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The reactions of difluorodiiodomethane with nucleophiles

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Dedicated to Dr. P. Tarrant on the occasion of his 85th birthday

Abstract

Treatment of difluorodiiodomethane with phenoxides (ArO^-) in DMF at room temperature gives $ArOCF_2I$ in 7–15%, the carbonates ($ArOCO_2Ar$) being the major products, while with thiophenoxides affords difluoromethylene derivatives ($ArSCF_2I$, $ArSCF_2SAr$, and $ArSCF_2H$) also in low yields. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Difluorodichloromethane (CF_2Cl_2, CFC-12) and difluorodibromomethane (CF_2Br_2) are still useful industrial sources of many fluorine-containing materials [1–3], although they were shown to cause the depletion of ozone layer [4,5]. However, their analogue, difluorodiiodomethane (**1**), has been much less developed, probably because this reagent was difficult to prepare [6]. The first report on compound **1** by Dolbier et al was involved with its photo- or benzoyl-peroxide induced reactions with alkenes [7]. After our finding of a simple, good method to synthesize **1** [8], we were attracted to study its properties as a difluorocarbene or iododifluormethyl radical source. It was found that **1** can be used as a trifluoromethylating agent for aza-aromatic compounds and enamines when irradiated in dimethyl foramide (DMF) [9]. Different from CF_2Br_2, diethyl iododifluoromethylphosphonate [$ICF_2P(O)(OEt)_2$] could be straightly obtained in near quantitative yield by simple treatment of **1** with triethylphosphite in diethyl ether [10]. Like perfluoroaklyl iodides, **1** can add to electron-rich alkenes by $PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$ [11], unactivated Zn or Fe [12]. Lead tetraacetate is even able to induce the addition reaction of **1** to poly- or perfluoroalkenes [13]. All the resultant adducts bearing iododifluoromethyl unit may further react with alkenes and alkynes to afford the various CF_2-containing compounds [10,14]. However, the desired vinyl iodides, $ICF_2CH{=}CIR$, derived from the addition reactions of **1** with alkynes, could not obtained trigged by either lead tetraacetate in alcohol [13] or aqueous hydrogen peroxide in acetone [15]. Instead, non-fluorinated compounds, i.e., β-iodo-α,β-unsaturated carboxylic esters and their acids were formed respectively. These unexpected data promoted us to do some simple fundamental research on the reactions of **1**, e.g. with nucleophiles. We, herein, present the results of **1** with alkoxide and thionate ions.

2. Results and discussion

First, we tried to use the simple ethoxide ion **(2a)** as a nucleophile reacting with **1**. It was found that **1** reacted with **2a** quickly in DMF at room temperature. When the reaction was completed, before and after treatment of the reaction mixture with water, to our surprise, none of ^{19}F NMR signals were detected, that is, difluoromethylene derivatives, e.g. $EtOCF_2I$, $EtOCF_2OEt$, $EtOCF_2H$ were not formed. Instead, diethylcarbonate **(3a)** as well as fluoride ion were the main products in spite of changing the ratio of **1/2a** from 1:4 to 2:1 (see entry 1, 2, Table 1). A higher alcohol, i.e., acetyl alcohol (1-hexadecanol) gave similar results with a moderate yield of the corresponding carbonate **3b** (entry 3, Table 1).

Interestingly, for phenoxide and substituted phenoxides, a small amount (7–15%) of desired products, aryldifluoroiodoethers **4** can be isolated and characterized if the ratio of **1**: phenoxides is kept at 2:1 (entry 6, 10, 11, 12, 15, 17, Table 1).

Lesser amounts (∼4%), even none, of **4**, were observed when the ratios being 1:1 and 1:4 (entry 4, 5 and 16 Table 1). In all these cases, the major products were still the corre-

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Table 1
The reaction of **1** with RO^- (**2**) in DMF at room temperature for 0.5 h

