Journal of Fluorine Chemistry, *43* (1989) 53–66

Received: June 29, 1988; accepted: November 3, 1988

NUCLEOPHILIC ADDITION OF DIFLUOROMETHYL PHENYL SULFONE TO ALDEHYDES AND VARIOUS TRANSFORMATIONS OF THE RESULTING ALCOHOLS

G. PATRICK STAHLY

Ethyl Technical Center, P. O. Box 14799, Baton Rouge, Louisiana 70898 (U.S.A.)

SUMMARY

Nucleophilic addition of difluoromethyl phenyl sulfone (1) to various aldehydes occurred in a two phase system (50% aqueous sodium hydroxide, dichloromethane, Aliquat® 336) to give difluoro(phenylsulfonyl)methyl substituted alcohols (2-8). The product alcohol derived from para-tolualdehyde was converted to the difluoromethylated alcohol by desulfonylation and to the α, ß, ß-trifluorostyrene by a fluorination-elimination sequence. In the absence of aldehydes, 1 reacted in the two phase system to give difluoro(phenylsulfonyl)methyl phenyl sulfide (9). The pathway of the latter conversion was studied.

INTRODUCTION

Difluoromethyl phenyl sulfone (1) can be easily synthesized using inexpensive $CHClF_2$ (Freon-22®) as the source of the fluorinated carbon atom. However, only a few studies of the chemistry of this material have been published. It was shown that 1 is deprotonated by base to give the difluoro(phenylsulfonyl)methide ion, which affords difluorocarbene by expulsion of the benzenesulfinate ion [1]. In another case, treatment of 1 with potassium tert-butoxide in the presence of an α,ß-unsaturated ketone resulted in Michael addition rather than α-elimination to produce

0022-1139/89/$3.50

difluorocarbene [2]. As part of an effort to uncover other nucleophilic reactions of 1, I found that 1 reacts with aldehydes under the influence of base to give difluoromethyl-(phenylsulfonyl) alcohols. These products can be further transformed into various fluorine-containing materials.

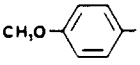
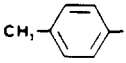
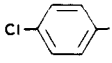
RESULTS AND DISCUSSION

Reaction of sulfone 1 and various aldehydes in a two phase system consisting of 50% aqueous sodium hydroxide, an organic solvent (dichloromethane or toluene), and a catalytic amount of Aliquat® 336 (standard conditions) afforded alcohols 2-8 (Table 1). It is known that similar conditions bring about addition of non-fluorinated sulfones to aldehydes [3].

TABLE 1

$PhSO_2CHF_2$ + RCHO $\xrightarrow[CH_2Cl_2]{50\%\ NaOH}$ R-CH(OH)CF_2SO_2Ph

1 2-8

R	Product Number	Yield (%)
	2	90
	3	89
	4	80
	5	88
	6	81
$(CH_3)_2CH-$	7	73
$(CH_3)_3C-$	8	90

The data in Table 1 show that aromatic aldehydes as well as α-branched aliphatic aldehydes gave addition products in good yields. In certain cases other reactions occurred rather than the desired addition. For example, 1-hexanal afforded aldol products and 4-nitrobenzaldehyde afforded Cannizzaro products. It is known that non-α-branched aldehydes readily undergo aldol reactions [4] and that electron withdrawing substituents increase the rate of the Cannizzaro reaction of aromatic aldehydes [5]. In fact, the latter reaction was shown to compete with the desired addition in certain cases. Cannizzaro products were observed in the product mixtures arising from reactions of benzaldehyde, 4-chlorobenzaldehyde, and 2-furaldehyde. Use of excesses of the aldehydes allowed the desired reactions to occur in good yields based on sulfone.

Treatment of 1 under standard conditions in the absence of any aldehyde resulted in a slow but clean conversion to sulfide-sulfone 9. Supportive evidence for the structure of 9 was obtained by its oxidation to bis-sulfone 10. A plausible mechanistic explanation for the formation of 9 is outlined in Scheme 1.

