PAPERS

Sterically Crowded Sulfonate Esters: Novel Leaving Groups with Hindered S–O Cleavage

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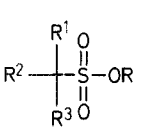
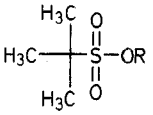
Reagents and procedures for the preparation of *tert*-butyl sulfonate esters **2** and 2,2,2-trifluoro-1,1-diphenylethane sulfonate esters **3** (TDE-sulfonates) are described. In these new sulfonates, S–O-scission is reduced significantly by steric hindrance.

In the alkylation by esters of sulfonic acids (e.g. tosylates, mesylates, triflates), a competing sulfur-oxygen-scission often occurs by attack of the nucleophile (hydroxide ion,[1] alcoholates,[2] carboxylic acid anions,[3] phenolates,[4] thiolates,[5] amines,[5,6] ammonia,[7] alkyl lithium/sodium reagents,[8] dialkylcuprates,[9] Grignard reagents,[10] anion radicals,[11] hydride anion[12]) on the central sulfur atom.

Having met competing S–O-cleavage in several projects, we looked for sulfonic esters in which the substitution at sulfur is sterically prohibited or at least severely hindered by a voluminous alkyl group. From a number of esters **1** (R^1, R^2, R^3 = alkyl, aryl), the *t*-butyl sulfonates **2** and the 2,2,2-trifluoro-1,1-diphenylethane sulfonates **3** (TDE-sulfonates) offered remarkable advanatages.[13–15] As to their nucleofugality, the anion of **2** is expectedly somewhat weaker than the anions of common alkyl sulfonates and the TDE-sufonate ist located between tosylate and triflate, within the region of unsubstituted tresylate **1** ($R^1 = CF_3$, $R^2 = R^3 = H$).[16] In this paper we present detailed protocols for the preparation of the respective reagents and of exemplary esters/amides.



1



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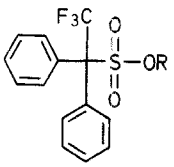


3

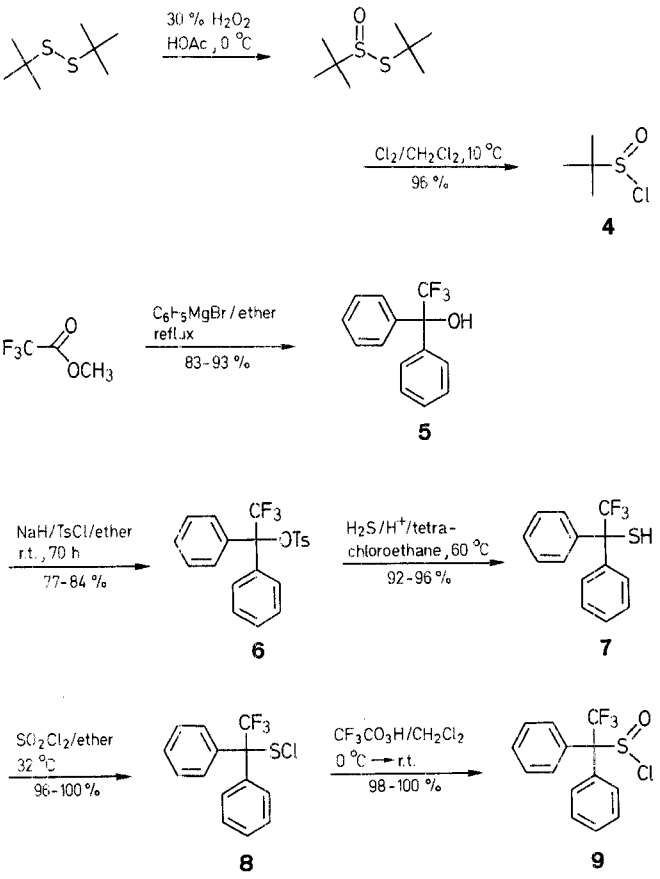
t-Butylsulfinyl chloride **(4)** is obtained in 96% yield from di-*t*-butyldisulfide following published procedures,[17] which have been optimized (Scheme **A**).

Starting material for the reagents **8** and **9** is the alcohol **5**,[18] easily available in high yield (83–93%) from methyl trifluoroacetate and the phenyl Grignard reagent. From **5** and sodium hydride/tosyl chloride, the crystalline tosylate **6**[19] is obtained and this is reacted with hydrogen sulfide in 1,1,2,2-tetrachloroethane at 60 °C to give the mercaptan **7** quantitatively. Crude **7** is transformed into the crystalline sulfenyl chloride **8** by treatment with sulfuryl chloride; after oxidation with exactly one equivalent of trifluoroperacetic acid, the sulfinyl chloride **9** is isolated as a viscous oil which slowly partially crystallizes. Reagent **9** is, in contrast to **8**, rather labile and it can be kept, even at – 70 °C, (nitrogen atmosphere) only for a limited time.