Entry	**2**	**1**:**2**	Conversion of ROH (%)	Yield (%)	
				3	**4**
1	**2a**	1:4	–	70	0
2	**2a**	2:1	–	99	0
3	**2b**	1:4	–	50	0
4	**2c**	1:4	–	62	0
5	**2c**	1:1	79	51	4
6	**2c**	2:1	71	40	13[a]
7[b]	**2c**	2:1	57	47	7
8[c]	**2c**	2:1	68	40	9
9[d]	**2c**	2:1	60	40	11
10	**2d**	2:1	60	45	10
11	**2e**	2:1	65	37	15
12	**2f**	2:1	68	30	15
13[b]	**2f**	2:1	62	45	7
14	**2g**	2:1	–	–	11
15	**2h**	2:1	62	38	12[e]
16	**2i**	1:1	82	52	4
17	**2i**	2:1	72	28	12

[a] A F^- (14%) was determined.
[b] In diglyme (DG) at 40°C.
[c] In the presence of *p*-DNB (20 mol%).
[d] The reaction performed in the dark.
[e] A F^- (22%) was determined.

sponding carbonates, accompanied by some sodium fluoride.

$$\underset{\mathbf{1}}{CF_2I_2} + \underset{\mathbf{2}}{RO^-} \rightarrow \underset{\mathbf{3}}{ROCO_2R} + \underset{\mathbf{4}}{ROCF_2I} + F^-$$

R = C_2H_5(**a**), *n*-$C_{16}H_{33}$(**b**), C_6H_5(**c**), *o*-$CH_3C_6H_4$(**d**), *p*-$CH_3C_6H_4$(**e**), *m*-$CH_3C_6H_4$(**f**), *o*-ClC_6H_4(**g**), *o*-BrC_6H_4(**h**), *o*-$CH_3OC_6H_4$(**i**)

Similar to phenoxides, the condensation of sodium thiophenoxide (**5a**), or *p*-chlorothiophenoxide (**5b**), with **1** in DMF at room temperature for 5 h gave three difluoromethylene derivatives **7**, **8** and **9** in low yields besides major product diphenyl disulfide **6**.

$$\underset{\mathbf{1}}{CF_2I_2} + \underset{\mathbf{5}}{ArS^-} \rightarrow \underset{\mathbf{6}}{ArSSAr} + \underset{\mathbf{7}}{ArSCF_2I} + \underset{\mathbf{8}}{ArSCF_2SAr} + \underset{\mathbf{9}}{ArCF_2H}$$

Ar = C_6H_5(**5a**), *p*-ClC_6H_4(**5b**)

The reactions of **1** with phenoxide and thiophenoxide ions were carried out in DMF according to the literature [16,17]. However, in order to eliminate the generation of fluoride ion resulting from the known reaction of diflurocarbene with DMF [18], diglyme (DG) was also employed as a solvent in some cases. The yields of **3** from phenoxides are comparable in these two solvents (entry 6 vs. 7, 12 vs. 13, Table 1) indicating that the formation of fluoride ion from free difluorocarbene and DMF is less important if not ruled out. However, better results were obtained in the reactions of **1** with **5b** in DG as compared with those in DMF(entry 3, 4 vs. 6, 8, Table 2).

Table 2
The reaction of **1** with ArS^- at room temperature

Entry	**5**	**1**:**5**	Solvent	Yield (%)			
				6	**7**	**8**	**9**
1	**5a**	1:1	DG	54	13	–	0
2	**5a**	2:1	DMF	–	5	13	12
3	**5b**	1:1	DG	28	34	6	0
4	**5b**	2:1	DG	28	35	9	0
5	**5b**	1:2	DG	–	0	43	0
6	**5b**	1:1	DMF	61	8	–	14
7	**5b**	2:1	DMF	68	6	2	7
8	**5b**	1:2	DMF	50	2	5	4
9[a]	**5b**	1:1	DG	–	20	0	0
10[a]	**5b**	1:1	DMF	69	0	0	0

[a] In the presence of *p*-DNB (20 mol%).

All the above results demonstrate, seemingly, that there are big differences between the reactivity of **1** and its analogues, i.e., difluorodibromo-, difluorodichloro- and difluorobromochloromethanes (CF_2X_2, X_2=Cl_2, Br_2, ClBr) with nucleophiles. Difluoroiodomethylalkylethers (**4a**, **b**) have never been obtained even at high ratio of **1**:**2** (2:1), the corresponding carbonates being the sole products although there was no report on the reactions of its counterparts with alkoxides. Unlike CF_2X_2, only very low yields of difluoroiodomethyl ethers or thioethers were obtained when **1** reacted with phenoxides or thiophenoxides even in the higher ratio of **1**: nucleophile (2:1), the carbonates **3** or diaryldisulfides **6** were the major products. However, in view of the fact that the CF_2-containing products, i.e., **4**, **7**, **8** and **9** were obtained, it is certain that there is some reactivity similarity between **1** and its analogues. In other words, the substitution approach of **1** like CF_2X_2 should follow one of two mechanisms or both: anionic chain mechanism or single electron transfer (ET) initiated radical process [16,17,19] (Schemes 1 and 2).

