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Synthesis and reactivity of benzylic sulfonium salts: benzylation of phenol and thiophenol under near-neutral conditions

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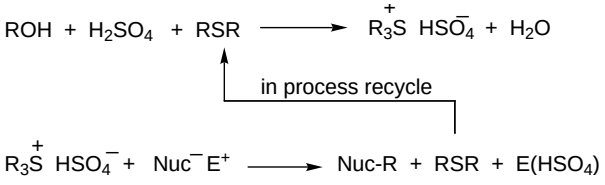
Abstract—A series of benzyldimethylsulfonium - and related hydrogensulfate salts have been synthesized from the ternary system $ArCH_2OH$:H_2SO_4: Me_2S or tetrahydrothiophene. The salts are generally stable crystalline solids, but anomalously high reactivity is observed for 9-(anthrylmethyl)dimethylsulfonium hydrogensulfate. Selected sulfonium salts have been used for the *O*- and *S*-benzylation of phenol and thiophenol, respectively, in a two phase system under near-neutral conditions. The benzylation of oximes and benzimidazole under basic conditions is also described.

1. Introduction

The synthesis and reactions of sulfonium salts have been widely studied. Prominent amongst the uses of such salts are their conversion into sulfonium ylides for use in the Corey epoxidation procedure[1] and for the alkylation of nucleophiles; examples of the latter include reactions with azide ion,[2] carboxylates,[3] nucleosides,[4] thiophenols,[5] amines,[6] cyanide,[7] amides,[8] enolates[9,10] and sulfenates.[11]

Investigations on sulfonium salts in our laboratories have been directed, in part, towards development of the ternary system CH_3OH:conc. H_2SO_4:Me_2S as an inexpensive procedure for production of trimethylsulfonium hydrogensulfate ($Me_3S^+HSO^-_4$)[12] thence its use through the sulfonium ylide for epoxidation.[13] In addition to environmental benefits in avoiding the use of toxic alkyl halides, the process has the advantage that dimethyl sulfide (bp 39°C), which mediates epoxide formation, can be recovered and recycled; it may be noted that the latter is an inexpensive bulk chemical that can be manipulated through standard industrial process technology. The above advantages would also accrue for alkylation of nucleophiles through sulfonium hydrogen sulfates (Scheme 1). Many industrial alkylation reactions involve the use of toxic or volatile alkyl halides or dialkyl sulfates with occasional use of undesirable bases such as sodium hydride; a process of the type outlined in Scheme 1 would circumvent these problems, to an extent.

The aims of the present project were to extend the scope of the ternary system as a method for generating a range of benzylsulfonium salts and to evaluate the utility of selected salts for the benzylation of nucleophiles, with particular regard to developing procedures that would operate under near-neutral conditions. It may be noted that conventional group protection, e.g. of phenols and amines, through benzylation involves the use of benzyl halides and strong bases[14] or of benzyl-2,2,2 trichloroacetimidate under acidic conditions.[15]



Scheme 1.

2. Results and discussion

2.1. Synthesis

A series of benzyldimethylsulfonium hydrogensulfate salts (**1a**–**j**) and related compounds (**4a**,**b**; Scheme 3) were prepared in variable yield (4–85%) from the ternary system $ArCH_2OH$ (1 mol equiv.): 98% H_2SO_4 (ca. 1 mol equiv.): Me_2S (excess); analogous compounds (**2a**; Scheme 2, **4c**,**d**) were prepared from related reactions of tetrahydrothiophene. These salts (**1a**–**j**, **2a**, **4c**,**d**) were generally stable, crystalline solids that were obtained in analytically pure form; exceptions were **1i** and **1j** which were characterized spectroscopically, but which could not be purified to analytical standard. The former (**1i**) was a deliquescent solid

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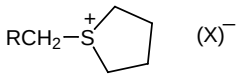
and the latter (**1j**) slowly decomposed at room temperature with loss of dimethyl sulfide, in a process that may be driven by formation of a relatively stable carbocation. Preparation of the parent salt (**1a**) was hampered by purification problems: a slight excess of sulfuric acid (0.3 mol equiv./mol equiv. of $PhCH_2OH$) was required to drive the reaction to completion and the salt (**1a**) could not be purified from this contaminant. This compound (**1a**) was more conveniently prepared from sulfuric acid, dimethyl sulfide and benzyl formate.[16] The ternary system $ArCH_2OH$:H_2SO_4:Me_2S was also successfully used in this work for the synthesis of 1- and 2-naphthylmethyl-(**1k**, **l**), 9-phenanthrylmethyl-(**1m**), 9-anthrylmethyl-(**1n**), 9-fluorenyl-(**1o**) and benzhydryl-(**1p**) dimethylsulfonium hydrogensulfates.

A useful technique for purification of compounds **1k**–**p** was found to be repeated batch sonication under solvents such as ethyl acetate in which sulfuric acid and water have higher solubility than the salts. Compounds **1k**–**p** were characterized analytically and spectroscopically, but 9-anthrylmethylsulfonium hydrogensulfate (**1n**) was found to be extraordinarily reactive and was additionally identified through solid state (CP MAS) ^{13}C NMR spectroscopy; the mode of reactivity of **1n** is discussed in a separate section below.

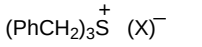
Also prepared in this work were sulfonium salts analogous to the above hydrogensulfates in which the counterion is Cl^- (**1q**), $CF_3CO_2^-$ (**1r**) and BF_4^- (**1s**–**u**, **2b**, **3b**, **4e** and **5**); with the exception of **5** the above were all obtained in analytically pure form. A notable feature of the present work is the isolation of anhydrous bis sulfonium salts (**4**); this contrasts with the analogous bis chloride salt (**4f**) which is normally used with ca. 2–5% water content.[17]

(1)	$[ArSMe_2]^+(X^-)$	
	Ar	X
a	$PhCH_2$	HSO_4
b	*o*-$ClC_6H_4CH_2$	HSO_4
c	*m*-$ClC_6H_4CH_2$	HSO_4
d	2,6-$Cl_2C_6H_3CH_2$	HSO_4
e	2,6-$F_2C_6H_3CH_2$	HSO_4
f	*o*-$O_2NC_6H_4CH_2$	HSO_4
g	*p*-$O_2NC_6H_4CH_2$	HSO_4
h	*p*-$MeOC_6H_4CH_2$	HSO_4
i	*p*-MeC_6H_4 CH_2	HSO_4
j	2,6-$(MeO)_2C_6H_3CH_2$	HSO_4
k	1-naphthylCH_2	HSO_4
l	2-naphthylCH_2	HSO_4
m	9-phenanthrylCH_2	HSO_4
n	9-anthrylCH_2	HSO_4
o	9-fluorenyl	HSO_4
p	Benzhydryl	HSO_4
q	$PhCH_2$	Cl
r	$PhCH_2$	CF_3CO_2
s	$PhCH_2$	BF_4
t	*o*-$ClC_6H_4CH_2$	BF_4
u	Benzhydryl	BF_4



(2)

	X	R
a	HSO_4	Ph
b	BF_4	Ph
c	HSO_4	Me



(3)

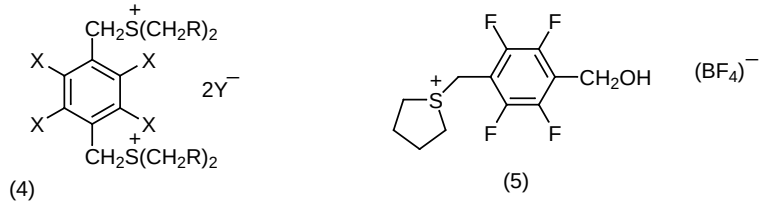
	X
a	HSO_4
b	BF_4

Scheme 2.