Table 1. *t*-Butyl Sulfinates **11** and *t*-Butyl Sulfonates **2** Prepared

Alcohol/ Phenol	Reaction Conditions	Sulfinates **11c–f** Yield (%)[a]	m.p. (°C)	Molecular Formula[b]	Sulfonates **2a–f** Yield (%)[a]	m.p. (°C) (solvent)	Molecular Formula[b]	m.p. of Corresponding Tosylate **13a–f**
10a	30 min, 0 °C	not isolated		–	65	34–35 (PE, 60–70 °C)[c]	$C_9H_{20}SO_3$ (208.3)	47–48[21]
10b	30 min, 0 °C	not isolated		–	84	between +2 and +20 °C (PE, 30–50 °C)[c]	$C_{13}H_{20}O_4S$ (272.4)	45[22]
10c	30 min, room temp.	78	90	$C_{10}H_{16}O_4S$ (232.3)	89	131 (MeOH)[13,15]	$C_{10}H_{16}O_5S$ (248.3)	134[13] (dec.)
10d	18 h, room temp.	76	81–82	$C_{10}H_{16}O_4S$ (232.3)	90	106–107 (EtOH)[13,15]	$C_{10}H_{16}O_5S$ (248.3)	134–135[13]
10e	70 h, room temp. and 5 h reflux	95	144–146	$C_{14}H_{24}O_6S$ (352.5)	85	169 (MeOH)	$C_{14}H_{24}O_8S$ (384.5)	173–174[13]
10f	16 h, room temp.	95	83–85	$C_{10}H_{12}N_2O_6S$ (288.3)	79	115 (ether)	$C_{10}H_{12}N_2O_7S$ (304.3)	123–124[5]

[a] Pure material after crystallization.
[b] Satisfactory microanalyses obtained: C ±0.22, H ±0.26, N ±0.06, S ±0.26; exception: **2a**, C −0.38; **2b**, C −0.34, S +0.55.
[c] PE = Petroleum ether.



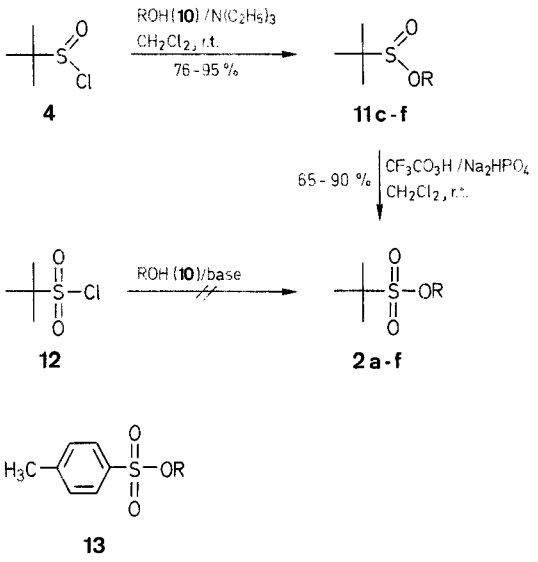
Scheme A

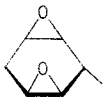
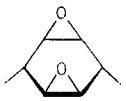
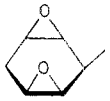
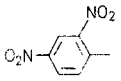
Table 2. IR and ^{1}H-NMR Data of New Compounds **11** and **2**

Compound	IR (KBr) ν(cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS), δ, *J* (Hz) H_α (Alcohol Part)	CMe_3
11c	1175, 1100	4.95 (d, 1H, *J* = 2.5, CHOSO)	1.29
11d	1180, 1120	5.05 (m, 1H, CHOSO)	1.27
11e	1190, 1120	5.07 (m, 2H, CHOSO)	1.26
11f	1185, 1140, 1125	8.83 (d, 1H, *J* = 2.5, 3′-H); 8.47 (dd, 1H, *J* = 2.5, 5′-H, 9.0); 7.73 (d, 1H, *J* = 9.0, 6′-H)[a]	1.41
2a	1370, 1330, 1300, 1215, 1140	3.90 (s, 2H, CH_2OSO_2)[a] [**13a**: 3.66][a,b]	1.46
2b	1395, 1335, 1275, 1210, 1145[c]	4.39 (m, 2H, CH_2OSO_2) [**13b**: 4.17][b]	1.46
2c	1360, 1325, 1300, 1260, 1200, 1135	5.49 (t, 1H, *J* = 3.0, $CHOSO_2$) [**13c**: 5.31][b]	1.56
2d	1335, 1310, 1280, 1260, 1205, 1135	5.43 (m, 1H, $CHOSO_2$) [**13d**: 5.13][b]	1.53
2e	1395, 1335, 1325, 1250, 1210, 1150	5.45 (m, 2H, CH—OSO_2) [**13e**: 5.12][b]	1.54
2f	1400, 1350, 1260, 1235, 1190, 1145	8.92 (d, 1H, *J* = 2.5, 3′-H); 8.58 (dd, 1H, *J* = 2.5, 5′-H, 9.0); 7.94 (d, 1H, *J* = 9.0, 6′-H)[a]	1.66

[a] 90 MHz.
[b] In brackets: values of corresponding tosylate **13**.
[c] Film.