In fact, the formation of all the products, except carbonates **3**, can be rationalized by both pathways. In order to distinguish these two mechanisms, the reactions with an addition of ET scavenger, i.e., *p*-dinitrobenzene (*p*-DNB) or in the dark were carried out. The results shown at entry 8, 9 in Table 1and entry 9, 10 in Table 2, seems uncertain

$$Nu^- + ICF_2I \longrightarrow NuI + CF_2I^-$$
$$CF_2I^- \longrightarrow CF_2{:} + I^-$$
$$Nu^- + CF_2{:} \longrightarrow NuCF_2^-$$
$$NuCF_2^- + ICF_2I \longrightarrow NuCF_2I + CF_2I^-$$
$$NuCF_2^- + H^+ \longrightarrow NuCF_2H$$
$$(ArS^- + ArSCF_2I \longrightarrow ArSCF_2SAr$$
$$ArSI + RS^- \longrightarrow ArSSAr)$$

Scheme 1. Anionic chain mechanism.

ET:

$$Nu^- + ICF_2I \longrightarrow Nu\cdot + ICF_2I^{\cdot -}$$

$$ICF_2I^{\cdot -} \longrightarrow ICF_2\cdot + I^-$$

$$ICF_2\cdot + Nu^- \longrightarrow ICF_2Nu^{\cdot -}$$

$$ICF_2Nu^{\cdot -} \longrightarrow NuCF_2\cdot + I^-$$

$$ICF_2Nu^{\cdot -} + ICF_2I \longrightarrow ICF_2Nu + ICF_2I^{\cdot -}$$

$$[ArS\cdot + ArS\cdot \longrightarrow ArSSAr$$

$$(ICF_2SAr)^{\cdot -} \longrightarrow ArSCF_2\cdot + I^-$$

$$ArSCF_2\cdot + ArS\cdot \longrightarrow ArSCF_2SAr$$

$$ArSCF_2\cdot + H\cdot \longrightarrow ArSCF_2H]$$

Scheme 2. Electron transfer.

because of insignificant decrease of the yields of the products in both cases as compared with those in very low yields without them.

The mechanism of the formation carbonates **3** is not yet clear. The disubstituted of **1**, i.e., $ArOCF_2OAr$ (**10**), might be expected to be the precursors of **3** because it is known that the CF_2 unit of $ROCF_2CFYH$ (Y = F, Cl, CF_3) resulting from the addition of alkoxides to fluorinated olefins can be easily hydrolyzed to the corresponding esters, ROCOCFXH, with elimination of fluoride ion [20,21]. An attempt to prepare **10c** from **4c** with phenoxide under the similar conditions met only failure.

$$\underset{\textbf{4c}}{C_6H_5OCF_2I} + C_6H_5O^- \not\dashrightarrow \underset{\textbf{10c}}{C_6H_5OCF_2OC_6H_5} \dashrightarrow \textbf{3c}$$

However, the disulfide **8b** was readily formed from **7b** and **5b** in good yield.

$$\underset{\textbf{7b}}{p\text{-}ClC_6H_4SCF_2I} + \underset{\textbf{5b}}{p\text{-}C_6H_5S^-} \rightarrow \underset{\textbf{8b}\ (65\%)}{p\text{-}ClC_6H_4SCF_2SC_6H_4Cl\text{-}p}$$

Similar to the previous report [16], the formation of **8b** was significantly suppressed by the presence of *p*-DNB (the conversion of **7b** was 30% vs. 60% in its absence for 10 min) indicating the ET mechanism being preferable.