2.2. Reactions of (9-anthrylmethyl)dimethylsulfonium hydrogensulfate

The anomalous reactivity of this poorly soluble salt (**1n**) was recognized through attempted acquisition of ^1H and ^{13}C NMR spectra in d^6-DMSO and d^7-DMF solutions. For example, both ^1H NMR spectra contained two sets of peaks, one set of which could be assigned to the desired salt (**1n**) by reference to the solid state (CP MAS) spectrum. Also present in the solution spectra were resonances arising from dimethyl sulfide, and evidence for formation of alkoxysulfonium (**6a**) and alkoxymethyleneiminium-(**6b**) salts, respectively (Scheme 4). Further evidence of the highly electrophilic character of the salt (**1n**) was apparent from solvolysis at ~50°C with separately, water, methanol and ethanol which led to the formation of **6c**–**e**, respectively. *N*,*N*-Dimethylformamide was also used as a (reactive) solvent to mediate the reaction of **1n** with nucleophiles, presumably in part, through the iminium salt (cf. **6b**); reactions with CN^-, SCN^-, AcO^- and $PhCH{=}NO^-$ leading to **6f**–**i**, respectively, exemplify this type of process. Attempts to use other solvents for mediation of reactions of **1n** with nucleophiles were unsuccessful. For example, treatment of **1n** with ethanol in dimethylsulfoxide afforded 9-anthraldehyde in a process akin to the Swern oxidation.[18] Solvolysis of the salt (**1n**) in acetonitrile and *N*,*N*-dimethylformamide followed by aqueous work up afforded [*N*-(9-anthrylmethyl)]acetamide (**6j**), albeit in poor yield (15%). When the salt (**1n**) was heated in a mixture of nitromethane and *N*,*N*-dimethylformamide, a complex mixture was obtained which could not be separated chromatographically. The ^1H NMR spectrum showed very broad peaks in the aliphatic (δ 4.0–4.6) and aromatic regions (δ 6.3–8.7) and the mass spectrum showed peaks corresponding to ions $[(anthrylCH_2)_n+H]^+$ (n=1–3). We suggest that the salt (**1n**) oligomerises in this solvent system in a process having analogy with the formation of poly[benzyl] from benzyl alcohol in anhydrous hydrogen fluoride.[19] Finally, treatment of **1n** with phenol in nitromethane under reflux afforded 9-anthraldehyde (46%, cf. reaction with ethanol in DMSO) and 9-(4-hydroxybenzyl)anthracene (**6k**) [20%]; the ring (*C*) alkylation of phenol observed in this process contrasts with the side-chain (*O*)-alkylation reactions described below.

The relatively high reactivity of **1n** may be contrasted with that of its structural analogues: for example, dimethyl(9-phenanthrylmethyl)sulfonium hydrogen sulfate (**1m**) is stable for one week at 100°C in d^7-DMF and is unreactive to water and alcohols in the absence of a base. The unusual behaviour of **1n** may have analogy in the



	X	R or R⌒R	Y
a	H	H	HSO_4
b	F	H	HSO_4
c	H	CH_2CH_2	HSO_4
d	F	CH_2CH_2	HSO_4
e	F	CH_2CH_2	BF_4
f	H	CH_2CH_2	Cl

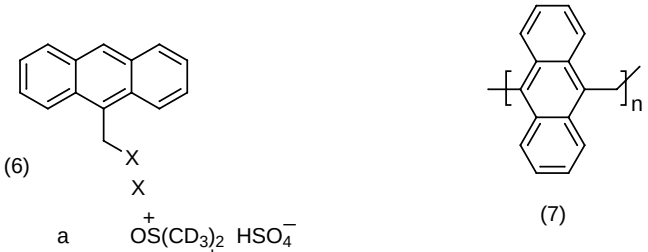
Scheme 3.

contrasting electrophilic reactivity of 9-chloromethylanthracene and 9-(anthrylmethyl)trialkylammonium salts (**6l**)[20] in which nucleophilic attack at the latter proceeds, initially at least, in *cine* fashion at the 10-position.

2.3. Reactions with *O*-, *S*- and *N*-centred nucleophiles

It is known that certain trialkylsulfonium salts,[21] including polymer-supported species,[22] can function as phase transfer catalysts. With this in mind, optimized conditions for conversion of phenol into benzyl ethers (**8a**–**f**; Scheme 5) were developed as follows: PhOH (1 mol equiv.)/sulfonium hydrogensulfate salt (1.05 mol equiv.)/$NaHCO_3$ (2.5 mol equiv.) in a mixture of toluene and water at 50°C. Yields were generally high (82–96%) with the exception of formation of **8e** (70%), which was accompanied by *p*-methoxybenzyl alcohol from hydrolysis of the salt **1h**. It was noted that the pH of the aqueous layer was 7.5 after thorough mixing of the reagents and the value fell to 6.5 at the end of the reaction. Benzylations were equally effective with sulfonium tetrafluoroborates (for **8a**,**d**; >96%) and a trifluoroacetate (**8d**, 96%). Thiophenol was also rapidly benzylated with salt **1d** in the two-phase system described above to give the thioether (**8g**) quantitatively.

A number of alkylations were also effected under basic conditions. For example, treatment of either *syn* or *anti*-benzaldoxime with the salt (**1b**) in the two phase system PhMe/aq. KOH afforded mixtures of predominantly *O*-(~50%) and *N*-alkylated products (~5%) [(**9**,**10**]. The regiochemistry of this process is similar to the outcome of base-promoted alkylation of *syn*-benzaldoxime with benzyl chloride;[23] in contrast, the reaction of *anti*-benzaldoxime with benzyl chloride affords exclusively the *N*-alkylated product (**10**).[23] It can be assumed that the *anti*-oxime isomerises rapidly under the reaction conditions. Alkylation of cyclohexanone oxime with salts **1b** and **1d** gave only products of *O*-(**11a**, **b**), and not *N*-alkylation, in variable yield (38, 75%). Finally, benzimidazole was benzylated under alkaline conditions in the two phase system (**1a**, **1b→12a**, **b**, respectively) in moderate yield (50, 59%). The selective exocyclic electrophilic reaction of **2a** contrasts with the reaction of benzimidazole with 1-methyltetrahydrothiophenium hydrogensulfate (**2c**) which results in products (**12c**, **d**) arising predominantly from endocyclic ring-opening (cf. reaction of the iodide analogue of **2c** with azide ion[24]).

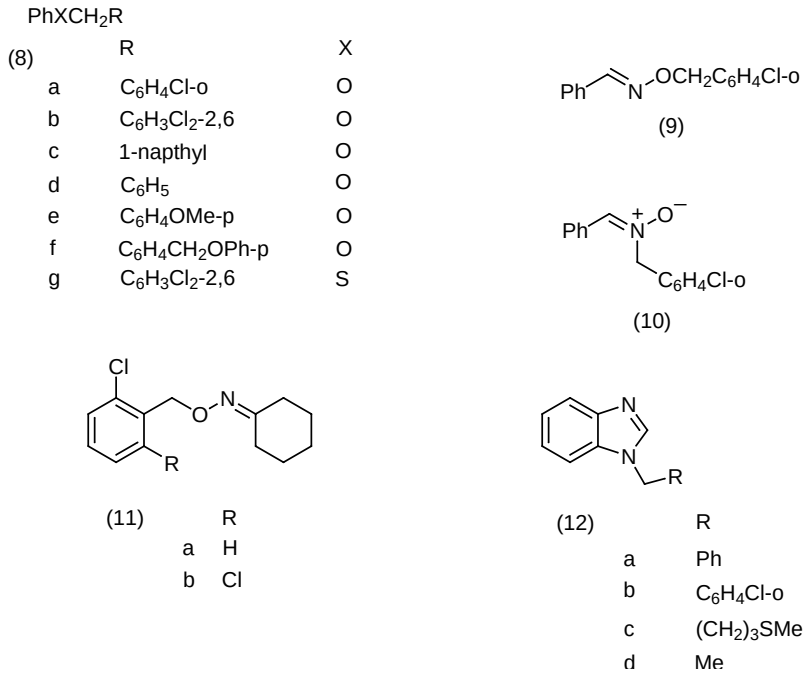


	X
a	$OS^+(CD_3)_2\ HSO_4^-$
b	$OC(D)=N^+(CD_3)_2\ HSO_4^-$
c	OH
d	OMe
e	OEt
f	CN
g	SCN
h	$OCOCH_3$
i	ON=CHPh
j	$NHCOCH_3$
k	C_6H_4OH-p
l	$NR_3^+\ Cl^-$

Scheme 4.