The sulfonates **2** were prepared in overall yields of 65–90% by the reactions of the alcohols/diols/phenols **10** with chloride **4** in the presence of triethylamine as a base, and subsequent oxidation of the sulfinates **11** by peracetic acid (Scheme **B**, Table 1). Emphasizing the efficiency of steric hindrance by the *t*-butyl group, direct esterification by sulfonyl chloride **12**[20] does not yield sulfonates **2**. The oxidation state of sulfur is evidenced by the chemical shift of the protons of the *t*-butyl group (see Table 2). The *t*-butyl sulfonate esters **2** are mostly well crystallizing compounds whose solubility in organic solvents is considerably higher than that of the corresponding tosylates **13**.



2,10,11	R	2,10,11	R
a	*t*-$C_4H_9CH_2$	d	
b	$C_6H_5CH_2O(CH_2)_2$	e	
c		f	

Scheme **B**

For the preparation of the TDE-sulfonates **3**, the alcohols/diols/phenols **10** (Scheme **C**, Table 3) are treated with sodium hydride and sulfenyl chloride **8** in tetrahydrofuran; the resulting sulfenates **14** are oxidized to **3** in buffered dichloromethane solution (Method A). In this manner, the overall yield is generally higher than from Method **B** which, however, is advantageous in the case of substrates containing e.g. epoxide or carboxylic acid ester functions. In the latter, the best results are obtained with *N*-methylimidazole as a base in dichloromethane solution. With sparingly soluble alcohols, this amine is also used as the solvent (example **10e**). Alcohols with bulky groups provide poor yields (e.g. **10a, e**). The application of both methods (A and B) is limited by the presence of groups sensitive towards oxidation, such as olefinic double bonds and sulfide and azo functions.

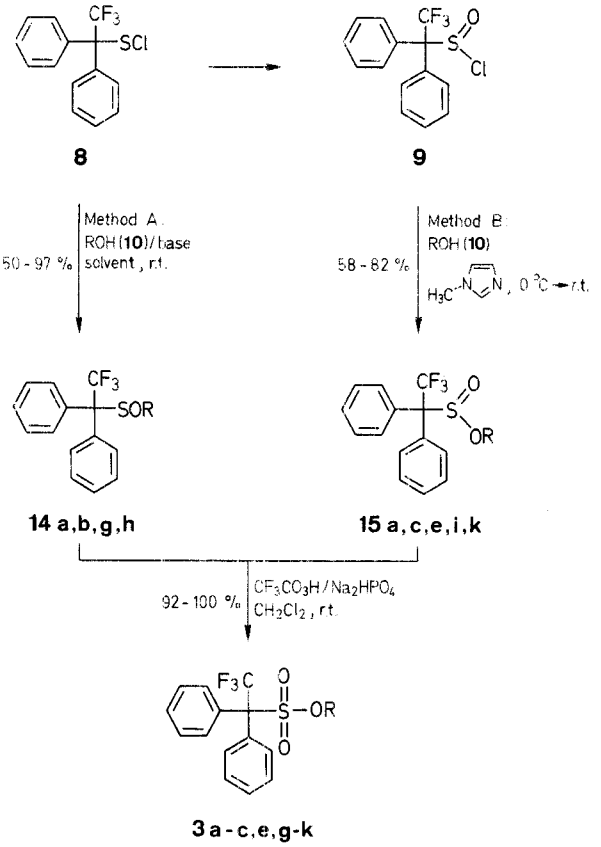
Analogous to the corresponding tosylates **13**, the TDE-sulfonates **3** crystallizes well and can thus be usually purified by crystallization after oxidation of the crude sulfinates **15**. The H_α-protons in the alcohol part of the esters **3** expose a characteristic high-field shift of 0.1–0.5 ppm (compared to **13**) in ^{1}H-NMR spectra (Table 4) as a consequence of the anisotropic effect of the TDE-aromatic groups.

It is noteworthy that, in addition to its application for syntheses of sterically hindered sulfenic/sulfinic/sulfonic acid esters, the stable TDE-sulfenylchloride **8** is suitable for derivatization of amines, ketones and aldehydes (Scheme **D**). Sulfenamide **16** (quantitatively obtained from **8** and 25% aqueous ammonia) condenses with carbonyl compounds (pyridinium-*p*-toluenesulfonate, magnesium sulfate, dichloromethane) to give the moisture-sensitive sulfenimines **17** (yield: 83–89%). With primary and secondary amines, **8** reacts smoothly to yield the weakly basic sulfenamides **18**; the latter are not protonated by 10% aqueous sulfuric acid.[13]

