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Photo-induced electron-transfer reaction of aryl perfluoroalkanesulfonates with anilines

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Abstract

Irradiation of mixtures of aryl perfluoroalkanesulfonates ($R_fSO_3C_6H_4X$-*p*, X = H, Cl and Me) (**1**) and aniline (**2a**), *N,N*-dimethylaniline (**2b**) or *N,N*-dimethylaniline (**2c**) results in the formation of 2-coupling products **3** and 4-coupling products **4**. However, in the reactions of **2b** and **2c**, in addition to **3** and **4**, arenes **5** and *N*-methylaniline (**6a**) or *N*-ethylaniline (**6b**) are also detected. The presence of *p*-dinitrobenzene, Bu^t_2NO and hydroquinone suppresses the reaction significantly. A photo-induced electron-transfer mechanism is proposed.

Introduction

It has been reported [1] that many aromatic compounds undergo electron-transfer reactions as acceptors, and of these aryl halides have been studied most widely. Although aryl diethyl phosphates afforded anilines upon treatment with potassium amide via an electron-transfer mechanism [2], a second important class of phenol derivatives, i.e. aryl perfluoroalkanesulfonates, were incapable of undergoing similar reactions because of the occurrence of a facile nucleophilic substitution reaction resulting in ready S–O bond cleavage [3]. Previously, the palladium-catalyzed coupling of aryl perfluoroalkanesulfonates (**1**) with alkynes, alkenes, organometallic reagents or other reagents such as carbon monoxide/alkanols was the only method reported as resulting in C–O bond cleavage in these compounds [4]. Aryl perfluoroalkanesulfonates (**1**) are readily prepared from perfluoroalkanesulfonyl fluorides and phenols [3], and it was considered desirable to investigate other simple approaches to the dehydroxylation of phenols. In this paper, we describe the results obtained from photochemical reactions of **1** with anilines.

Experimental

All melting points are uncorrected. ^1H NMR spectra were recorded on an XL-200 instrument (200 MHz) using TMS as an external standard. ^{19}F NMR spectra were undertaken on a Varian EM-360L model instrument (60 MHz) using CF_3COOH as an external standard. Mass spectra were recorded on a Finnigan-4401 instrument and IR spectra (KBr pellets) were obtained on a Shimadzu-440 model spectrometer. Gas–liquid chromatography was undertaken on a Shanghai-107 model instrument using a TQ column (2 m×3 mm). All reagents were purified before use. Silica gel (10–40 μ) was used for column chromatography.

Typical procedure

Under a nitrogen atmosphere, a stirred mixture of **2b** (12.1 g, 100 mmol) and **1b** (3.74 g, 10 mmol) contained in a Pyrex flask connected to a cold trap (−78 °C) was irradiated with a medium-pressure mercury lamp (450 W) at a distance of 8 cm for 21 h. Benzene (0.19 g, 22%) was obtained in the cold trap. The mixture in the flask was washed with aqueous $NaHCO_3$ solution (10%) (3×5 ml), dried ($MgSO_4$) and distilled under reduced pressure. GLC analyses indicated that *c*. 18% (based on **1b**) of *N*-methylaniline (**6a**) remained in the distillate. The residue was subjected to column chromatography on silica gel using ether petroleum ether (1:5) as eluent to give bis (*p*-dimethylaminophenyl)methane (**8**) (0.51 g, 20%), 2-dimethylaminobiphenyl (**3b**) (0.63 g, 32%) and 4-dimethylaminobiphenyl (**4b**) (0.43 g, 22%).

Compound **8**: M.p. 89–90 °C (lit. value [5] 91 °C). IR ν_{max} (cm^{-1}): 2860; 1605; 1560; 1510; 1440; 1335; 1220; 1155; 1060; 890; 825. ^1H NMR ($CDCl_3$) δ: 2.78 (12H, s, Me–H); 3.72 (2H, s, CH_2–H); 6.57 (4H, d, J = 9.0 Hz); 6.98 (4H, d, J = 9.0 Hz) ppm. MS *m/z*(%): 255 ($M^+ + 1$, 19); 254 (M^+, 80); 253 ($M^+ - H$, 100); 237 ($M^+ - CH_5$, 17); 210 (25).