$PhSO_2CF_2SPh$ (9)

$PhSO_2CF_2SO_2Ph$ (10)

SCHEME 1

$$PhSO_2CHF_2 \xrightarrow[CH_2Cl_2]{50\%\ NaOH} PhSO_2CF_2Na \longrightarrow PhSO_2Na + CF_2 \qquad (a)$$

$$PhSO_2Na + CF_2 \xrightarrow[CH_2Cl_2]{50\%\ NaOH} PhSSPh + COF_2 \qquad (b)$$

$$PhSO_2CF_2Na + PhSSPh \longrightarrow \underset{9}{PhSO_2CF_2SPh} + PhSNa \qquad (c)$$

The reaction products shown in equation (a) were established by Hine and Porter [1]. The intermediacy of the benzenesulfinate ion is supported by experimental results from the reaction of 1 and sodium para-toluenesulfinate under standard conditions, which gave a mixture of all possible compounds (9, 11-13)*.

$$PhSO_2CHF_2 \; (1) + MeC_6H_4SO_2^-Na^+ \xrightarrow[CH_2Cl_2]{50\%\ NaOH} RC_6H_4SO_2CF_2SC_6H_4R'$$

9: R=R'=H
11: R=Me, R'=H
12: R=H, R'=Me
13: R=R'=Me

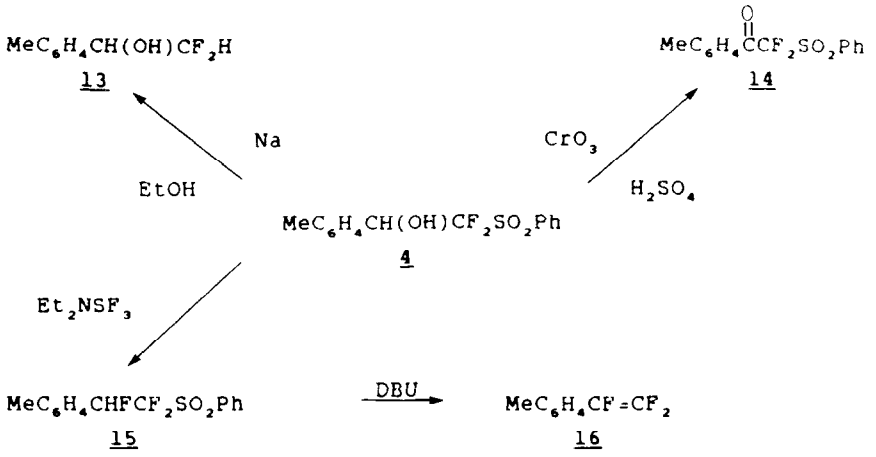
It was recognized that diphenyl disulfide might be an intermediate in the formation of 9 when sodium benzenesulfinate was exposed to standard conditions under an atmosphere of $CHClF_2$, affording a mixture of 1, 9, and diphenyl disulfide. The difluorocarbene formed under such conditions reacted with the benzenesulfinate ion either by addition, giving 1, or by deoxygenation, leading eventually to the disulfide. Such deoxygenation by carbenes has precedent. Dichlorocarbene was shown to react with dimethyl sulfoxide to give dimethyl sulfide and phosgene [6]. Presumably sodium benzenesulfinate is similarly deoxygenated by difluorocarbene to sodium thiophenoxide, which is readily dimerized by air [7].

---

* The location of methyl groups in compounds 11-13 was determined by mass spectrometry. The spectrum of the parent (9) exhibits the molecular ion (m/z 300) as well as fragments corresponding to the C_6H_5 (m/z 77) and $C_6H_5SCF_2$ (m/z 159) ions. The latter ions also result from compound 11, which is methylated only in the sulfone-bound aromatic ring. On the other hand, compounds methylated in the sulfide-bound ring give rise to C_7H_8 (m/z 96) and $C_7H_8SCF_2$ (m/z 173) ions. Thus, compound 11: m/z 314 (M^+), 159, and 77; compound 12: m/z 314 (M^+), 173, and 96; compound 13: m/z 328 (M^+), 173, and 96.