Table 3. TDE-Sulfenates **14**, TDE-Sulfinates **15** and TDE-Sulfonates **3** Prepared

Alcohol/ Phenol (R–OH)	Method	Base/ Solvent	Yield (%) **14**(A)/ **15**(B)	m.p. (°C) (solvent)	Molecular Formula[a]	Yield (%) **14/15** → **3**	m.p. (°C) (solvent)	Molecular Formula[a]	Overall Yield (%) **10** → **3**
10a	A	NaH/ THF	50[b]	22–26	$C_{19}H_{21}F_3OS$ (354.4)	98	99 (PE, 30–50°C)[d]	$C_{19}H_{21}F_3O_3S$ (384.4)	49[c]
10b	A	NaH/ THF	75[b] (94)	oil	$C_{23}H_{21}F_3O_2S$ (418.5)	100	39–41 (PE, 30–50°C/ ether)[d]	$C_{23}H_{21}F_3O_4S$ (450.5)	94[c]
10c	B	*N*-methyl-imidazole/ CH_2Cl_2	82[c]	126–129 (ether/ MeOH)	$C_{20}H_{17}F_3O_4S$ (410.4)	94	164–167 (dec.) (EtOAc/ cyclohexane)	$C_{20}H_{17}F_3O_5S$ (426.4)	77[c]
10e	B	*N*-methyl-imidazole	61[c]	124–125 (MeOH/ EtOAc)	$C_{34}H_{26}F_6O_6S_2$ (708.7)	92	212–214 (MeOH)	$C_{34}H_{26}F_6O_8S_2$ (740.7)	58[c]
10g	A	K-salt/ acetone	97[b]	73 (PE, 30–50°C/ ether)[d]	$C_{20}H_{14}F_3NO_3S$ (405.4)	93	141[c] (ether)	$C_{20}H_{14}F_3NO_5S$ (437.4)	90[c]
10h	A	NaH/ THF	69[b]	viscous oil	$C_{36}H_{36}F_6O_5S_2$ (726.8)	99	viscous oil[f]	$C_{36}H_{36}F_6O_9S_2$ (790.8)	68[b]
10i	B	*N*-methyl-imidazole/ CH_2Cl_2	not isolated	–	–	–	151–152 (ether)	$C_{20}H_{37}F_3O_6SSi$ (598.8)	64[c]
10k	B	*N*-methyl-imidazole/ CH_2Cl_2	58[c]	128 (MeOH)	$C_{27}H_{21}F_3O_6S$ (530.5)	96	178–180 (dec.) (ether)	$C_{27}H_{21}F_3O_7S$ (546.5)	56

[a] Satisfactory microanalyses obtained: C ±0.29, H ±0.14, N ±0.03, S ±0.31; exception: **3a**, H +0.42.
[b] After chromatography.
[c] After crystallization.
[d] PE = Petroleum ether.
[e] M.p. of corresponding tosylate **13g** = 96–97°C.[5]
[f] Corresponding tosylate **13h** is an oil.[23]



3,10 14,15	R	3,10 14,15	R
g	O_2N–	i	$(i\text{-}C_3H_7)_3SiO$–
h	$CH_2(CH_2OCH_2)_3CH_2$	k	C_6H_5–