3. Experimental

Boiling (melting) points were uncorrected. IR spectra were recorded on a Shimadzu IR-440 or Perkin-Elmer Jeol 983 spectrometer. ^{19}F NMR spectra were obtained on a Varian EM-360 spectrometer (56.4 MHz) using trifluoroacetic acid as external standard, downfield shift being designated as negative. ^1H NMR spectra were carried out on a FX-90Q (90 MHz) or Varian EM-360 (60 MHz) spectrometer with Me_4Si as an external standard. Mass spectral data spectra were taken on a Hewlett-Packard HP-5989A spectrometer and HRMS data were obtained on a Finnigan MAT-8430 spectrometer. All reactions were routinely monitored by using thin layer chromatography (TLC) or ^{19}F NMR spectroscopy.

*3.1. General procedure for the reactions of **1** with sodium phenoxides*

To a 25 ml three-necked round bottomed flask, equipped with stirrer, phenol **2c** (0.31 g, 3.3 mmol), NaH (75% in oil, 0.10 g, 3.3 mmol), and dry DMF (5 ml) were added under nitrogen. **1** (2.00 g, 6.6 mmol) was dropped into the flask accompanying with releasing heat. After 30 min, the mixture was poured into water. The aqueous layer was extracted three times with ether (3 × 20 ml). The combined extracts were washed with water (3 × 10 ml) and dried over Na_2SO_4. After the ether had been evaporated, the residue was subjected to chromatography on silica gel to give phenyl difluoroiodomethyl ether as an oil, **4c** (0.13 g, 13%), and diphenyl carbonate **3c** (0.14 g, 40%), and phenol **2c** (0.09 g, 29%).

4c: Colorless oil. IR (film) (cm^{-1}): 1591, 1491, 1458, 1385, 1182, 1129, 996, 859, 761, 698, 621. ^1H NMR (CCl_4) δ (ppm): 6.5. ^{19}F NMR (CCl_4) δ (ppm): −76.0. MS *m/z* (relative intensity): 270 (M^+, 1.24), 269 (10.06), 177 (CF_2I^+, 2.8), 144 (11.34), 143 (M^+−I, 100), 77 (96.65). HRMS: calc. for $C_7H_5F_2IO$: 269.9352; found: 269.9348.

4d: Colorless oil. IR (film) (cm^{-1}): 3422, 2921, 2852, 1592, 1481, 1385, 1231, 1176, 1128, 1002, 873, 819, 717, 690, 587. ^1H NMR (CCl_4) δ (ppm): 7.32 (4H, s), 2.44 (3H, s). ^{19}F NMR (CCl_4) δ (ppm): −76.3. MS *m/z* (relative intensity): 284 (M^+, 0.08), 283 (0.90), 177 (CF_2I^+, 1.51), 158 (6.48), 157 (M^+−I, 69.20), 127 (I^+, 2.70), 91 (100), 65 (19.47). HRMS: calc. for $C_8H_7F_2IO$: 283.9509; found: 283.9523.

4e: Colorless oil. IR (film) (cm^{-1}): 3469, 2925, 1593, 1505, 1221, 1182, 1127, 995, 868, 823, 780, 713, 682. ^1H NMR (CCl_4) δ (ppm): 7.16 (4H, s), 2.42 (3H, s). ^{19}F NMR (CCl_4) δ (ppm): −75.0. MS *m/z* (relative intensity): 284 (M^+, 0.13), 283 (1.41), 177 (CF_2I^+, 2.71), 158 (7.65), 157 (M^+−I, 79.15), 127 (I^+, 3.23), 91 (100), 65 (23.49). HRMS: calc. for $C_8H_7F_2IO$: 283.9509; found: 283.9519.

4f: Colorless oil. IR (film) (cm^{-1}): 3441, 2921, 1610, 1587, 1486, 1466, 1382, 1247, 1183, 1125, 992, 930, 871, 789, 698. ^1H NMR (CCl_4) δ (ppm): 6.64–7.24 (4H, m), 2.24 (3H, s). ^{19}F NMR (CCl_4) δ (ppm): −75.3. MS *m/z* (relative intensity): 284 (M^+, 9.48), 283 (100), 218 (7.81), 217 (97.27), 177 (CF_2I^+, 2.50), 157 (M^+−I, 6.78), 127 (I^+, 4.42), 90 (94.07). HRMS: calc. for $C_8H_7F_2IO$: 283.9508; found: 283.9504.

