield 14%). ^{19}F NMR: −43.3 ($C\underline{F}_2$, s). ^{1}H NMR: 7.15 (2H, H_3, d, $^{2}J_{HH}$ = 8 Hz) 7.22–7.54 (6H, M) 7.66 (2H, H_7, $^{2}J_{HH}$ = 7 Hz). 13C NMR: 121.4 (C_7, s) 122.7 (C_9) 126.6 (C_6, t, $^{4}J_{CF}$ = 1.4 Hz) 128.5 (C_5, t, $^{1}J_{CF}$ = 295 Hz) 129.1 (C_2) 129.4 (C_8) 130.1 (C_1) 136.0 (C_3, t, $^{4}J_{CF}$ = 1 Hz) 150.7 (C_4, t, $^{3}J_{CF}$ = 2 Hz). MS (CI NH_3): *m/z* = 252 (67%, $M^{+\bullet}$) 233 (11%, M^+−F) 159 (100%, $PhSCF_2$) 143 (39%, $PhOCF_2$) 109 (6%, PhS) 77 (63%, Ph). HRMS: *m/z* calc. for $C_{13}H_{10}F_2OS$: 252.0450, found: 252.0425.

4.1.3. [(Difluorophenylmethyl)selanyl]benzene **5**

A mixture of diphenyl diselenide (125 mg, 0.4 mmol) and sodium borohydride (45 mg, 1.2 mmol, 3 eq.) in ethanol (0.2 mL) was stirred for 30 min under argon [2]. The halide 1 (65 mg, 0.4 mmol, 1 eq.) in DMF (3 mL) was added. The mixture was irradiated in a Pyrex tube under argon at 100 °C with a 500 W halogen lamp (distance 15 cm) for 8 h. After addition of water (25 mL) at room temperature, the mixture was extracted with ether (3 mL × 20 mL). The organic layer was dried over magnesium sulfate and concentrated in vacuo. The product was purified by preparative thin layer chromatography on silica gel (pentane/ether: 95/5) (white crystals; m.p.: 75 °C, yield: 45%). ^{19}F NMR: −70.5 ($C\underline{F}_2$, s). ^{1}H NMR: 7.20–7.67 (10H, H_{arom}, M).

4.1.4. (Difluorophenoxymethyl)benzene **6**

The reaction temperature and time were, respectively, 100 °C and 24 h (elution with pentane; colourless oil, yield: 75%) [6]. ^{19}F NMR: −65.8 ($C\underline{F}_2$, s). ^{1}H NMR: 7.23–7.51 (8H, H_1–H_2–H_3–H_9, M) 7.76–7.78 (2H, H_7, d, $^{3}J_{HH}$ = 8 Hz). ^{13}C NMR: 121.9 (C_7) 122.2 (C_5, t, $^{1}J_{CF}$ = 262 Hz) 125.6 (C_3, t, $^{5}J_{CF}$ = 2 Hz) 125.6 (C_9) 128.5 (C_8) 129.4130.8 (C_1) 133.9 (C_4, t, $^{2}J_{CF}$ = 31 Hz) 150.6 (C_6, t, $^{3}J_{CF}$ = 2 Hz). MS (CI NH_3): *m/z* = 220 (8%, $M^{+\bullet}$) 127 (100%, $PhCF_2$) 77 (6%, Ph). Elemental analysis calc. for $C_{13}H_{10}F_2O$: C (70.9%) H (4.5%); found: C (71.1%) H (4.5%).

4.1.5. 1,1′-[Difluoromethylene(bis)oxy]dibenzene **7**

The reaction temperature and time were, respectively, 150 °C and 24 h (elution with pentane) (colourless oil; yield: 37%) [7]. ^{19}F NMR: −55.8 (CF_2, s). ^{1}H NMR: 7.24–7.27 (6H, H_1–H_2, M) 7.36–7.41 (4H, H_3, M). ^{13}C NMR: 120.9 (C_5, t, $^{1}J_{CF}$ = 254 Hz) 121.0 (C_3) 125.87 (C_1) 129.5 (C_2) 150.4 (C_4). MS (CI NH_3): *m/z* = 236 (100%, $M^{+\bullet}$) 217 (17%, $M^{+\bullet}$−F) 143 (32%, $PhOCF_2$) 77 (78%, Ph). Elemental analysis calc. for $C_{13}H_{10}F_2O_2$: C (66.1%) H (4.3%); found: C (66.0%) H (4.3%).

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