3. Conclusion

The inexpensive ternary system $ArCH_2OH$:H_2SO_4:Me_2S provides a useful procedure for the preparation of a variety of benzylic sulfonium hydrogensulfates. 9-(Anthrylmethyl)-dimethylsulfonium hydrogen sulfate (**1n**) has considerably higher reactivity than analogous benzylic salts synthesized in this work. Selected benzylic sulfonium salts have been used for the benzylation of phenol and thiophenol under near-neutral conditions in procedures that could be valuable in the chemistry of protecting groups.



Scheme 5.

4. Experimental

4.1. General

Solvents used were dried under reflux and freshly distilled under a dry nitrogen atmosphere before use. Drying agents were: Na–benzophenone {for petroleum ether (bp 60–80°C), diethyl ether, tetrahydrofuran (THF), and toluene}; and P_2O_5 (for dichloromethane). Infrared (IR) spectra were recorded on Perkin–Elmer 580 and 1600 instruments and calibrated against polystyrene. ^1H, ^{13}C and ^{19}F NMR spectra in solution were recorded at 200.13, 50.32 and 376.5 MHz, unless otherwise stated, respectively, on a Bruker WP 200 SY spectrometer; ^1H and ^{19}F Chemical shifts (ppm) are reported relative to tetramethylsilane and trichlorofluoromethane as references, respectively, and coupling constants are quoted in Hz. The solid state CPMAS $^{13}C\{^1H\}$ NMR spectrum (75.43 MHz) was recorded at the University of Durham, UK.

4.2. Synthesis of sulfonium salts

4.2.1. Benzyldimethylsulfonium hydrogensulfate (1a). 98% Sulfuric acid (6.5 g, 65 mmol) was added dropwise to a mechanically stirred solution of benzyl alcohol (5.4 g, 50 mmol) in dimethyl sulfide (12.4 g, 0.2 mol) over ca. 30 min and the resultant mixture was stirred at ambient temperature overnight. The lower layer was separated and evaporated under reduced pressure to give benzyldimethylsulfonium hydrogensulfate (**1a**) as a colorless oil; δ_H (d_6-DMSO), 2.8 (s, 6H, CH_3); 4.7 (s, 2H, CH_2); 7.5 (s, 5H, Ar–H); δ_C (d_6-DMSO), 24.1 (CH_3); 45.9 (CH_2); 128.8 (quaternary C) 129.7, 130.0, 131.2; *m/z* (FAB for salt AB) 153 (69%, A^+), 91 (100, A^+–$S(CH_3)_2$), 403 (2.4, A_2B^+ cluster), 653 (0.05, $A_3B_2^+$ cluster), 903 (0.05, $A_4B_3^+$ cluster); (Found: A_2B^+ 403.1093 (FAB). $C_{18}H_{27}O_4S_3$ requires: 403.1071).

This compound (**1a**) was also prepared in quantitative yield by the reaction of 98% sulfuric acid (5.0 g, 50 mmol), benzyl formate (8.59 g, 55 mmol) and dimethyl sulfide (20 cm^3), by analogy with a literature procedure.[16]

4.3. General procedure for benzylic sulfonium salts (1b–e)

98% Sulfuric acid was added dropwise to a mechanically stirred solution of the appropriate alcohol in dimethyl sulfide over ca. 30 min. at ambient temperature. After stirring overnight at ambient temperature, a white precipitate was observed. The dimethyl sulfide and water were removed by evaporation under reduced pressure and the residue was treated as outlined below.

4.3.1. 2-Chlorobenzyldimethylsulfonium hydrogensulfate (1b). From H_2SO_4 (7.0 g, 70 mmol), 2-chlorobenzyl alcohol (10.0 g, 70 mmol) and Me_2S (17.6 g, 280 mmol). The residue was treated with acetone (50 cm^3) and the resultant slurry was filtered. The solid was washed with ice-cold acetone (10 cm^3), and then dried under high vacuum to give 2-chlorobenzyldimethylsulfonium hydrogensulfate (**1b**) as a colorless, crystalline solid (8.8 g, 44%); mp 143–144°C (EtOH/EtOAc); ν_{max} (KBr)/cm^{-1}, 2940, 1470, 1430, 1290, 1170, 1000; δ_H (d_6-DMSO), 2.9 (s, 6H, CH_3); 4.8 (s, 2H, CH_2); 7.4–7.7 (m, 4H, Ar–H); δ_C (d_6-DMSO), 24.4 (CH_3); 44.0 (CH_2); 128.5, 130.6, 132.2, 134.0 (4×CH); 127.2, 134.5 (2 quaternary C's); *m/z* (FAB for salt AB) 187 (^{35}Cl isotope) [100%, A^+]), 125 (51, A^+–$S(CH_3)_2$), 471 (3.5, A_2B^+ cluster), 756 (0.27, $A_3B_2^+$ cluster); (Found: C, 38.0; H, 4.7%. $C_9H_{13}ClO_4S_2$ requires: C, 38.0; H, 4.60%).

4.3.2. 3-Chlorobenzyldimethylsulfonium hydrogensulfate (1c). From H_2SO_4 (7.0 g, 70 mmol), 3-chlorobenzyl-alcohol (10.0 g, 70 mmol) and Me_2S (17.6 g, 280 mmol).

The residual clear yellow syrup was triturated with diethyl ether to give a white paste, which was filtered on a glass sinter. The resulting solid was washed with ice-cold ethanol (5 cm^3) and dried under high vacuum to give 3-chlorobenzyldimethylsulfonium hydrogensulfate (**1c**) as a white powder (780 mg, 4%); mp 86–88°C (EtOH); ν_{max} (KBr)/cm^{-1}, 3000, 1580, 1480, 1430, 1210, 1050; δ_H (d_6-DMSO), 2.85 (s, 6H, CH_3); 4.7 (s, 2H, CH_2); 7.45–7.65 (m, 4H, Ar–H); δ_C (d_6-DMSO), 24.2 (CH_3), 45.2 (CH_2); 129.9, 130.0, 130.8, 131.6 (4×CH); 131.4, 134.1 (2 quaternary C's); *m/z* (FAB for salt AB) 187 (^{35}Cl isotope) [100%, A^+]), 125 (27, A^+–$S(CH_3)_2$), 471 (2.4), (A_2B^+ cluster); (Found: C, 37.8; H, 4.6; S, 22.6%. $C_9H_{13}ClO_4S_2$ requires: C, 38.0; H, 4.6; S, 22.5%).

4.3.3. 2,6-Dichlorobenzyldimethylsulfonium hydrogensulfate (1d). From H_2SO_4 (14.0 g, 140 mmol), 2,6-dichlorobenzyl alcohol (24.8 g, 140 mmol) and Me_2S(35.2 g, 560 mmol). Ethyl acetate (100 cm^3) was added to the residue and the resultant slurry was filtered. The solid was washed with ethyl acetate (50 cm^3) and finally dried under high vacuum to give 2,6-dichlorobenzyldimethylsulfonium hydrogensulfate (**1d**) as a colorless, crystalline solid (27.5 g, 62%); mp 160–161°C (EtOH/EtOAc); ν_{max} (KBr)/cm^{-1}, 2950, 1580, 1560, 1430, 1290, 1170, 1010; δ_H (d_6-DMSO), 3.1 (s, 6H, CH_3); 4.9 (s, 2H, CH_2); 7.5–7.55 (m, 3H, Ar–H); δ_C (d_6-DMSO), 25.8 (CH_3); 43.2 (CH_2); 126.5, 130.2 (2×CH); 133.4, 136.9 (2 quaternary C's); *m/z* (FAB for salt AB) 221 (^{35}Cl isotopes) [(100%, A^+)], 159 (32, A^+–$S(CH_3)_2$), 541 (2.2, A_2B^+ cluster); (Found: C, 33.9; H, 3.9%. $C_9H_{12}Cl_2O_4S_2$ requires: C, 33.9; H, 3.8%).