Finally, the rapid reaction of 1 with disulfides was demonstrated. Treatment of an equimolar mixture of 1 and diphenyl disulfide under standard conditions afforded 9 in 92% yield. In addition, reaction of 1 and di-para-tolyl disulfide gave only compound 12 (see footnote p. 56).

In order to demonstrate the utility of alcohols 2-8 as intermediates to other fluorinated materials, some reactions of one of these (compound 4) were carried out. The transformations are outlined in Scheme 2.



SCHEME 2

Desulfonylation of 4 was accomplished using sodium and ethanol in tetrahydrofuran and afforded the known difluoroalcohol 13 [8] in 49% isolated yield. This reaction completes a sequence ($CHClF_2$ → 1 → 4 → 13) which demonstrates the utility of 1 as a transfer agent of the difluoromethide ion from $CHClF_2$ to tolualdehyde.

Jones oxidation of 4 gave ketone 14 in 95% isolated yield.

Treatment of 4 with diethylaminosulfur trifluoride (DAST) afforded trifluorosulfone 15 in 71% isolated yield. Elimination of benzenesulfinic acid from 15 gave the known [9] styrene 16. Trifluorostyrenes are useful as polymer precursers [10] and the sequence 1 → 4 → 15 → 16 demonstrates a potentially general method for production of ring-functionalized analogs.

EXPERIMENTAL

General

Melting points were determined with a Fischer-Johns hot stage melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian EM-390 or a GE/NIC NT-360 spectrometer. Chemical shifts are reported in parts per million relative to tetramethylsilane (^{1}H) or fluorotrichloromethane (^{19}F). Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer. Mass spectra were obtained on a Finnigan 4023 gas chromatograph/mass spectrometer equipped with a 50-M SE-52 fused silica capillary column. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparative thin layer chromatography (PTLC) was carried out on commercially prepared silica gel plates (Analtech) and visualization was by ultraviolet light. Petroleum ether refers to the fraction of bp 35-60°C. Aliquat® 336 is tricaprylylmethylammonium chloride.

Sulfone 1 was synthesized essentially as previously described. Difluoromethylation of thiophenol was carried out in a Fisher-Porter aerosol compatibility bottle under $CHClF_2$ gas, but otherwise conditions were as described by Miller and Thanassi for the analogous reaction of phenol [11]. Hydrogen peroxide oxidation of the resulting difluoromethyl phenyl sulfide afforded 1, as reported by Hine and Porter [1].

2,2-Difluoro-1-phenyl-2-phenylsulfonylethanol (2)

A mixture of 100 mg (0.52 mmol) of difluoromethyl phenyl sulfone (1), 1.0 mL of dichloromethane, 1.0 mL of 50% aqueous sodium hydroxide and 20 mg (0.050 mmol) of Aliquat 336 was stirred vigorously for 10 min and treated with a solution of 0.16 mL (1.6 mmol) of benzaldehyde in 0.5 mL of dichloromethane. Vigorous stirring was continued for 4 h and the resulting mixture was poured into 20 mL of 1M HCl. Extraction of the aqueous mixture with three 10 mL portions