4g: Colorless oil. IR (film) (cm^{-1}): 3426, 1584, 1478, 1448, 1378, 1231, 1176, 1120, 1068, 1005, 866, 759, 713, 699, 575, 566. ^1H NMR (CCl_4) δ (ppm): 7.13 (4H, s). ^{19}F NMR (CCl_4) δ (ppm): −74.6. MS *m/z* (relative intensity): 305 (2.72), 304 (35.01), 303 (10.70), 302 (100), 239 (17.01), 237 (50.73), 177 (3.31), 127 (4.01), 112 (10.79), 110 (33.32). HRMS: calc. for $C_7H_4ClF_2IO$: 303.8962; found: 303.8986.

4h: Colorless oil. IR (film) (cm^{-1}): 3394, 2280, 1578, 1472, 1444, 1227, 1174, 1118, 1051, 1033, 1004, 865, 759, 704, 655. ^1H NMR (CCl_4) δ (ppm): 6.90–7.90 (4H, m). ^{19}F NMR (CCl_4) δ (ppm): −74.6. MS *m/z* (relative intensity): 349 (6.02), 348 (70.54), 346 (70.80), 283 (4.63), 282 (66.21), 280 (67.91), 177 (6.33), 157 (4.02), 156 (46.61), 154 (47.39), 127 (12.28), 75 (100). HRMS: calc. for $C_7H_4Br^{79}F_2IO$: 347.8457; found: 347.8474. calc. for $C_7H_4Br^{81}F_2IO$: 349.8437; found: 349.8477.

3h: White solid. m.p. 74–76°C. IR (KBr) (cm^{-1}): 1783, 1472, 1445, 1238, 1197, 1159, 1045, 1028, 1006, 760, 740. ^1H NMR (CCl_4) δ (ppm): 6.7–8.2 (m). MS *m/z* (relative intensity): 374 (6.51), 372 (12.73), 370 (6.48), 293 (35.19), 291 (35.20), 201 (8.26), 199 (8.44), 168 (100), 157 (30.95), 155 (32.29), 75 (28.74), 63 (39.62). Analysis: calc. for $C_{13}H_8Br_2O_3$: C, 41.97%; H, 2.17%; found: C, 41.90%; H, 2.10%.

4i: Colorless oil. IR (film) (cm^{-1}): 3008, 2942, 2840, 1604, 1502, 1465, 1441, 1384, 1308, 1285, 1266, 1176, 1120, 1047, 1029, 996, 866, 784, 754, 690. ^1H NMR (CCl_4) δ (ppm): 6.70–7.50 (4H, m), 3.84 (3H, s). ^{19}F NMR (CCl_4) δ (ppm): −76.1. MS *m/z* (relative intensity): 300 (0.50), 299 (4.34), 174 (11.30), 173 (100), 92 (37.57), 79 (44.09), 77 (68.01), 63 (14.51). HRMS: calc. for $C_8H_7F_2IO_2$: 299.9457; found: 299.9450.

3i: White needle. m.p. 88–89°C. IR (KBr) (cm^{-1}): 1783, 1472, 1445, 1238, 1197, 1159, 1045, 1028, 1006, 760, 740. ^1H NMR (CCl_4) δ (ppm): 6.7–8.2 (m), 4.00 (3H, s). MS *m/z* (relative intensity): 374 (6.51), 372 (12.73), 370 (6.48), 293 (35.19), 291 (35.20), 201 (8.26), 199 (8.44), 168 (100), 157 (30.95), 155 (32.29), 75 (28.74), 63 (39.62). Analysis: calc. for $C_{15}H_{14}O_5$: C, 65.75%; H, 5.15%; found: C, 65.76%; H, 5.11%.

*3.2. General procedure for the reactions of **1** with sodium thiophenoxides*

To a 25 ml three-necked round bottomed flask, equipped with stirrer, **5a** (0.54, 4.9 mmol), NaH (75% in oil, 0.16 g, 5 mmol), and DG (5 ml) were added under nitrogen. **1** (1.50 g, 5 mmol) was dropped into the flask slowly. After 5 h, the mixture was poured into water. The aqueous layer was extracted three times with ether (3 × 20 ml). The combined extracts were washed with water (3 × 10 ml) and dried over Na_2SO_4. After the ether had been evaporated, the residue was subjected to chromatography on silica gel to give thiophenyl difluoroiodomethyl ether as an oil, **7a** (0.18 g, 13%), and diphenyldisulfide **6a** (0.28 g, 54%).