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Compound **3b**: Oil [6]. IR ν_{max} (cm^{-1}): 2960; 1500; 1450; 1380; 1200; 1145; 960; 760. ^1H NMR ($CDCl_3$) δ: 2.63 (6H, s, Me−H); 6.42–7.12 (4H, m); 7.34 (5H, s) ppm. MS *m/z*(%): 198 ($M^+ + 1$, 100); 197 (M^+, 46); 196 (32); 181(24); 152(21); 99(10); 76(12).

Compound **4b**: M.p. 119–121 °C (lit. value [7] 120 °C). IR ν_{max} (cm^{-1}): 2960; 1615; 1530; 1450; 1205; 1040; 780. ^1H NMR ($CDCl_3$) δ: 2.52 (6H, s, Me−H); 6.85 (2H, d, $J = 9.0$ Hz); 7.26 (2H, d, $J = 9.0$ Hz); 7.40 (5H, s) ppm. MS *m/z*(%): 198 ($M^+ + 1$, 18); 197 (M^+, 100); 196 (83); 181 (17); 153 (15); 98 (25); 76 (11).

2-Aminobiphenyl (**3a**): M.p. 53–55 °C (lit. value [8] 51–53 °C). IR ν_{max} (cm^{-1}): 3545; 3500 (NH_2); 1615; 1350; 1105; 1065; 970; 860. ^1H NMR ($CDCl_3$) δ: 3.14 (2H, s, NH_2−H); 6.60–7.15 (4H, m); 7.37 (5H, s) ppm. MS *m/z*(%): 170 ($M^+ + 1$, 25); 169 (M^+, 100); 168 (82); 120 (17); 77 (7).

4-Aminobiphenyl (**4a**): M.p. 52 °C (lit. value [8] 53–54 °C). IR ν_{max} (cm^{-1}): 3500; 3450 (NH_2); 1610; 1245; 1180; 1050; 965. ^1H NMR ($CDCl_3$) δ: 3.12 (2H, s, NH_2−H); 6.85 (2H, d, $J = 6.5$ Hz); 7.15 (2H, d, $J = 6.5$ Hz); 7.34 (5H, s) ppm. MS *m/z*(%): 170 ($M^+ + 1$, 24); 169 (M^+, 100); 168 (48); 120 (18); 83 (24).

2-Diethylaminobiphenyl (**3c**): Oil [9]. IR ν_{max} (cm^{-1}): 2960; 2900; 1610; 1600; 1500; 1450; 1395; 1355; 1265; 1140; 1070; 1005; 965; 815. ^1H NMR ($CDCl_3$) δ: 1.34 (6H, t, $J = 6.0$ Hz); 2.45 (4H, q, $J = 6.0$ Hz); 6.65–7.25 (4H, m); 7.43 (5H, s) ppm. MS *m/z*(%): 226 ($M^+ + 1$, 81); 225 (M^+, 21); 211 (70); 210 (21); 181 ($ArN{=}CH_2^+$, 100); 154 (23); 106 (37).

4-Diethylaminobiphenyl (**4c**): M.p. 135–137 °C (no m.p. quoted in lit. [10]). IR ν_{max} (cm^{-1}): 2955; 1605; 1600; 1495; 1390; 1345; 1265; 1145; 1075; 975; 825. ^1H NMR ($CDCl_3$) δ: 1.34 (6H, t, $J = 6.0$ Hz, Me−H); 2.41 (4H, q, $J = 6.0$ Hz, CH_2−H); 6.63 (2H, d, $J = 8.5$ Hz); 7.30 (2H, d, $J = 8.5$ Hz); 7.45 (5H, s) ppm. MS *m/z*(%): 226 ($M^+ + 1$, 100); 225 M^+, 43); 196 (21), 77 (9).