4.3.4. 2,6-Difluorobenzyldimethylsulfonium hydrogensulfate (1e). From H_2SO_4 (2.5 g, 25 mol), 2,6-difluorobenzyl alcohol (4.6 g, 32 mmol) and Me_2 S (12.8 g, 200 mmol). Ethanol (10 cm^3) was added to the residue and the resultant slurry was filtered. The solid was washed with ethanol (10 cm^3) and finally dried under high vacuum to give 2,6-difluorobenzyldimethylsulfonium hydrogensulfate (**1e**) as a colorless, crystalline solid (2.3 g, 25%); mp 147–148°C (EtOH); ν_{max} (KBr)/cm^{-1}, 2980, 1630, 1590, 1470, 1220, 1030; δ_H (d_6-DMSO), 2.9 (s, 6H, CH_3); 4.8 (s, 2H, CH_2); 7.25–7.35 (m, 2H, Ar–H); 7.55–7.7 (m, 1H, Ar–H); δ_C (d_6-DMSO), 24.3 (CH_3); 34.0 (CH_2); 105.1 (t, J_{C-F}=19 Hz, C_1); 112.8 (d, J_{C-F}=22 Hz, C_3,C_5); 133.6 (t, J_{C-F}=10 Hz, C_4); 161.4 ($J_{C2-F2,\ C6-F6}$=249 Hz, $J_{C2-F6,\ C6-F2}$=6.5 Hz, C_2,C_6); δ_F (C_2D_6SO), −111.49 (overlapping dd, J_{HF} and J_{HF}~8 Hz); *m/z* (FAB for salt AB) 189 (100%, A^+), 475 (5.7, A_2B^+ cluster), 762 (0.6, $A_3B_2^+$ cluster); (Found: C, 37.5; H, 4.3; S, 22.2%. $C_9H_{12}F_2O_4S_2$ requires: C, 37.8; H, 4.2; S, 22.4%).

4.3.5. Dimethyl-(2-nitrobenzyl)sulfonium hydrogensulfate (1f). 98% Sulfuric acid (5.0 g, 50 mmol) was added dropwise to a mechanically stirred solution of 2-nitrobenzyl alcohol (7.67 g, 50 mmol) in dimethyl sulfide (100 cm^3) over ca. 30 min., at 0°C. At first, a white solid formed but after stirring overnight at ambient temperature yellow oil appeared as the lower of two layers. The dimethyl sulfide (top) layer was decanted and the lower layer was triturated under ethyl acetate. The resulting slurry was filtered and the solid product was washed with ice-cold ethyl acetate (5×10 cm^3) and then dried under high vacuum to give dimethyl-(2-nitrobenzyl)sulfonium hydrogensulfate (**1f**) as a yellowish white, crystalline solid (5.68 g, 38%); mp 178–180°C (EtOH/EtOAc); ν_{max} (KBr)/cm^{-1}, 3459, 3393, 3019, 2548, 1609, 1577, 1526, 1430, 1339, 1238, 1061, 1009, 848, 710, 577; δ_H (d_6-DMSO), 3.0 (s, 6H, CH_3); 5.0 (s, 2H, CH_2); 7.7–7.9 (m, 3H, Ar–H); 8.2 (d, *J*=7.5 Hz, 1H, Ar–H); δ_C (d_6-DMSO), 25.1 (CH_3); 44.8 (CH_2); 124.6, 148.7 (2 quaternary C's); 126.4, 131.9, 135.0, 135.2 (4×CH). *m/z* (FAB for salt AB) 198 (100% A^+), 136 (53, A^+–$S(CH_3)_2$), 493 (3.8, A_2B^+ cluster); (Found: C, 36.5; H, 4.5; N, 4.5%. $C_9H_{13}NO_6S_2$ requires: C, 36.6; H, 4.4; N, 4.7%).

4.3.6. Dimethyl-(4-nitrobenzyl)sulfonium hydrogensulfate (1g). 98% Sulfuric acid (5.0 g, 50 mmol) was added dropwise to a mechanically stirred solution of 4-nitrobenzyl alcohol (7.67 g, 50 mmol) in dimethyl sulfide (120 cm^3) over ca. 20 min., at 0°C. After stirring overnight at ambient temperature, yellow oil formed as the lower of two layers. The upper dimethyl sulfide layer was decanted and the lower layer was sonicated under ethyl acetate for 6 h before trituration with acetone. The resulting slurry was filtered and the solid was washed with ice-cold ethyl acetate (5×10 cm^3) and then dried under high vacuum to give dimethyl-(4-nitrobenzyl)sulfonium hydrogensulfate (**1g**) as a colorless crystalline solid (6.10 g, 41%); mp 130.5–131.5°C (EtOH/EtOAc); ν_{max} (KBr)/cm^{-1}, 3408, 3003, 2916, 1606, 1522, 1422, 1352, 1223, 1110, 1080, 1048, 1011, 860, 710, 590; δ_H (d_6-DMSO), 2.9 (s, 6H, CH_3); 4.9 (s, 2H, CH_2); 7.7 (d, *J*=8.7 Hz, 2H, Ar–H); 8.3 (d, *J*=8.7 Hz, 2H, Ar–H); δ_C (d_6-DMSO), 24.2 (CH_3); 44.8 (CH_2); 124.6, 132.7 (2×CH); 136.6, 148.5 (2 quaternary C's); *m/z* (FAB for salt AB) 198 (54%, A^+), 136 (29, A^+–$S(CH_3)_2$), 31 (100), 493 (1.5, A_2B^+ cluster); (Found: C, 36.5; H, 4.5; N, 4.6%. $C_9H_{13}NO_6S_2$ requires: C, 36.6; H, 4.4; N, 4.7%).

4.3.7. 4-Methoxybenzyldimethylsulfonium hydrogensulfate (1h). 98% Sulfuric acid (10.0 g, 100 mmol) was added dropwise to a mechanically stirred solution of 4-methoxybenzyl alcohol (13.82 g, 100 mmol) in dimethyl sulfide (100 cm^3) over ca. 20 min. After stirring for 4 h at ambient temperature, a thick, white paste was observed. The upper dimethyl sulfide layer was decanted and the paste was sonicated under ethyl acetate for 6 h before immediate recrystallization to give 4-methoxybenzyldimethylsulfonium hydrogensulfate **1h** as a colorless, crystalline solid (22.5 g, 85%); mp 83–84°C (EtOH/EtOAc); ν_{max} (KBr)/cm^{-1}, 3400, 3001, 1610, 1514, 1426, 1253, 1027, 841, 750, 585; δ_H (d_6-DMSO), 2.8 (s, 6H, SMe); 3.75 (s, 3H, OMe); 4.65 (s, 2H, CH_2); 7.0 (d, *J*=8.7 Hz, 2H, Ar–H); 7.4 (d, *J*=8.7 Hz, 2H, Ar–H); δ_C (d_6-DMSO), 23.6 (SMe); 44.8 (CH_2); 55.7 (OMe); 115.0, 132.7 (2×CH); 120.2, 160.5 (2 quaternary C's); *m/z* (FAB for salt AB) 167 (5.9%, A^+), 121 (100, A^+–$S(CH_3)_2$).

This sulfonium salt was very unstable until it had been recrystallized, after which it was stable at 4°C for a few weeks.

4.3.8. Dimethyl-(4-methylbenzyl)sulfonium hydrogensulfate (1i). 98% Sulfuric acid (10.0 g, 100 mmol) was added dropwise to a mechanically stirred solution of

dimethyl sulfide (80 cm^3) and 4-methylbenzyl alcohol (12.22 g, 100 mmol) over ca. 30 min at 0°C. The mixture was stirred at ambient temperature overnight. The upper dimethylsulfide layer was decanted and the aqueous layer was sonicated under ethyl acetate (100 cm^3) for 6 h and then diethyl ether (100 cm^3) for 4 h. The resulting colorless oil was triturated at −20°C in the presence of diethyl ether (50 cm^3) and the colorless crystals produced were separated by cold filtration to give dimethyl-(4-methybenzyl)sulfonium hydrogensulfate (**1i**) as a deliquescent, colorless, crystalline solid; δ_H (d_6-DMSO), 2.3, s, 3H (CH_3–C); 2.8, s, 6H (CH_3–S); 4.7, s, 2H (CH_2); 7.3 (d, *J*=8 Hz, 2H, Ar–H); 7.4 (d, *J*=8 Hz, 2H, Ar–H); δ_C (d_6-DMSO); 21.3 (*C*H_3–C); 23.9 (*C*H_3–S) 45.7 (CH_2); 130.3, 131.1 (2×CH); 125.7, 139.6 (2 quaternary C's); *m/z* (FAB for salt AB) 167 (63%, A^+), 105 (100, A^+–$S(CH_3)_2$), 431 (1.4, A_2B^+ cluster); (Found: A_2B^+ 431.1417 (FAB). $C_{20}H_{31}O_4S_3$ requires: 431.1385).