7a: Colorless oil. ^1H NMR (CCl_4) δ (ppm): 7.1–7.8 (m). ^{19}F NMR (CCl_4) δ (ppm): −63.0. MS *m/z* (relative intensity): 286 (M^+, 0.26), 177 (CF_2I^+, 0.74), 159 (M^+-I, 100), 109 (12.29), 77 (47.74). Analysis: calc. for $C_7H_5F_2IS$: C, 29.37%; H, 1.74%; found: C, 29.11; H, 1.61.

7b: Colorless oil. b.p. 70–76°C/1 mm Hg. IR (film) (cm^{-1}): 2109, 1897, 1801, 1571, 1474, 1461, 1390, 1301, 1058, 838, 806, 750, 706, 683, 639, 610. ^1H NMR (CCl_4) δ (ppm): 7.1–7.7 (m). ^{19}F NMR (CCl_4) δ (ppm): −61.0. MS *m/z* (relative intensity): 319 (0.40), 196 (2.90), 195 (34.55), 194 (9.46), 193 (100), 143 (11.23), 111 (18.14). Analysis: calc.for $C_7H_4ClF_2IS$: C, 26.20%; H, 1.24%; found: C, 25.65%; H, 1.06%.

8b: White needle. m.p. 136–138°C. IR (film) (cm^{-1}): 3083, 1907, 1715, 1635, 1570, 1474, 1452, 1390, 1270, 1095, 1084, 1048, 1026, 1017, 970, 956, 898, 877, 827, 753, 711, 660. ^1H NMR (CCl_4) δ (ppm): 7.3–7.7 (m). ^{19}F NMR (CCl_4) δ (ppm): −28.0. MS *m/z* (relative intensity): 337 (9.17), 335 (12.74), 195 (77.22), 193 (100), 143 (25.61), 111 (37.69). Analysis: calc. for $C_{13}H_8Cl_2F_2I_2S_2$: C, 49.29%; H, 2.37%; found: C, 49.24%; H, 2.17%.

9b: colorless oil. b.p. 46–52/1 mm Hg. IR(film) (cm^{-1}): 2970, 1898, 1643, 1573, 1476, 1443, 1391, 1320, 1298, 1071, 1043, 1018, 830, 792, 765, 743, 705, 683, 604. ^1H NMR ($CDCl_3$) δ (ppm): 7.41 (4H, m), 7.00–6.62 (1H, t, $J_{HF} = 56.6$ Hz). ^{19}F NMR ($CDCl_3$) δ (ppm): 13.83 (d, $J_{FH} = 56.6$ Hz). MS *m/z* (relative intensity): 196 (40.52), 195 (17.50), 194 (100), 146 (37.85), 145 (29.87), 144 (97.54), 143 (56.47), 108 (55.35).

*3.3. The preparation of **8b** from **7b** and the inhibition of the experiment*

The thiophenol **5b** (0.07 g, 0.5 mmol), NaH (75% in oil, 0.02 mg, 0.5 mmol) were reacted in DMF (5 ml) under nitrogen for an hour. To this solution, **7b** (0.15 g, 0.5 mmol) was added. The mixture was stirred at room temperature for an hour. After work-up as usual, **8b** (0.11 g, 65%) was obtained.

A parallel experiment, i.e., with and without *p*-PNB (20 mmol%), of the same procedure(0.5 mmol of **7b** and 0.5 mmol of *p*-$ClC_6H_4S^-$ in DMF) were run under nitrogen at room temperature. After 10 min, the conversion of **7b** was 60% determined by the decrease of signal $ICF_2SC_6H_4Cl$-*p* (−61.0 ppm) in ^{19}F NMR spectroscopy while that was only 30% in the presence of *p*-PNB. Both reactions did not continue if the experiments were exposed to air at this moment.

*3.4. The attempt to prepare **10c** from **4c***

The phenol **2c** (0.28 g, 3 mmol) and NaH (75% in oil, 0.09 g, 3 mmol) were reacted in DMF (5 ml) under nitrogen for an hour. Then, **4c** (0.27 g, 1 mmol) was added and the mixture was stirred at room temperature for 5 h. After work-up as usual, **4c** was recovered 0.15 g (55%) and none of **3c** was detected.

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