of dichloromethane followed by combination, drying ($MgSO_4$), and concentration in vacuo of the organic layers gave a residue which was purified by preparative TLC (two 2mm plates eluted with dichloromethane), affording 140 mg (90% yield) of 2 as a solid. Crystallization from toluene provided an analytical sample: mp 77-79°C; IR (neat) 3503, 3064, 2922, 1447, 1335, 1312, 1197, 1154, 1113, 1089, 996, 738, 715, 698, 685, 585, 558 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.54 (broad s, 1H), 5.54 (dd, 1H, J_{HF} = 21, 3 Hz), 7.20-8.10 (m, 10H); ^{19}F NMR ($CDCl_3$) -106.4 ppm (dd, 1F, J_{FF} = 238 hz, J_{HF} = 3Hz), -121.6 ppm (dd, 1F, J_{FF} = 238 Hz, J_{HF} = 21 Hz); mass spectrum (70 eV) m/z (relative intensity) 298 (8, M^+), 156(18), 109(31), 107(100), 79(30), 78(18), 77(56), 51(20). Anal. Calcd. for $C_{14}H_{12}F_2O_3S$: C, 56.37; H, 4.06%. Found: C, 56.58; H, 4.08%.

The following compounds were prepared by similar procedures.

2,2-Difluoro-1-(4-methoxyphenyl)-2-phenylsulfonylethanol(3)

From 100 mg (0.52 mmol) of 1, 0.20 mL (1.6 mmol) of 4-methoxybenzaldehyde, 1.5 mL of dichloromethane, 1 mL of 50% aqueous sodium hydroxide and 20 mg (0.050 mmol) of Aliquat 336 was obtained a product mixture which was purified by PTLC (two 2 mm plates eluted with dichloromethane) to give 152 mg (89% yield) of 3 as a solid. Crystallization from toluene provided an analytical sample: mp 93-95°C; IR (KBr) 3512, 3062, 2932, 1608, 1511, 1447, 1328, 1313, 1249, 1180, 1158, 1116, 1085, 1029, 995, 792, 683, 600, 595, 579 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.62 (d, 1H, J = 3Hz), 3.77 (s, 3H), 5.50 (apparent dt, 1H, J = 21, 3Hz), 6.80-7.02 (m, 2H), 7.26-8.13 (m, 7H); ^{19}F NMR ($CDCl_3$) -104.6 ppm (dd, 1F, J_{FF} = 236 Hz, J_{HF} = 2 Hz), -119.9 ppm (dd, 1F, J_{FF} = 237 Hz, J_{HF} = 21 Hz); mass spectrum (70 eV) m/z (relative intensity) 328 (12, M^+), 137(100), 109(20), 77(20). Anal. Calcd. for $C_{15}H_{14}F_2O_4S$: C, 54.87; H, 4.30%. Found: C, 54.90; H, 4.33%.

2,2-Difluoro-1-(4-methylphenyl)-2-phenylsulfonylethanol (4)

From 100 mg (0.52 mmol) of 1, 0.19 mL (1.6 mmol) of 4-methylbenzaldehyde, 1.5 mL of dichloromethane, 1 mL of 50% aqueous sodium hydroxide and 20 mg (0.050 mmol) of Aliquat 336 was obtained a product mixture which was purified by PTLC (one 2mm plate eluted with dichloromethane) to give 129 mg (80% yield) of 4 as a solid. Crystallization from toluene provided an analytical sample: mp 98-100°C; IR (KBr) 3534, 3059, 3031, 2920, 1450, 1325, 1314, 1159, 1106, 1087, 1002, 782, 722, 683 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H), 3.38 (d, 1H, J = 3 Hz), 5.51 (apparent dt, 1H, J = 21, 3 Hz), 7.10-8.10 (m, 9H); ^{19}F NMR ($CDCl_3$) -104.5 ppm (dd, 1F, J_{FF} = 237 Hz, J_{HF} = 2 Hz), -119.7 ppm (dd, 1F, J_{FF} = 238 Hz, J_{HF} = 21 21 Hz); mass spectrum (70 eV) m/z (relative intensity) 312 (6, M^+), 121(100), 93(20), 77(26). Anal. Calcd. for $C_{15}H_{14}F_2O_3S$: C, 57.68; H, 4.52%. Found: C, 57.62; H, 4.66%.