Due to the extremely hygroscopic nature of this salt, it was not possible to obtain a melting point, an accurate yield, or an analytically pure sample.

4.3.9. 2,6-Dimethoxybenzyldimethylsulfonium hydrogensulfate (1j). 2,6-Dimethoxybenzyl alcohol. 2,6-Dimethoxybenzoic acid (21.5 g, 128 mmol) was added in portions to a mechanically stirred suspension of lithium aluminium hydride (21.5 g, 565 mmol) in dry THF (300 cm^3) at 0°C. The mixture was allowed to warm to ambient temperature and then heated under reflux for 20 h. Successive dropwise addition of water (20 cm^3), 6 M sodium hydroxide solution (20 cm^3) and finally water (65 cm^3), all with vigorous stirring precipitated the metals as their insoluble hydroxides. The mixture was filtered and the resulting solid was washed with THF (2×50 cm^3) and the combined solvents evaporated under reduced pressure. The crude residue was dissolved in ethyl acetate (100 cm^3) and the solution was washed with water (50 cm^3) followed by saturated brine (50 cm^3). This solution was dried ($MgSO_4$), filtered, and the solvent evaporated under reduced pressure to give 2,6-dimethoxybenzyl alcohol as a colorless, crystalline solid (15.46 g, 80%); mp 54–56°C (lit. 25 55.5–56°C); δ_H (d_6-DMSO), 3.8 (s, 6H, OCH_3); 4.35 (t, *J*=6 Hz, 1H, OH); 4.5 (d, *J*=6 Hz, 2H, CH_2); 6.6 (d, *J*=8 Hz, 2H, Ar–H); 7.25 (t, *J*=8 Hz, 1H, Ar–H); δ_C (d_6-DMSO), 51.9 (CH_2); 56.0 (OCH_3); 104.3, 117.7 (2×CH); 129.4, 158.8 (2 quaternary C's).

98% Sulfuric acid (3.0 g, 30 mmol) was added dropwise to a mechanically stirred solution of dimethyl sulfide (12.4 g, 0.2 mol) and 2,6-dimethoxybenzyl alcohol (5.05 g, 30 mmol, prepared as above) over ca. 30 min. The mixture was stirred at ambient temperature overnight. The lower layer was separated and evaporated under reduced pressure to give crude 2,6-dimethoxybenzyldimethylsulfonium hydrogensulfate (**1j**) as a white paste (7.5 g, 80% approx.); δ_H (d_6-DMSO), 2.85 (s, 6H, SCH_3); 3.85 (s, 6H, OCH_3); 4.55 (s, 2H, CH_2); 6.8 (d, *J*=6.5 Hz, 2H, Ar–H); 7.4 (t, *J*=6.5 Hz, 1H, Ar–H); δ_C (d_6-DMSO); 24.8 (CH_3); 36.4 (CH_2); 56.5 (OCH_3); 104.0 (*C*–CH_2); 104.8, 132.4 (2×CH); 159.2 (*C*–OCH_3); *m/z* (FAB for salt AB) 213 (11% A^+), 151 (100, A^+–$S(CH_3)_2$), 523 (0.45, A_2B^+ cluster). This compound was found to be extremely unstable and it proved impossible to obtain an analytically pure sample.

4.3.10. Dimethyl-(1-naphthylmethyl)sulfonium hydrogensulfate (1k). 98% Sulfuric acid (580 mg, 5.8 mmol) was added dropwise to a mechanically stirred solution of 1-naphthalenemethanol (913 mg, 5.8 mmol) in dimethyl sulfide (30 cm^3) over ca. 5 min. at ambient temperature. The mixture was stirred at ambient temperature overnight, whereupon a thick, brownish sludge formed. The upper layer of excess dimethyl sulfide was then decanted and ethyl acetate (20 cm^3) was added. The mixture was placed in a sonic bath for 1 h, after which time the ethyl acetate was decanted and a fresh portion added. This procedure was repeated until the product was a fine powder. The product was filtered on a glass sinter, dried under vacuum and the residual solid was recrystallized to give dimethyl-(1-naphthylmethyl)sulfonium hydrogensulfate (**1k**) as an off-white, crystalline solid. (920 mg, 53%); mp 156.5–158°C (EtOH); ν_{max} (KBr)/cm^{-1}, 2984, 2932, 1596, 1512, 1404, 1284, 1171, 1070, 1002, 887, 850, 808, 778, 575; ν_H (d_6-DMSO), 2.9 (s, 6H, CH_3); 5.2 (s, 2H, CH_2); 7.5–7.7 (m, 4H, Ar–H); 8.0 (m, 2H, Ar–H); 8.4 (d, *J*=8 Hz, 1H, Ar–H); δ_C (d_6-DMSO), 24.6, (CH_3); 44.3 (CH_2); 124.2, 126.1, 127.1, 129.4, 131.0, 131.2 (7×CH), 125.0, 131.6, 134.0 (3 quaternary C's). *m/z* (FAB for salt AB), 203 (30%, A^+), 141 (100, A^+–$S(CH_3)_2$), 503 (1.1, A_2B^+ cluster), 804 (0.08, $A_3B_2^+$ cluster); (Found: C, 52.1; H, 5.3%. $C_{13}H_{16}O_4S_2$ requires: C, 52.0; H, 5.4%).

4.3.11. Dimethyl-(2-naphthylmethyl)sulfonium hydrogensulfate (1l). This was prepared as above (for **1k**) from 98% sulfuric acid (3.0 g, 30 mmol), 2-naphthalenemethanol (4.745 g, 30 mmol) and dimethyl sulfide (100 cm^3) to give dimethyl-(2-naphthylmethyl)sulfonium hydrogensulfate (**1l**) as a colorless crystalline solid. (5.2 g, 58%); mp 108.5–109°C (EtOH/EtOAc); ν_{max} (KBr)/cm^{-1}, 3019, 1598, 1502, 1420, 1336, 1171, 1052, 1006, 854, 825, 758; δ_H (d_6-DMSO), 2.85 (s, 6H, CH_3); 4.85 (s, 2H, CH_2); 7.6 (m, 3H, Ar–H); 8.0 (m, 4H, Ar–H); δ_C (d_6-DMSO), 24.2, (CH_3); 46.3 (CH_2); 127.4, 127.7, 127.9, 128.2, 128.5, 129.5, 130.9 (7×CH), 126.3, 133.2, 133.5 (3 quaternary C's). *m/z* (FAB for salt AB), 203 (46%, A^+), 141 (100, A^+–$S(CH_3)_2$), 503 (2.0, A_2B^+ cluster); (Found: C, 51.8; H, 5.3%. $C_{13}H_{16}O_4S_2$ requires: C, 52.0; H, 5.4%).

4.3.12. Dimethyl-(9-phenanthrylmethyl)sulfonium hydrogensulfate (1m). 9-Phenanthrenemethanol. Sodium borohydride (284 mg, 7.5 mmol, 3 equiv.) was suspended in a solution of 9-phenanthrene carboxaldehyde (516 mg, 2.5 mmol) in dry THF (10 cm^3). Isopropanol (5 cm^3) was added and the mixture stirred until reaction was complete (t.l.c.). After the addition of water (2 cm^3) the solvents were evaporated under reduced pressure. The crude product was dissolved in chloroform (20 cm^3) and the solution was washed with water (10 cm^3) then saturated brine (10 cm^3), and finally dried ($MgSO_4$). The mixture was filtered and the filtrate was evaporated under reduced pressure to give 9-phenanthrenemethanol as a colorless, crystalline solid (496 mg, 95%); mp 146–148.5°C (lit. 26 149–149.5°C); δ_H (d_6-DMSO), 5.0 (d, *J*=5.4 Hz, 2H, CH_2); 5.4 (t, *J*=5.4 Hz, 1H, OH); 7.6–7.7 (m, 4H, Ar–H); 7.85 (s, 1H, H_{10}); 7.95 (m, 1H, Ar–H); 8.1 (m, 1H, Ar–H); 8.75–8.9 (m, 2H, Ar–H); δ_C (d_6-DMSO), 61.9 (CH_2); 123.2; 123.7, 124.7, 124.7, 127.0, 127.0, 127.2, 127.3, 128.8 (9×CH) 129.9, 130.3, 130.4, 131.7, 136.5 (5 quaternary C's).