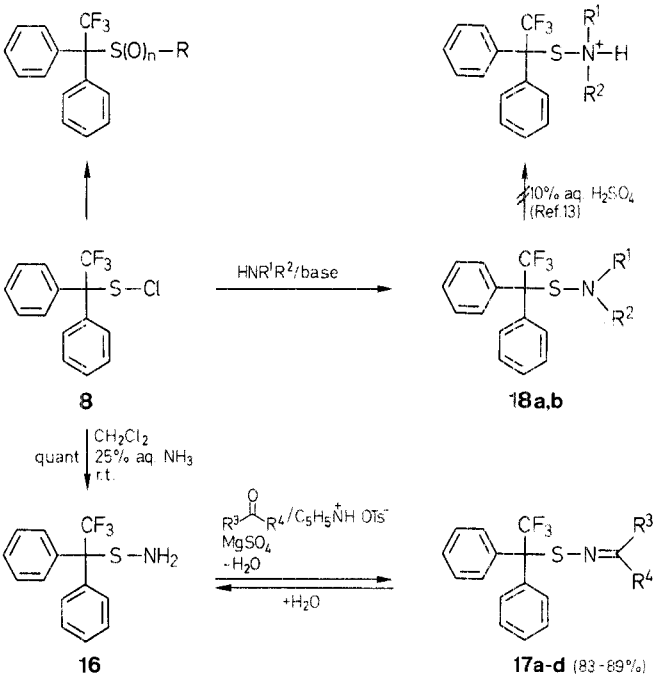
For **a–c, e** see Scheme **B**

Scheme **C**

Table 4. IR and ^{1}H-NMR Data of New Compounds **14**, **15** and **3**

Compound	IR (KBr) ν (cm^{-1})	^{1}H-NMR ($CDCl_3$), δ, J (Hz) H_x (Alcohol Part)	H_{arom}
14a	1145	3.31 (s, 2H, CH_2–OS)	7.22–7.53[b]
14b	1145[a]	3.82 (m, 2H, CH_2–OS)	7.39–7.48 (*o*)
			7.22–7.35 (*m*, *p*)[c]
14g	1150	7.11 (AA'XX', 2H);	7.38–7.46 (*o*)
		8.08 (AA'XX', 2H)	7.28–7.36 (*m*, *p*)
14h	1145[a]	3.78 (m, 4H, CH_2–OS)	7.37–7.47 (*o*)
			7.24–7.34 (*m*, *p*)
15a	–	3.56, 3.37 (AB, 2H, J = 9)	7.19–7.69[d]
15c	1135	4.77 (t, 1H, J = 3.0, CH–OSO)	7.48–7.62 (*o*)
			7.37–7.46 (*m*, *p*)
15e	1175, 1145	4.77 (m, CH–OSO)	7.48–7.57 (*o*[e]) 7.32–7.48 (*m*, *p*[e], *o*, *m*, *p*[e,f])
15k	1180, 1150	4.90 (t, 1H, J = 1.5, CH–OSO)	7.38–7.64[g]
3a	1365, 1175	3.36 (s, 2H, CH_2–SO_2) [**13a**: 3.66][d,h]	7.56–7.73 (*o*) 7.34–7.49 (*m*, *p*)
3b	1380, 1180	3.71 (m, 2H, CH_2–OSO_2) [**13b**: 4.17][h]	7.55–7.62 (*o*) 7.24–7.44 (*m*, *p*)[c]
3c	1375, 1175	4.98 (t, 1H, J = 3.0, CH–OSO_2) [**13c**: 5.31][h]	7.57–7.69 (*o*) 7.35–7.49 (*m*, *p*)
3e	1360, 1175	4.77 (m, 2H, CH–OSO_2) [**13e**: 5.12][h]	7.56–7.64 (*o*) 7.36–7.50 (*m*,,*p*)
3g	1375, 1170	6.82 (AA'XX'), 8.09 (AA'XX') [**13g**: 7.19; 8.19][d,h]	7.56–7.66 (*o*) 7.34–7.52 (*m*, *p*)
3h	1370, 1175[a]	3.67 (m, 4H, CH_2–OSO_2) [–][h]	7.56–7.64 (*o*) 7.31–7.48 (*m*, *p*)
3i	1380, 1180	4.57 (t, 1H, J = 1.5, CH–OSO_2) [–][h]	7.58–7.66 (*o*) 7.37–7.53 (*m*, *p*)
3k	1375, 1180	4.82 (t, 1H, J = 1.5, CH–OSO_2) [–][h]	7.40–7.67[g]

[a] Film.
[b] CCl_4, 90 MHz.
[c] Overlapped by the signals of benzyl group.
[d] 90 MHz.
[e] Diasteromer 1.
[f] Diastereomer 2.
[g] Overlapped by the signals of benzoyl group.
[h] In brackets: values of corresponding tosylate **13**.



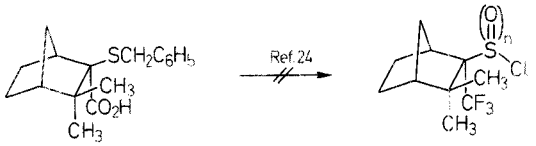
17	R^3	R^4
a	H	C_6H_5
b	CH_3	CH_3
c	$-(CH_2)_5-$	
d	CH_3	$CH_2CO_2CH_3$

18	R^1	R^2
a	H	$CH_2C_6H_5$
b	$-(CH_2)_5-$	

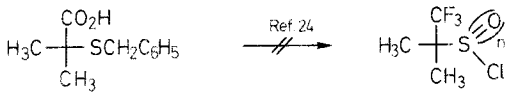
Scheme **D**

In connection with synthetic studies requiring the availability of sterically demanding tertiary sulfenyl/sulfinyl halides containing a trifluoromethyl substituent, the preparation of reagents **20** and **22** *via* fluorination of carboxylic acids (**19** and **21**)

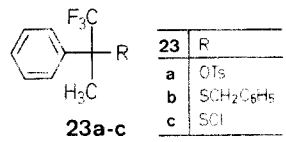
by sulfur tetrafluoride has been unsuccessful,[24] probably for steric reasons. In connection with the development of bulky sulfonic acid esters of modified reactivity (between **2** and **3**, e.g. **24**), sulfenyl chloride **23c** was synthesized *via* **23a, b** on a limited scale.[13]



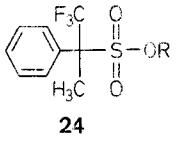
19 **20**



21 **22**



23a-c



24

Considering the ready availability of the starting materials and the simplicity of the work up, the new reagents are generally useful for producing sulfonate esters which in S_N2 reactions are very resistant, if not inert, towards competing S–O-scission. Details of the preparation of compounds **17,18** and **23a–c** and **24** will be reported later elsewhere.