1-(4-Chlorophenyl)-2,2-difluoro-2-phenylsulfonylethanol (5)

A reaction mixture generated from 100 mg (0.52 mmol) of 1, 225 mg (1.6 mmol) of 4-chlorobenzaldehyde, 1.5 mL of dichloromethane, 1 mL of 50% aqueous sodium hydroxide and 20 mg (0.050 mmol) of Aliquat 336 was poured into 20 mL of 1N HCl. Extraction of the aqueous mixture with three 10 mL portions of ethyl acetate followed by combination, drying ($MgSO_4$), and concentration in vacuo of the organic layers gave a residue which was purified by preparative TLC (two 2 mm silica gel plates eluted with 10% ethyl acetate in toluene), affording 153 mg (88% yield) of 5 as a solid. Crystallization from toluene provided an analytical sample: mp; 100-102°C; IR (KBr) 3530, 3060, 2921, 1491, 1446, 1332, 1157, 1120, 1113, 1090, 1016, 1005, 784, 723, 683, 589, 538 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.62 (broad s, 1H), 5.56 (dd, 1H, J = 20, 3 Hz), 7.26-8.13 (m, 9H); ^{19}F NMR ($CDCl_3$) -104.8 ppm (dd, 1F, J_{FF} = 238 Hz, J_{HF} = 3 Hz), -119.2 ppm (dd, 1F, J_{FF} = 238 Hz, J_{HF} = 20 Hz); mass spectrum (70 eV) m/z (relative intensity) 332 (9, M^+), 143(44), 141(100), 77(33). Anal. Calcd. for $C_{14}H_{11}ClF_2O_3S$: C, 50.53; H, 3.33%. Found: C, 50.49; H, 3.41%.

α-(Difluoro[phenylsulfonyl]methyl)-2-furanmethanol (6)

From 100 mg (0.52 mmol) of 1, 0.13 mL (1.6 mmol) of 2-furaldehyde, 1.5 mL of dichloromethane, 1 mL of 50% aqueous sodium hydroxide, and 20 mg (0.050 mmol) of Aliquat 336 was obtained a product mixture which was subjected to preparative TLC (two 2 mm silica gel plates eluted with dichloromethane), affording a mixture of 6 and 2-furanmethanol. The mixture was dissolved in 5 mL of toluene and the resulting solution was washed with three 5 mL portions of water. Drying ($MgSO_4$) and concentration in vacuo of the toluene layer gave 121 mg (81% yield) of 6 as a solid. Crystallization from toluene provided an analytical sample: mp 72-74°C; IR (KBr) 3501, 3114, 2943, 1448, 1338, 1314, 1201, 1161, 1107, 1089, 1078, 1065, 1017, 994, 924, 800, 770, 757, 711, 686, 600, 586, 532 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.24 (broad s, 1H); 5.66 (dd, 1H, J = 17 Hz, 4 Hz), 6.41-6.69 (m, 2H), 7.48-8.20 (m, 6H); ^{19}F NMR ($CDCl_3$) -106.7 ppm (dd, 1F, J_{FF} = 237 Hz, J_{HF} = 4 Hz); -116.7 ppm (dd, 1F, J_{FF} = 237 Hz, J_{HF} = 17 Hz); mass spectrum (70 eV) m/z (relative intensity) 288 (5, M^+), 97(100), 77(20), 51(20). Anal. Calcd. for $C_{12}H_{10}F_2O_4S$: C, 50.00; H, 3.50%. Found: C, 49.87; H, 3.59%.