98% Sulfuric acid (1.34 g, 13.4 mmol) was added dropwise to a mechanically stirred solution of 9-phenanthrenemethanol (2.78 13.4 mmol, prepared as above) in dimethyl sulfide (150 cm^3) over ca. 5 min., at ambient temperature. After 1 h, a thick, grey paste formed. The upper dimethyl sulfide layer was decanted and ethyl acetate (50 cm^3) was added. The mixture was placed in a sonic bath for 1 h, after which time the ethyl acetate was decanted and a fresh portion added. This procedure was repeated until the product was a fine powder. The product was filtered on a glass sinter and dried under vacuum to give dimethyl-(9-phenanthrylmethyl)sulfonium hydrogensulfate (**1m**) as an off-white powder which became pale brown after recrystallization (1.96 g, 42%); mp 177–179°C (H_2O/EtOH/EtOAc); ν_{max} (KBr)/cm^{-1}, 3020, 1498, 1431, 1306, 1227, 1170, 1067, 1002, 852, 770, 754, 728; δ_H (d_6-DMSO), 2.95 (s, 6H, CH_3); 5.2 (s, 2H, (CH_2); 7.7–7.9 (m, 4H, Ar–H); 8.0–8.15 (m, 2H, Ar–H); 8.45 (m, 1H, Ar–H); 8.85–9.0 (m, 2H, Ar–H); δ_C (d_6-DMSO), 25.0 (CH_3), 45.3 (CH_2), 123.5, 124.3, 125.0, 127.9, 127.9, 128.0, 128.8, 129.5, 132.5 (9×CH), 123.7, 129.8, 130.8, 130.9, 131.0 (5 quaternary C's); *m/z* (FAB for salt AB) 253 (27%, A^+), 191 (100, A^+–$S(CH_3)_2$) 602 (0.67, A_2B^+ cluster); (Found: C, 58.4; H, 5.2%. $C_{17}H_{18}O_4S_2$ requires: C, 58.3; H, 5.2%).

4.3.13. (9-Anthrylmethyl)dimethylsulfonium hydrogensulfate (1n). This was prepared as above for **1m** from H_2SO_4 (2.0 g, 20 mmol), 9-anthracenemethanol (4.16 g, 20 mmol) and Me_2S (150 cm^3). Compound (**1n**) was a yellowish green powder (6.01 g, 86%); mp 150–150.5°C (dec.); ν_{max} (KBr)/cm^{-1}, 3005, 1624, 1436, 1220, 1062, 884, 850, 743, 584; δ_H (d_6-DMSO), 3.0 (s, 6H, CH_3); 5.7 (s, 2H, CH_2); 7.5–9.0 (m, 9H, Ar–H). δ_C (CP MAS), 26.9 (CH_3), 38.8 (CH_2) 116.9, 123.3, 126.0, 130.2; *m/z* (FAB for salt AB) 253 (3.1%, A^+), 191 (100, A^+–$S(CH_3)_2$); (Found: C, 57.7; H, 5.2; S, 18.1%. $C_{17}H_{18}O_4S_2$ requires: C, 58.3; H, 5.2; S, 18.3%).

4.3.14. 9-Fluorenyldimethylsulfonium hydrogensulfate (1o). This was prepared as above for **1m** from H_2SO_4 (2.0 g, 20 mmol), 9-hydroxyfluorene (3.64 g, 20 mmol) and Me_2S (200 cm^3). Compound (**1o**) was an off-white powder (3.05 g, 45%); mp 148–150°C; ν_{max} (KBr)/cm^{-1}, 2997, 2908, 1412, 1286, 1178, 1069, 1006, 850, 733, 574; δ_H (d_6-DMSO), 2.65 (s, 6H, CH_3); 6.2 (s, 1H, H-9); 7.55.(t, *J*=7.5 Hz, 2H, ArH); 7.65 (t, *J*=7.5 Hz, 2H, Ar–H); 7.9 (d, *J*=7.5 Hz, 2H, Ar–H); 8.1 (d, *J*=7.5 Hz, 2H, Ar–H); δ_C (d_6-DMSO), 22.0 (CH_3); 55.1 (C-9); 121.9, 127.0, 129.1, 131.3 (4×CH); 135.4, 141.8 (2 quaternary C's); *m/z* (FAB for salt AB), 227 (24^+, A^+), 165 (100, A^+ $S(CH_3)_2$) 551 (1.1, A_2B^+ cluster), 875 (0.07, $A_3B_2^+$ cluster); (Found: 551.1436. A_2B^+ cluster requires: 551.1385).

4.3.15. Benzhydryldimethylsulfonium hydrogensulfate (1p). This was prepared as above for **1m** from H_2SO_4 (10.0 g, 0.1 mol), benzhydrol (18.42 g, 0.1 mol) and Me_2S (100 cm^3). Compound (**1p**) was a colorless crystalline solid (22.70 g, 70%); mp 118–119°C; ν_{max} (KBr)/cm^{-1}, 2921, 2618, 1315, 1169, 1062, 847, 713, 581; δ_H (d_6-DMSO), 2.8 (s, 6H, CH_3); 6.3 (s, 1H, CH–S); 7.4–7.5(m, 6H, Ar–H); 7.65–7.75 (m, 4H, Ar–H); δ_C (d_6-DMSO), 24.6 (CH_3); 63.9 (CH–S); 129.0, 130.2 (CH); 134.2 (quaternary C); *m/z* (FAB for salt AB), 229 (3.7%, A^+), 167 (100, A^+–$S(CH_3)_2$), 554 (0.36, A_2B^+ cluster); (Found: C, 55.15; H, 5.5%; $C_{15}H_{18}O_4S_2$ requires: C, 55.2; H, 5.6%).

4.3.16. Benzyldimethylsufonium chloride (1q). Gaseous hydrogen chloride was bubbled through a mixture of dimethyl sulfide (29 cm^3, 0.4 mol) and diethyl ether (29 cm^3) for ca. 20 min. Benzyl alcohol (4.32 g, 40 mmol) was added and the solution was stirred overnight. The solvents were evaporated under reduced pressure and the residue was partitioned between distilled water and diethyl ether. The aqueous layer was separated and the water evaporated under high vacuum to leave benzyldimethylsulfonium chloride (**1q**) as a colorless oil. (5.65 g, 75%); δ_H (d_6-DMSO), 2.95 (s, 6H, CH_3); 4.9 (s, 2H, CH_2); 7.5 (m, 5H, Ar–H); δ_C (d_6-DMSO), 24.1 (CH_3); 46.0 (CH_2); 128.8 (quaternary C) 129.7, 130.0, 131.1 (3×CH); *m/z* (FAB for salt AB) 153 (100%, A^+), 91 (85, A^+–$S(CH_3)_2$), 341 (8.3, A_2B^+ cluster), 529 (0.16, $A_3B_2^+$ cluster).

4.3.17. Benzyldimethylsulfonium trifluoroacetate (1r). Trifluoroacetic acid (22.8 g, 0.2 mol) was added dropwise to a mechanically stirred solution of benzyl alcohol (10.8 g, 0.1 mol) in dimethyl sulfide (29 cm^3, 0.4 mol) over ca. 30 min and the mixture was stirred at ambient temperature overnight. The solvents were evaporated under reduced pressure and the residue was partitioned between distilled water and diethyl ether. The aqueous layer was separated, the water was evaporated under reduced pressure, and the residual solid was triturated with diethyl ether. The slurry was filtered and the solid was dried under high vacuum to give benzyldimethylsulfonium trifluoroacetate (**1r**) as a colorless, crystalline solid (5.32 g, 20%); mp 64–65.5°C (EtOH/EtOAc); ν_{max} (KBr)/cm^{-1}, 3452, 3018, 2930, 1687, 1426, 1203, 1127, 700; δ_H (d_6-DMSO), 2.8 (s, 6H, CH_3); 4.7 (s, 2H, CH_2); 7.45 (m, 5H, Ar–H); δ_C (d_6-DMSO), 24.1 (CH_3); 46.0 (CH_2); 128.8 (quaternary C) 129.8, 130.0, 131.1 (3×CH); *m/z* (FAB for salt AB) 153 (100%, A^+), 91 (76, A^+–$S(CH_3)_2$), 419 (8.3, A_2B^+ cluster); (Found: C, 49.3; H, 5.0%; $C_{11}H_{13}F_3O_2S$ requires: C, 49.6; H, 4.9%).