Elemental analyses: Analytische Abteilung des Chemischen Laboratoriums Freiburg i.Br. Infrared spectra: Perkin Elmer 457 Grating Infrared Spectrophotometer. ^{1}H-NMR spectra: Bruker WM 250, Varian EM 360/390; unless otherwise noted, 250 MHz data are given. Chromatography: TLC on thin layer plates silica gel 60 F_{254} (Merck); column chromatography on silica gel 60, particle size 0.063–0.2 mm (Macherey-Nagel). Melting points: Monoskop IV from Bock, Frankfurt and apparatus by Tottoli from Buchi, Flawil.

t-Butylsulfinyl Chloride (4):[17]

The solution of di-*t*-butyldisulfide (89.2 g, 0.5 mol) and hydrogen peroxide (0.625 mol, as a 30% aqueous solution) in acetic acid (500 mL) is stirred at 0°C, until all the disulfide is consumed [24–48 h; control by direct ^{1}H-NMR measurement of the reaction mixture: disulfide: δ = 1.30 (s), thiosulfinate: δ = 1.39 (s) and 1.54 (s)]. The mixture is poured onto ice water (500 mL) extracted with CH_2Cl_2 (2 × 300 mL), and washed in turn with aqueous $NaHSO_3$ (200 mL), $NaHCO_3$ (200 mL), and water (200 mL). Dry chlorine (39 g; 0.55 mol) is passed into the dried (Na_2SO_4) solution (total ca. 500 mL) at an internal temperature of less than 10°C. After distillation of CH_2Cl_2 (atmospheric pressure), the residue is fractionated through a 20 cm Vigreux column to give **4** as a pale yellowish oil; yield: 67.4 g (96%); b.p. 54–57°C/15 mbar (Lit.[17] b.p. 53–54°C/19 mbar).

2,2,2-Trifluoro-1,1-diphenylethanol (5):[18]

To a solution of phenylmagnesium bromide [3.0 mol; from magnesium (72.0 g, 3.0 mol) and bromobenzene (471 g, 3.0 mol)] in ether (1.2 L) methyl trifluoroacetate (128 g, 1.0 mol) is added dropwise (temperature below 20°C). After refluxing for 1 h, the mixture is hydrolysed carefully by concentrated NH_4Cl solution. The yellow ether layer is decanted, and the salts are washed with ether (2 × 150 mL). The inorganic material is dissolved in a mixture of ice water and concentrated hydrochloric acid (total ca. 1 l, pH < 7) and extracted again with ether (2 × 150 mL). After washing the combined organic extracts with $NaHCO_3$ solution (400 mL) and then water (400 mL), the solvent is removed from the dried solution ($MgSO_4$) by heating the residue to 135°C. Crystallization from petroleum ether (b.p. 30–50°C) or distillation gives colourless **5**; yield: 210–235 g (83–93%); b.p. 137–140°C/16 mbar; (Lit.[18] b.p. 109–110°C/2 mbar).

^{1}H-NMR (CCl_4/TMS): δ = 2.80 (OH); 7.25–7.7 (H_{arom}).

2,2,2-Trifluoro-1,1-diphenylethanol-4-methylbenzenesulfonate (6):

Into a 2 l three necked round bottomed flask fitted with mechanical stirrer, dropping funnel and reflux condenser (with drying tube), a solution of alcohol **5** (88.3 g, 0.35 mol) in ether (150 mL) is added during 15 min to a suspension of sodium hydride (80%, 12.6 g, 0.42 mol, 1.2 equiv.) in dry ether (1 L). After 1 h at room temp., a solution of *p*-toluenesulfonyl chloride (80.1 g, 0.42 mol) in ether (350 mL) is added over 10 min, and the mixture is vigorously stirred at room temperature for 70 h. After careful hydrolysis of the remaining sodium hydride, ice water (500 mL) is added. The organic layer is separated, and the aqueous phase is extracted with ether (2 × 300 mL). The combined extract is dried ($MgSO_4$) and concentrated under reduced pressure (< 20°C). Crystallization at −30°C affords colourless crystals; m.p. 53°C; yield: 109–120 g (77–84%). **6** is unstable at room temp., but can be stored at −30°C for several months without decomposition.

$C_{21}H_{17}F_3O_3S$	calc.	C 62.06	H 4.22	S 7.89
(406.4)	found	62.00	4.34	7.79

IR (KBr): ν = 1365 (OSO_2), 1260, 1190 (OSO_2), 1165, 955, 920, 835, 695, 660, 545 cm^{-1}.

^{1}H-NMR (Acetone-d_6/TMS): δ = 2.40 (s, 3H, CH_3); 7.28 (d, 2H, AA', XX'); 7.32–7.50 (m, 12 H_{arom}).