2-Dimethylamino-4′-chlorobiphenyl (**3d**): M.p. 67–69 °C. Analysis: Calc. for $C_{14}H_{14}NCl$: C, 72.55; H, 6.10; N, 6.05; Cl, 15.30%. Found: C, 71.99; H, 5.62; N, 5.87; Cl, 15.52%. IR ν_{max} (cm^{-1}) 2955; 1605; 1545; 1385; 1200; 1095; 945; 875. ^1H NMR (acetone-d_6) δ: 3.02 (6H, s, Me−H); 6.72–7.12 (4H, m); 7.43 (2H, d, $J = 8.5$ Hz); 7.55 (2H, d, $J = 8.5$ Hz) ppm. MS *m/z*(%): 234 ($M^+ + 1$, ^{37}Cl, 5); 233 (M^+, ^{37}Cl, 38); 232 ($M^+ - H$, ^{35}Cl, 41); 231 (M^+, ^{35}Cl, 100); 108 (21); 76 (11); 57 (44); 43 (68).

4-Dimethylamino-4′-chlorobiphenyl (**4d**): M.p. 189–191 °C (lit. value [11] 192 °C). IR ν_{max} (cm^{-1}): 2960; 1455; 1285; 1105; 960; 785. ^1H NMR (acetone-d_6) δ: 3.00 (6H, s); 6.86 (2H, d, $J = 8.5$ Hz); 7.42 (2H, d, $J = 8.5$ Hz); 7.55 (2H, d, $J = 8.0$ Hz); 7.63 (2H, d, $J = 8.0$ Hz) ppm. MS *m/z*(%): 234 (M^+1, ^{37}Cl, 5); 233 (M^+, ^{37}Cl, 33); 232 (M^+, ^{35}Cl, 38); 231 (M^+, ^{35}Cl, 100); 230 (79); 215 (13); 152 (25); 116 (32); 107 (25); 76 (16).

2-Dimethylamino-4′-methylbiphenyl (**3e**): Oil. Analysis: Calc. for $C_{15}H_{17}N$: C, 85.25; H, 8.12; N, 6.62%. Found: C, 85.20; H, 7.96; N, 6.43%. IR ν_{max} (cm^{-1}): 2820; 1610; 1500; 1440; 1420; 1330; 1290; 1130; 1010; 945; 880; 820. ^1H NMR ($CDCl_3$) δ: 2.45 (6H, s, NMe_2−H); 2.76 (3H, s, ArMe−H); 6.65–7.13 (6H, m); 7.42 (2H, d, $J = 8.5$ Hz) ppm. MS *m/z*(%): 212 ($M^+ + 1$, 23); 211 (M^+, 100); 210 (93); 197 (19); 196 (19); 152 (13).

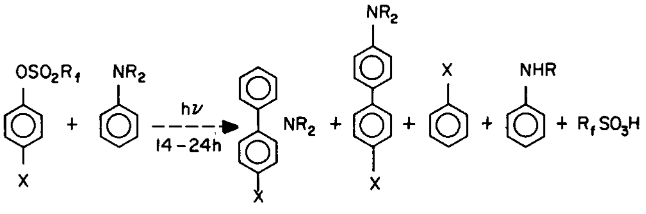
4-Dimethylamino-4′-methylbiphenyl (**4e**): M.p. 120–122 °C. Analysis: Calc. for $C_{15}H_{17}N$: C, 85.25; H, 8.12; N, 6.62%. Found: C, 85.42; H, 8.06; N, 6.23%. IR ν_{max} (cm^{-1}): 2820; 1605; 1505; 1460; 1330; 1290; 1240; 1020; 985; 895; 875. ^1H NMR ($CDCl_3$) δ: 2.34 (3H, s, ArMe−H); 2.62 (6H, s, NMe_2−H); 6.63 (2H, d, $J = 8.0$ Hz); 7.05 (2H, d, $J = 7.0$ Hz); 7.24 (2H, d, $J = 8.0$ Hz); 7.40 (2H, d, $J = 7.0$ Hz) ppm. MS *m/z*(%): 212 ($M^+ + 1$, 33); 211 (M^+, 100); 210 (82); 196 (11); 152 (12).

Results and discussion

Treatment of **1** with anilines **2** under UV irradiation for 14–24 h gave the corresponding aminobiphenyls (**3**, **4**) and arenes (**5**) in good yield (Scheme 1).

The reaction between **1** and **2** (molar ratio, 1:10) proceeded in the absence of solvents at a reaction temperature of *c.* 80 °C as a result of irradiation, which is essential for the reaction. Representative results of the reaction are listed in Table 1. It can be seen from the table that varying the R_f group in **1** has little effect on the product yield.