The diethyl ether layer described above was evaporated under reduced pressure to leave benzyl trifluoroacetate as a colorless liquid (10.2 g, 50%); bp 174–178°C/760 Torr (lit. 27 175°C/760 Torr); ν_{max} (KBr)/cm^{-1}, 3550, 3039, 1784, 1500, 1457, 1395, 1347, 1148, 907; δ_H (d_6-DMSO), 5.3 (s, 2H, CH_2); 7.35 (m, 5H, Ar–H); δ_C (d_6-DMSO), 69.5 (CH_2); 114.5 (q, J_{C-F}=248 Hz, CF_3); 128.6, 128.8, 129.2 (3×CH); 133.2 (quaternary C); 157.4 (q, $^2J_{CF}$=42 Hz, C═O);.

4.3.18. 1-Benzyltetrahydrothiophenium hydrogensulfate (2a). 98% Sulfuric acid (10.0 g, 0.1 mol) was added dropwise to a mechanically stirred solution of benzyl alcohol (10.8 g, 0.1 mol) in tetrahydrothiophene (26.4 g, 0.3 mol) over ca. 20 min at 0°C. The resultant mixture was allowed to warm to ambient temperature and stirred overnight. The lower dark green aqueous layer was separated and sonicated under ethyl acetate (100 cm^3) for 4 h. The ethyl acetate was decanted and any residual solvents evaporated under reduced pressure to give the crude product as an extremely viscous oil. This oil was cooled to −18°C and crystallization occurred. The solid was separated and washed with a little ice-cold ethanol to give pure 1-benzyltetrahydrothio-

phenium hydrogensulfate (**2a**) as a very hygroscopic, colorless, crystalline solid (2.75 g, 10%); mp 76–79°C; ν_{max} (KBr)/cm^{-1}, 3389, 2944, 1494, 1456, 1417, 1200, 1072, 1011, 883, 844, 772, 707; δ_H (d_6-DMSO), 2.05–2.3 (m, 4H, C*H*$_2$–CH$_2$–S); 3.3–3.55 (m, 4H, CH$_2$–C*H*$_2$–S); 4.55 (s, 2H, PhCH$_2$); 7.45 (m, 3H, Ar–H); 7.55 (m, 2H, Ar–H); δ_C (d_6-DMSO), 28.6 (*C*H$_2$–CH$_2$–S); 42.9 (CH$_2$–*C*H$_2$–S); 45.2 (benzyl CH$_2$); 129.8, 129.9, 130.9 (3×CH); 130.4 (quaternary C); *m/z* (FAB for salt AB) 179 (83%, A$^+$), 91 (100, A$^+$–(CH$_2$)$_4$S), 455 (2.9, A$_2$B$^+$ cluster), 731 (0.11, A$_3$B$_2^+$ cluster), 1005 (0.31, A$_4$B$_3^+$ cluster); (Found: C, 46.9; H, 6.1%. $C_{11}H_{16}O_4S_2$ requires: C, 47.8; H, 5.8%).

4.3.19. Tribenzylsulfonium hydrogensulfate (3a). 98% Sulfuric acid (3.0 g, 30 mmol) was added dropwise to a mechanically stirred mixture of benzyl formate (4.49 g, 33 mmol) in dibenzyl sulfide (6.43 g, 30 mmol) over ca. 5 min, at 0°C. The mixture was stirred overnight at ambient temperature, after which time a white precipitate had formed. This was separated and washed with ice-cold diethyl ether (20 cm^3), and then recrystallized to give tribenzylsulfonium hydrogensulfate (**3a**) as a colorless, crystalline solid (10.2 g, 92%); mp 167–168°C (H$_2$O/EtOH/EtOAc), (lit. 28 170–175°C); δ_H (d_6-DMSO), 4.9 (s, 6H, CH$_2$); 7.3 (m, 15H, Ar–H); δ_C (d_6-DMSO), 45.2 (CH$_2$); 129.2 (quaternary C); 129.5, 129.7, 130.8 (3×CH); *m/z* (FAB for salt AB) 91 (100%, A$^+$–(PhCH$_2$)$_2$S), 305 (31, A$^+$), 707 (1.2, A$_2$B$^+$ cluster); (Found: C, 63.0; H, 5.9%. $C_{21}H_{22}O_4S$ requires: C, 62.7; H, 5.5%).

4.4. General procedure for the preparation of tetrafluoroborate salts (1s–u, 2b, 3b)

The appropriate sulfide (0.1 mol) and the alcohol (50 mmol) were dissolved in dichloromethane (50 cm^3). A 54% w/w solution of tetrafluoroboric acid in diethyl ether (7 cm^3, 8.1 g, equivalent to 4.4 g of HBF_4, 50 mmol) was added dropwise over ca. 5 min. at 0°C. The mixture was stirred overnight at ambient temperature. The solvents were evaporated under reduced pressure to give a thick, colorless oil, which was triturated with diethyl ether to crystallise the salt. The following were prepared:

4.4.1. Benzyldimethylsulfonium tetrafluoroborate (1s). Colorless, crystalline solid (10.04 g, 84%); mp 103–104°C (H$_2$O/EtOH/EtOAc); ν_{max} (KBr)/cm^{-1}, 3420, 3025, 1470, 1438, 1053, 703; δ_H (d_6-DMSO), 2.8 (s, 6H, CH$_3$); 4.7 (s, 2H, CH$_2$); 7.5 (m, 5H, Ar–H); δ_C (d_6-DMSO), 24.1 (CH$_3$); 46.1 (CH$_2$); 128.6 (quaternary C) 129.8, 130.1, 131.1 (3×CH); *m/z* (FAB for salt AB) 153 (100%, A$^+$), 91 (74, A$^+$–S(CH$_3$)$_2$), 393 (8.3, A$_2$B$^+$ cluster); (Found: C, 44.6; H, 5.4%; $C_9H_{13}BF_4S$ requires: C, 45.0; H, 5.5%).

4.4.2. 2-Chlorobenzyldimethylsulfonium tetrafluoroborate (1t). Colorless, crystalline solid (9.35 g, 68%); mp 69–70°C (H$_2$O/EtOH/EtOAc); ν_{max} (KBr)/cm^{-1}, 3442, 3037, 2935, 1473, 1425, 1053, 762; δ_H (d_6-DMSO), 2.9 (s, 6H, CH$_3$); 4.7 (s, 2H, CH$_2$); 7.45–7.65 (m, 4H, Ar–H); δ_C (d_6-DMSO), 24.7 (CH$_3$); 44.3 (CH$_2$); 127.0, 134.5 (2 quaternary C's) 128.6, 130.7, 132.2, 133.8 (4×CH); *m/z* (FAB for salt AB) 187 (100%, A$^+$), 125 (58, A$^+$–S(CH$_3$)$_2$), 461 (3.1, A$_2$B$^+$ cluster); (Found: C, 39.3; H, 4.4%; $C_9H_{12}BClF_4S$ requires: C, 39.4; H, 4.4%).

4.4.3. Benzhydryldimethylsulfonium tetrafluoroborate (1u). Colorless, crystalline solid (14.56 g, 92%); mp 155–160°C dec.; ν_{max} (KBr)/cm^{-1}, 3480, 2981, 2905, 1630, 1494, 1455, 1425, 1028, 732, 626; δ_H (d_6-DMSO), 2.8 (s, 6H, CH$_3$); 6.1 (s, 1H, CH–S); 7.5–7.7(m, 10H, Ar–H); δ_C (d_6-DMSO), 24.8 (CH$_3$); 64.6 (CH–S); 128.9, 128.9, 130.2 (3×CH); 133.9 (quaternary C); *m/z* (FAB for salt AB), 229 (3.7%, A$^+$), 167 (100, A$^+$–S(CH$_3$)$_2$) 544 (0.36, A$_2$B$^+$ cluster); this compound could not be purified to analytical standard. (Found: C, 56.0; H, 5.3%; $C_{15}H_{17}BF_4S$ requires C, 57.0; H, 5.4%).