2,2,2-Trifluoro-1,1-diphenylethanethiol (7):

(***Caution:*** A distasteful odour is present during the work-up procedure.) A strong stream of hydrogen sulfide is passed into a stirred solution of tosylate **6** (101.6 g, 0.25 mol) in dry 1,1,2,2-tetrachloroethane (400 mL) for 10 min. After addition of *p*-toluenesulfonic acid (0.2 g, 1.2 mmol), the mixture is heated at 60°C within 30 min while vigorous stirring and the stream of hydrogen sulfide is continued. The mixture is held at this temperature for further 30 min, cooled to room temperature and washed with water (2 × 100 mL). The organic layer is extracted with 10% sodium hydroxide (2 × 200 mL), and the mercaptan is liberated by addition of concentrated hydrochloric acid (ca. 80 mL, ice bath). Extraction with ether (2 × 300 mL), drying ($MgSO_4$) and evaporating under reduced pressure gives a light yellow oil, which is pure enough for further reactions (purity > 97%); yield: 61.7–64.4 g (92–96%). Redistillation of the crude product (25.9 g) gives an analytically pure pale yellow oil (25.2 g, 97%); b.p. 154–155°C/16 mbar, m.p. between +2 and +20°C.

$C_{14}H_{11}F_3S$	calc.	C 62.67	H 4.13	S 11.95
(268.3)	found	62.43	3.90	11.72

IR (Film): ν = 2570 (S–H), 1490, 1445, 1250, 1160, 750, 720, 695 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 2.82 (s, 1H, SH); 7.22–7.33 (m, 6H, *m*-, *p*-H_{arom}); 7.38–7.47 (m, 4H, *o*-H_{arom}).

2,2,2-Trifluoro-1,1-diphenylethanesulfenyl Chloride (8):

To a solution of the mercaptan **7** (64.4 g, 0.24 mol) in dry ether (200 mL) in a 500 mL two necked round bottomed flask fitted with a dropping funnel, a reflux condenser and a gas outlet tube, sulfuryl chloride (35.6 g, 0.26 mol) is added dropwise at a rate which keeps the ether boiling gently (ca. 15 min). After completion of the addition, the solution is held at room temperature for a further 15 min [TLC, petroleum ether (b.p. 30–50°C), R_F **(7)** = 0.63, R_F **(8)** = 0.74; detection by iodine or molybdatophosphoric acid]. The excess sulfuryl chloride is hydrolysed by water (ice bath), and the mixture is poured onto ice water (200 mL). The bright yellow organic layer is separated, washed with 2% NaCl (2 × 200 mL) and with saturated $NaHCO_3$ solution (2 × 200 mL) (*caution!* neutralization of acid causes vigorous liberation of gas!), dried ($MgSO_4$) and evaporated under reduced pressure. Crystallization of the viscous yellow oil (69.9–72.7 g, 96–100%) from petroleum ether (50 mL, b.p. 30–50°C) at −70°C affords lemon-yellow spheroidal crystals; yield: 64.3–69.4 g (92–96%); m.p. 35°C.

$C_{14}H_{10}ClF_3S$	calc.	C 55.54	H 3.33	S 10.59
(302.7)	found	55.37	3.14	10.77

IR (KBr): ν = 1440, 1245, 1160, 740, 715, 690 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 7.34–7.42 (m, 6H, *m*-, *p*-H_{arom}); 7.43–7.51 (m, 4H, *o*-H_{arom}).

2,2,2-Trifluoro-1,1-diphenylethanesulfinyl Chloride (9):

A solution of trifluoroperacetic acid (30.0 mmol, 1.0 equiv. prepared by adding the exact amount, as determined by titration, of ca 85%

hydrogen peroxide into trifluoroacetic acid anhydride) in CH_2Cl_2 20 mL) is added dropwise to a solution of sulfenyl chloride **8** (9.08 g, (30.0 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The solution is stirred for 1 h at 0 °C and 1 h at room temp., washed quickly with ice water (2 × 30 mL) and with cold $NaHCO_3$ solution (30 mL), dried ($MgSO_4$) and evaporated *in vacuo* (under 20 °C, traces of solvent is removed under high vacuum), affording a mostly yellowish-green (occasionally orange-brown) coloured viscous oil; yield: 9.37–9.56 g (98–100%). Quick work up is necessary to obtain a good quality reagent **9**, which is used in further reactions without purification. An analytical sample is obtained by incomplete crystallization (20–30%) at −30 °C (N_2, after several weeks); square crystals, m.p. 42–43 °C (petroleum ether, b.p. 30–50 °C). Storage at room temp. results in complete decomposition within hours and at −30 °C noticeable darkening occurs within weeks (data are given for the crystalline material).