Only the 2- and 4-aminobiphenyl derivatives were formed as coupling products; the 3-amino isomers were not detected. The reactions involving **2b** and **2c** gave



(1) (2) (3) (4) (5) (6) (7)

1a: $R_f = CF_3$, X = H
1b: $R_f = H(CF_2)_2O(CF_2)_2$, X = H
1c: $R_f = H(CF_2)_6O(CF_2)_2$, X = H
1d: $R_f = CF_3$, X = Cl
1e: $R_f = H(CF_2)_2O(CF_2)_2$, X = Cl
1f: $R_f = H(CF_2)_2O(CF_2)_2$, X = Me
2a: R = H
2b: R = Me
2c: R = Et

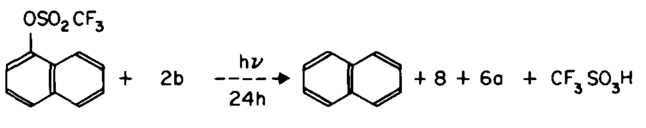
3a and **4a**: X = H, R = H
3b and **4b**: X = H, R = Me
3c and **4c**: X = H, R = Et
3d and **4d**: X = Cl, R = Me
3e and **4e**: X = R = Me
5a: X = H
5b: X = Cl
5c: X = Me
6a: R = Me
6b: R = Et

Scheme 1.

TABLE 1. Photo-induced reactions of phenyl perfluoroalkanesulfonates (**1**) with anilines (**2**) (**1**/**2** = 1:10)

Entry No.	1	2	Time (h)	Conversion[a] (%)	Product (%)			
					3[b]	4[b]	5[c]	6[c]
1	**1a**	**2a**	18	68	**3a**(42)	**4a**(22)	–	
2	**1b**	**2a**	20	70	**3a**(40)	**4a**(25)	–	
3	**1c**	**2a**	24	72	**3a**(41)	**4a**(23)	–	
4	**1a**	**2b**	20	85	**3b**(34)	**4b**(21)	**5a**(24)	**6a**(25)
5	**1b**	**2b**	21	84	**3b**(32)	**4b**(20)	**5a**(22)	**6a**(22)
6[d]	**1b**	**2b**	21	52	**3b**(24)	**4b**(14)	**5a**(12)	**6a**(10)
7[e]	**1b**	**2b**	21	45	**3b**(21)	**4b**(10)	**5a**(12)	**6a**(12)
8[f]	**1b**	**2b**	21	42	**3b**(21)	**4b**(10)	**5a**(10)	**6a**(9)
9[g]	**1b**	**2b**	20	42	**3b**(20)	**4b**(11)	**5a**(10)	**6a**(11)
10	**1a**	**2c**	18	78	**3c**(30)	**4c**(21)	**5a**(17)	**6b**(18)
11	**1b**	**2c**	20	75	**3c**(38)	**4c**(20)	**5a**(14)	**6b**(15)
12	**1d**	**2b**	14	82	**3d**(34)	**4d**(24)	**5b**(18)	**6a**(18)
13	**1e**	**2b**	18	84	**3d**(32)	**4d**(22)	**5b**(11)	**6a**(10)
14	**1f**	**2b**	20	64	**3e**(22)	**4e**(17)	**5c**(20)	**6a**(22)
15	**1g**	**2b**	24	54			**5d**(50)	**6a**(48)

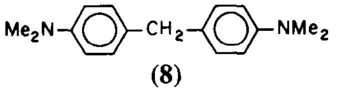
[a] Determined by ^{19}F NMR spectroscopy.
[b] Isolated yields based on **1**.
[c] Determined by GLC methods.
[d] 20 mol% of *p*-DNB added.
[e] 20 mol% of Bu^t_2NO added.
[f] 20 mol% of HQ added.
[g] The reaction proceeded in MeCN (**1b**/**2b** = 1:3).



(1g) **(5d)**

Scheme 2.

mixtures of arenes **5** and N-alkylanilines (**6a** or **6b**), respectively. Unexpectedly, compound **8** (*c.* 20%) was also obtained from the reaction involving **2b**.