1,1-Difluoro-3-methyl-1-phenylsulfonyl-2-butanol (7)

From 100 mg (0.52 mmol) of 1, 0.15 mL (16 mmol) of 2-methylpropanal, 1.5 mL of dichloromethane, 1 mL of 50% aqueous sodium hydroxide, and 20 mg (0.050 mmol) of Aliquat 336 was obtained a product mixture which was purified by PTLC (one 2 mm plate eluted with dichloromethane followed by two 1 mm alumina plates eluted with toluene) to give 101 mg (73% yield) of 7 as an oil: IR (neat) 3522, 3066, 2967, 1447, 1333, 1312, 1161, 1138, 1110, 1084, 1069, 1029, 996, 756, 714, 686, 634, 600, 591, 536 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 apparent t, 6H, J = 6 Hz), 2.05-2.45 (m, 1H), 3.13 (broad s, 1H), 4.39 (apparent dt, 1H, J = 22, 5 Hz), 7.50-8.13 (m, 5H); ^{19}F NMR ($CDCl_3$) -106.9 ppm (dd, 1F, J_{FF} = 235 Hz, J_{HF} =7 Hz), -115.6 ppm (ddd, 1F, J_{FF} = 235 Hz, J_{HF} = 22, 8 Hz); mass

spectrum (70 eV) m/z (relative intensity) 264 (2, M^+), 143(37), 142(59), 125(25), 78(100), 77(80), 73(65), 55(37), 51(59), 43(86), 41(52), 39(31). Anal. Calcd. for $C_{11}H_{14}F_2O_3S$: C, 49.99; H, 5.34%. Found: C, 50.08; H, 5.37%.

1,1-Difluoro-3,3-dimethyl-1-phenylsulfonyl-2-butanol (8)

From 100 mg (0.52 mmol) of 1, 0.17 mL (16 mmol) of 2,2-dimethylpropanal, 1.5 mL of dichloromethane, 1 mL of 50% aqueous sodium hydroxide, and 20 mg (0.050 mmol) of Aliquat 336 was obtained a product mixture which was purified by PTLC (one 2 mm plate eluted with dichloromethane) to give 130 mg (90% yield) of 8 as a solid. Crystallization from toluene-hexane provided an analytical sample: mp 91-94°C; IR (KBr) 3505, 3057, 2969, 1479, 1449, 1347, 1328, 1314, 1280, 1158, 1119, 1092, 1080, 1042, 989, 756, 708, 687, 594, 527 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (s, 9H), 3.22 (broad d, 1H), 4.14 (apparent dd, ^1H, J = 25, 4 Hz), 7.50-8.11 (m, 5H); ^{19}F NMR ($CDCl_3$) -101.1 ppm (dd, 1F, J_{FF} = 232 Hz, J_{HF} = 2 Hz), -116.0 (dd, 1F, J_{FF} = 232 Hz, J_{HF} = 25 Hz); mass spectrum (70 eV) m/z (relative intensity) 278 (1, M^+), 77(38), 57(100), 51(29), 41(50). Anal. Calcd. for $C_{12}H_{16}F_2O_3S$: C, 51.78; H, 5.80%. Found: C, 51.69; H, 5.77%.

Difluoro(phenylsulfonyl)methyl phenyl sulfide (9)

A mixture of 300 mg (1.6 mmol) of 1, 3 mL of dichloromethane, 3 mL of 50% aqueous sodium hydroxide, and 60 mg (0.15 mmol) of Aliquat 336 was stirred vigorously for 66 h and poured into a solution of 5 mL of 37% HCl in 20 mL of water. Extraction of the aqueous mixture with three 10 mL portions of dichloromethane followed by combination, drying ($MgSO_4$), and concentration in vacuo of the organic layers gave a residue which was purified by preparative TLC (two 2 mm silica gel plates eluted with 30% dichloromethane in petroleum ether), affording 149 mg of 9 as an oil: IR (neat)

3063, 1474 1446, 1441, 1349, 1181, 1170, 1101, 1068, 751, 726, 715, 685, 578, 557, 546 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.20-8.10 (m); ^{13}C NMR ($CDCl_3$) 128.2 (t, J_{CF} = 326 Hz), 129.3, 130.8, 131.0, 135.5, 137.3; mass spectrum (70 eV) m/z (relative intensity) 300 (2, M^+), 186(22), 159(100), 125(63), 109(24), 77(100), 65(20), 51(78), 50(23), 39(22). Anal. Calcd. for $C_{13}H_{10}F_2O_2S_2$: C, 51.99; H, 3.36%. Found: C, 52.12; H, 3.41%.