$C_{14}H_{10}ClF_3OS$	calc.	C 52.76	H 3.16	S 10.06
(318.7)	found	52.85	3.24	10.26

IR (Film): ν = 1490, 1445, 1175, 1155, 745, 710, 690, 460 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 7.38–7.51 (m, 8H); 7.53–7.59 (m, 2H).

t-Butyl Sulfinates 11; General Procedure:

A solution of *t*-butylsulfinyl chloride (**4**; 1.41 g, 10.0 mmol) in CH_2Cl_2(10 mL) is added dropwise to a stirred solution of alcohol/phenol **10** (10.0 mmol) and triethylamine (1.21 g, 12.0 mmol) in CH_2Cl_2 (25–50 mL), (TLC control; conditions see Table 1). [For diol **10e** (5.0 mmol) the following reagents are used: **4** (20.0 mmol), **10e** (5.0 mmol), triethylamine (22.0 mmol) and solvent (100 mL). The mixture is diluted with the same solvent (total volume 50–100 mL), washed with 10% sulfuric acid (50 mL), water (50 mL) and $NaHCO_3$ solution (50 mL) and dried ($MgSO_4$). After evaporation *in vacuo*, the crude sulfinates **11** are crystallized or oxidized without purification to sulfonates **2**.

TDE-Sulfenates 14; General Procedure:

A solution of alcohol **10** (10.0 mmol) in dry THF (10 mL) is added dropwise into a stirred suspension of sodium hydride (288 mg, 12.0 mmol) in THF (10 mL) (for diol **10e**: NaH (24.0 mmol), solvent (25/75 mL). After stirring for 3–24 h at room temperature, the reagent **8** in THF (10 mL) is added, and the mixture is stirred for a further 3 h at room temperature (TLC control; the products **14** have R_F values slightly lower than **8**). The excess sodium hydride is hydrolyzed by addition of water, and ice water (50 mL) is added. The products **14** are obtained by extraction with ether (2 × 30 mL), drying ($MgSO_4$) and evaporating the solvent. They are then chromatographed or oxidized directly (exception: **14g** is obtained by treatment of a suspension of potassium-*p*-nitrophenolate in dry acetone with **8** and crystallized after suction filtration).

TDE-Sulfinates 15; General Procedure:

To a stirred solution of alcohol **10** (4.0 mmol) in dry CH_2Cl_2 (10 mL) reagent **9** (1.40 g, 4.4 mmol) and *N*-methylimidazole (411 mg, 5.0 mmol) (for **10e**; 2.4 equiv **9** in pure *N*-methylimidazole) are added dropwise at 0 °C. The mixture is stirred for 30 min to 18 h between 0 °C and room temperature (TLC; products **15** have much higher R_F values than the starting materials **10**). The mixture is diluted with CH_2Cl_2 (20 mL), washed with 10% sulfuric acid (20 mL), water (20 mL), $NaHCO_3$ solution (20 mL), dried ($MgSO_4$), and evaporated to dryness *in vacuo*. The crude products (often as a foam) are crystallized or oxidized directly.

Sulfonates 2/3 from 11/14/15; General Procedure:

To a stirred mixture of **11/14/15** in CH_2Cl_2 (20–60 mL/mmol) with Na_2HPO_4 as buffer (1.3 molar equiv for each equiv peracid) is added at 0 °C a solution of trifluoroperacetic acid (1.1–1.2 molar equiv for one oxidation step; 1.15 equiv. trifluoroacetic acid anhydride and 85% hydrogen peroxide form 1.0 equiv peracid) in CH_2Cl_2 (ca. 1 mL/mmol). (In the case of *t*-butyl derivatives **11** oxidation can be carried out also by use of *m*-chloroperbenzoic acid). After 1–3 h stirring at room temp. (exception: **10g**, 16 h), the mixture is poured onto ice water. The organic layer is separated, washed with $NaHSO_3$ and $NaHCO_3$ solutions, and evaporated to dryness under reduced pressure. Recrystallization affords pure sulfonates **2/3**.

2,2,2-Trifluoro-1,1-diphenylethanesulfenamide 16:

A solution of sulfenyl chloride **8** (908 mg, 3.0 mmol) in CH_2Cl_2 (5 mL) is added dropwise into a well-stirred 25% aqueous ammonia solution (25 mL). After 5 min, the colourless mixture is diluted with water (20 mL) and CH_2Cl_2 (20 mL). The organic layer is separated, dried ($MgSO_4$) and evaporated *in vacuo*. The crude product **16** (850 mg, 100% yield) is pure enough for further reactions. An analytical sample is obtained by chromatography [silica gel, 35 × 2.5 cm, petroleum ether (b.p. 30–50 °C)/ether, 20:1; R_F **(8)** = 0.83, R_F **(16)** = 0.42)]; yield: 810 mg (95%) colourless oil; m.p. between +1 and +20 °C.

$C_{14}H_{12}F_3NS$	calc.	C 59.35	H 4.27	N 4.94	S 11.32
(283.3)	found	59.19	4.20	4.89	11.24

IR (Film): ν = 3400, 3310, 1490, 1440, 1250, 1150, 745, 715, 695 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 2.29 (br. s, 2H, NH_2); 7.29–7.41 (m, 10 H_{arom}).

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