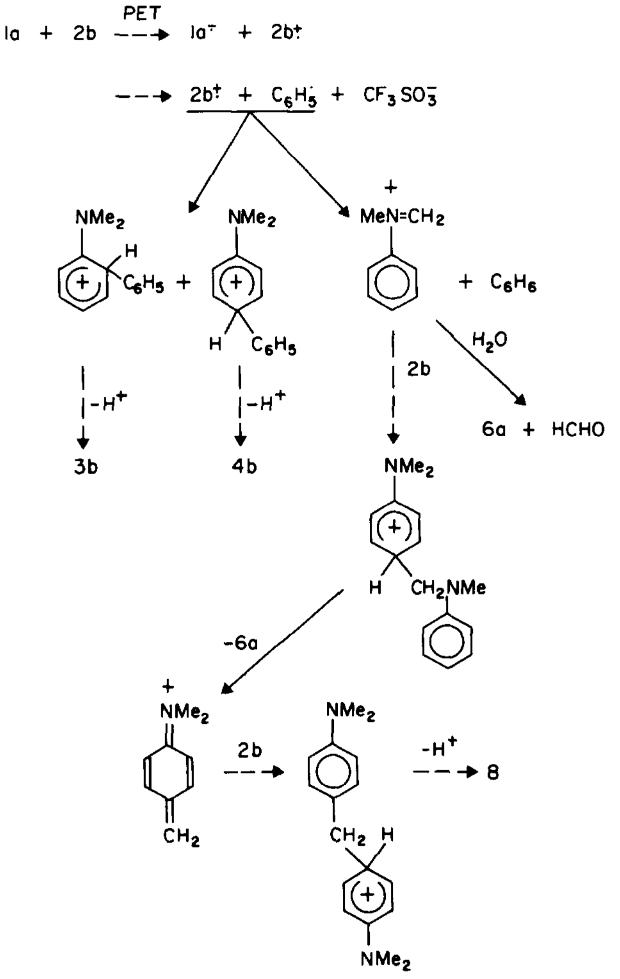


(8)

However, analogous products were not produced in the reaction of **1** with **2a** or **2c**. Treatment of 1-naphthyl trifluoromethanesulfonate (1 g) with **2b** under similar conditions gave naphthane (**5d**) (50%), together with **6a** (48%) and **8** (18%). No coupling products corresponding to **3** and **4** were obtained (Scheme 2).

It has been reported that methyl benzenesulfonate does not undergo C–O bond cleavage when irradiated in methanol [12]. Thus, it seems reasonable to infer that UV irradiation does not directly initiate C–O bond cleavage in **1**. Since electron scavengers such as *p*-dinitrobenzene (DNB) and Bu^t_2NO and the free-radical inhibitor hydroquinone (HQ) suppress the reaction significantly (see Table 1), the latter may involve an electron-transfer mechanism, i.e. **1** accepting an electron from **2** to generate the radical anion $\mathbf{1}^{\cdot-}$ and cation $\mathbf{2}^{\cdot+}$. The radical anion $\mathbf{1}^{\cdot-}$ then decomposes to yield an aryl radical which either combines with $\mathbf{2}^{\cdot+}$ to give the coupled products **3** and **4** or abstracts hydrogen from the α-carbon of an R group giving arenes **5** and anilines **6** (Scheme 3). The formation of **8** may take place in a similar manner to that reported [13, 14] as shown in Scheme 3 (using the reaction of **1a** with **2b** as an example).

It has also been reported that the amine **6a** is produced in the photo-induced reaction of **2b** with aryl halides, i.e. the aryl radicals formed do not attack the aromatic ring but only abstract hydrogen from a methyl group of **2b** [14, 15]. In the present work using **2b** and **2c**, both phenylation and hydrogen abstraction by the intermediate phenyl radicals occurred. However, in the reaction of **2a** with **1**, the phenyl radical only attacked the benzene ring of the radical cation $\mathbf{2a}^{\cdot+}$ resulting in the formation of **3a** and **4a**. The reaction of the naphthyl derivative **1g** with **2b** did not give the cor-



Scheme 3.

responding coupling products, probably because of the greater steric hindrance of the naphthyl radical.

Acknowledgement

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