Bis(phenylsulfonyl)difluoromethane (10)

A mixture of 300 mg (1.0 mmol) of difluoro(phenylsulfonyl)methyl phenyl sulfide (9), 0.30 mL (3.0 mmol) of 30% hydrogen peroxide, and 1 mL of glacial acetic acid was heated at reflux for 1 h, allowed to cool to room temperature, and poured into 10 mL of water. The resulting aqueous mixture was extracted with two 10 mL portions of diethyl ether. The organic layers were combined, washed with one 10 mL portion of 10% Na_2CO_3 and one 10 mL portion of water, dried ($MgSO_4$), and concentrated *in vacuo* to give a solid residue which was crystallized from dichloromethane-hexane to give 271 mg (82% yield) of 10: mp 112-114°C; IR (KBr) 3094, 3066, 2920, 1446, 1364, 1354, 1194, 1171, 1136, 1120, 1081, 750, 729, 716, 679, 570, 555, 530 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.52-8.18 (m); ^{19}F NMR ($CDCl_3$) -106.3 ppm (s); mass spectrum (H_2O CI) m/z (relative intensity) 333 (100, M+1), 141 (28), 77 (28). Anal. Calcd. for $C_{13}H_{10}F_2O_4S_2$: C, 46.98; H, 3.03%. Found: C, 46.92; H, 3.04%.

2,2-Difluoro-1-(4-methylphenyl)ethanol (13)

A solution of 2.0 g (6.4 mmol) of 2,2-difluoro-1-(4-methylphenyl)-2- phenylsulfonylethanol (4) and 1.9 mL (32 mmol) of absolute ethanol in 20 mL of dry tetrahydrofuran was treated with 0.74 g (32 mmol) of sodium spheres. After 90 min. 1 mL of methanol followed by 1 mL of water were added to decompose unreacted sodium, and the mixture was poured into 100 mL of 1M HCl. The resulting aqueous mixture

was extracted with three 50 mL portions of dichloromethane. Combination, drying ($MgSO_4$), and concentration of the organic layers afforded an orange liquid which was short path distilled to give 0.54g (49% yield) of 13; bp 58°C at 0.6 torr (lit [8] 60-62°C at 0.5-0.6 torr); mass spectrum (70 eV) m/z (relative intensity) 172 (17, M^+), 121 (100), 93 (68), 91 (75), 77 (64), 65 (25), 51 (46), 39 (24).

Difluoro(phenylsulfonyl)methyl 4-Methylphenyl Ketone(14)

A mixture of 0.30 g (0.96 mmol) of 4, 0.78 g (1.4 mmol CrO_3) of Jones reagent (solution of 2.3 mL of 96% H_2SO_4, 10 mL of water, and 2.7 g CrO_3), and 3 mL of acetone was heated at reflux for 30 min. After cooling to room temperature the mixture was treated with a little sodium bisulfite to discharge the yellow color and filtered. The filtrate was concentrated in vacuo to give a residue which was dissolved in dichloromethane and dried ($MgSO_4$). Removal of the solvent gave 0.28 g (95% yield) of 14. An analytical sample was obtained by crystallization from toluene-hexane: mp 79-80°C; IR (KBr) 3071, 1684, 1605, 1446, 1352, 1314, 1277, 1146, 1084, 756, 687, 600, 564, 553, 527 cm^{-1}; H^1 NMR ($CDCl_3$) δ 2.42 (s, 3H), 7.28-8.14 (m, 9H); ^{19}F NMR ($CDCl_3$, relative to $CFCl_3$) -102.3 ppm (s); mass spectrum (70 eV) m/z (relative intensity) 310 (3, M^+), 119 (100), 91 (29). Anal. Calcd. for $C_{15}H_{12}F_2O_3S$:C, 58.05; H, 3.90%. Found C, 57.96; H, 4.19%.

2-(4-Methylphenyl)-1-phenylsulfonyl-1,1,2-trifluoroethane (15)

A solution of 0.24 mL (1.8 mmol) of diethylaminosulfur trifluoride in 5 mL of dichloromethane was cooled to -78°C (dry ice-acetone bath) and treated dropwise with a solution of 0.50 g (1.6 mmol) of 4 in 2 mL of dichloromethane. The cooling bath was removed, and 30 min later 2 mL of saturated $NaHCO_3$ was added with vigorous stirring. The organic layer

was removed, washed with one 2 mL portion of water, dried ($MgSO_4$), and concentrated in vacuo to give a residue which was crystallized from toluene-hexane, affording 0.36g (71% yield) of 15: mp 80-82°C; IR (KBr) 2924, 1447, 1352, 1185, 1163, 1117, 1054, 1013, 787, 757, 720, 686, 603, 567, 553 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.36 (s, 3H), 6.10 (ddd, 1H, J_{HF} = 44 18.5 Hz), 7.16-8.07 (m, 9H); ^{19}F NMR ($CDCl_3$) -44.0 ppm (dt, 1F J = 44, 16 Hz), -109.3 ppm (dd, 1F, J = 247, 15 Hz), -118.8 ppm (dt, 1F, J = 248, 17 Hz); mass spectrum (70 eV) m/z (relative intensity) 314 (11, M^+), 172 (41), 123 (100), 77 (31). Anal. Calcd. for $C_{15}H_{13}F_3O_2S$:C, 57.32; H, 4.17%. Found: C, 56.90; H, 4.47%.

1-(4-Methylphenyl)-1,2,2-trifluoroethene (16)

A solution of 25 mg (0.080 mmol) of sulfone 15 and 60 μL (0.40 mmol) of 1.8-diazabicyclo[5.4.0]undec-7-ene in 0.5 mL of benzene was kept in an oil bath at 50-60°C for 2 hours. GC/MS analysis of the solution indicated the presence of a minor amount of starting material and a major amount of styrene 16: mass spectrum (70 eV) m/e (relative intensity) 172 (100, M^+), 171 (37), 151 (30).

ACKNOWLEDGEMENTS

The valuable technical assistance of Mr. D. R. Bell is greatly appreciated. Thanks are due to Dr. L. S. Simeral and Ms. P. K. Landry for NMR data and to Dr. V. O. Brandt and Dr. J. P. Kleiman for GC/MS data.

REFERENCES

1 J. Hine and J. J. Porter, J. Am. Chem. Soc., 82 (1960) 6178.

2 J. A. Edwards, J. H. Fried, and J. S. Mills, U. S. Pat. 3 705 182 (1972).

3 G. Cardillo, D. Savoia, and A. Umani-Ronchi, Synthesis (1975) 453.

4 A. T. Nielsen and W. J. Houlihan, Org. React. 16 (1968) 14.

5 T. A. Geissman, Org. React., 2 (1944) 97.

6 R. Oda, M. Miemo, and Y. Hayashi, Tetrahedron Lett.
7 (1967), 2363.

J. Xan, E. A. Wilson, L. D. Roberts, and N. H. Horton,
8 J. Am. Chem. Soc., 63 (1941) 1139.

C. H. DePuy, A. L. Schultz, J. Org. Chem., 39 (1974)
9 878.

G. V. Kazennikova, T. V. Talalaeva, A. V. Zimin, A. P.
10 Siminov, and K. A. Kocheshkov, Izv. Akad. Nauk SSSR, Otdel, Khim. Nauk (1961) 1063; Chem. Abstr. (1961) 55, 27153i.

J. M. Antonucci in 'Fluoropolymers'; L. A. Wall, Ed.;
11 Wiley Interscience, 1972, Chapter 2.

T. G. Miller and J. W. Thanassi, J. Org. Chem., 25
12 (1960) 2009.