4.4.4. 1-Benzyltetrahydrothiophenium tetrafluoroborate (2b). Colorless, crystalline solid (11.75 g, 88%); mp 79–79.5°C (H$_2$O/EtOH/EtOAc); ν_{max} (KBr)/cm^{-1}, 3420, 2944, 1458, 1036, 770, 703; δ_H (d_6-DMSO), 2.1–2.3 (m, 4H, C*H*$_2$–CH$_2$–S); 3.3–3.5 (m, 4H, CH$_2$–C*H*$_2$–S); 4.5 (s, 2H, PhCH2); 7.45 (m, 3H, Ar–H); 7.55 (m, 2H, Ar–H); δ_C (d6-DMSO), 28.6 (CH$_2$–CH$_2$–S); 43.0 (CH$_2$–CH$_2$–S); 45.4 (benzyl CH2); 129.9, 130.0, 130.8 (3×CH); 130.2 (quaternary C); *m/z* (FAB for salt AB) 179 (100%, A$^+$), 91 (87, A$^+$–(CH$_2$)$_4$S), 445 (2.3, A$_2$B$^+$ cluster); (Found: C, 49.5; H, 5.6%. $C_{11}H_{15}BF_4S$ requires: C, 49.65; H, 5.7%).

4.4.5. Tribenzylsulfonium tetrafluoroborate (3b). Colorless, crystalline solid (10.80 g, 55%); mp 170–171°C (EtOH); ν_{max} (KBr)/cm^{-1}, 2991, 1497, 1456, 1423, 1254, 1070, 775, 708; δ_H (d_6-DMSO), 4.8 (s, 6H, CH$_2$); 7.3 (m, 15H, Ar–H); δ_C (d_6-DMSO), 45.4 (CH$_2$); 129.0 (quaternary C); 129.6, 129.8, 130.8 (3×CH); *m/z* (FAB for salt AB) 91 (100%, A$^+$–(PhCH$_2$)$_2$S), 305 (52, A$^+$), 697 (1.4, A$_2$B$^+$ cluster); (Found: C, 64.3; H, 5.6%. $C_{21}H_{21}BF_4S$ requires: C, 64.3; H, 5.4%).

4.4.6. 1-Methyltetrahydrothiophenium hydrogensulfate (2c). 98% Sulfuric acid (10.0 g, 0.1 mol) was added dropwise to a mechanically stirred mixture of tetrahydrothiophene (17.6 g, 0.2 mol) and methanol (4 cm^3, 3.2 g, 0.1 mol) over ca. 30 min. The mixture was stirred at ambient temperature overnight, and the lower layer was separated and evaporated under reduced pressure to afford 1-methyltetrahydrothiophenium hydrogensulfate (**2c**) as a colorless oil; δ_H (d_6-DMSO), 2.0–2.3 (m, 4H, C*H*$_2$CH$_2$S); 2.8 (s, 3H, CH$_3$); 3.2–3.5 (m, 4H, CH$_2$C*H*$_2$ S); δ_C (d_6-DMSO), 25.3 (CH$_3$); 28.1 (*C*H$_2$CH$_2$S); 44.7 (CH$_2$*C*H$_2$ S); *m/z* (FAB for salt AB) 103 (100%, A$^+$), 303 (2.3, A$_2$B$^+$ cluster); [Found: A$_2$B$^+$ 303.0784; $C_{10}H_{23}O_4S_3$ requires: 303.0758].

4.5. Synthesis of bis sulfonium salts

4.5.1. 1,4-Phenylene bis-(methylene) bis-(dimethylsulfonium hydrogensulfate) (4a). 98% Sulfuric acid (4.0 g, 40 mmol) was added dropwise to a mechanically stirred solution of 1,4-benzenedimethanol (2.76 g, 20 mmol) in dimethyl sulfide (100 cm^3) over ca. 15 min. After stirring overnight at ambient temperature, the lower aqueous layer was separated and sonicated under ethyl acetate for 5 h before trituration with ethanol. The resulting slurry was filtered and the solid was dried under high vacuum to give the title compound (**4a**) as a colorless, crystalline solid (4.11 g, 49%); mp 164–165°C (dec.) (EtOH); ν_{max} (KBr)/cm^{-1}, 2982, 2486, 1432, 1290, 1167, 1070, 1006, 851; δ_H (d_6-DMSO), 2.85 (s, 12H, CH$_3$); 4.75 (s, 4H, CH$_2$); 7.6 (s,

4H, Ar–H); δ_C (d_6-DMSO), 23.9 (CH_3); 45.2 (CH_2); 130.2 (quaternary C); 132.0 (CH); *m/z* (FAB for salt AB_2) 165 (100%, $A–S(CH_3)_2^+$), 325 (57, AB^+ cluster), 747 (1.3, $A_2B_3^+$ cluster); (Found: C, 33.9; H, 5.2%. $C_{12}H_{22}O_8S_4$ requires: C, 34.1; H, 5.25%).

4.5.2. (2,3,5,6-Tetrafluoro-1,4-phenylene) bis-(methylene) bis-(dimethyl sulfonium hydrogensulfate) (4b). 98% Sulfuric acid (10.0 g, 100 mmol) was added dropwise to a mechanically stirred solution of 1,4-(2,3,5,6-tetrafluoro)-benzenedimethanol (5.26 g, 50 mmol) in dimethyl sulfide (100 cm^3) over ca. 15 min. After stirring for 4 h at ambient temperature the lower dark brown aqueous layer was separated and sonicated under ethyl acetate for 4 h. The resulting mixture contained some solid and was left for three days to crystallise. The solids were separated, triturated with hot ethanol, then filtered, and the residual material was dried under high vacuum to give the *title compound* **4b** as a colorless, crystalline solid (10.04 g, 41%); mp 200–202°C (H_2O, EtOH); ν_{max} (KBr)/cm^{-1}, 3003, 2475, 1496, 1435, 1299, 1224, 1061, 1017, 875, 843; δ_H (d_6-DMSO), 2.95 (s, 12H, CH_3); 4.9 (s, 4H, CH_2); δ_C (100.6 MHz d_6-DMSO), 24.0 (CH_3); 33.5 (CH_2); 109.9 (*C*–CH_2); 145.3 (dd, $^1J_{CF}$=250 Hz; $^2J_{CF}$=11 Hz); δ_F (C_2D_6SO), −138.8 (s); *m/z*(FAB for salt AB_2) 238 (33%, $A–S(CH_3)_2^+$), 335 (72, $AB–S(CH_3)_2^+$), 397 (6.8, AB^+ cluster); (Found: C, 29.0; H, 3.6%. $C_{12}H_{18}F_4O_8S_4$ requires: C, 29.15; H, 3.7%).

4.5.3. 1,1′-[1,4-Phenylene bis-(methylene)] bis-(tetrahydrothiophenium hydrogensulfate) (4c). 98% Sulfuric acid (8.0 g, 80 mmol) was added dropwise to a mechanically stirred solution of 1,4-benzenedimethanol (5.53 g, 40 mmol) in tetrahydrothiophene (80 cm^3) over ca. 15 min. After stirring overnight at ambient temperature, the (lower) dark red aqueous layer was separated and sonicated under ethyl acetate for 4 h. This mixture was left to crystallise for two weeks. The resultant solid was slurried with ethanol and ground in a mortar and pestle. This slurry was filtered and the solid was recrystallized from a mixture of water, ethanol and acetone and finally dried under high vacuum to give the title compound (**4c**) as a colorless, crystalline solid (13.90 g, 85%); mp 183.5–185°C (H_2O/EtOH/acetone); ν_{max} (KBr)/cm^{-1}, 3408, 3998, 2486, 1405, 1187, 1020, 882, 826, 700, 572; δ_H (d_6-DMSO), 2.1–2.3 (m, 8H, C*H*$_2$–CH_2–S); 3.35–3.5 (m, 8H, CH_2–C*H*$_2$–S); 4.6 (s, 4H, benzyl CH_2); 7.65 (s, 4H, Ar–H); δ_C (d_6-DMSO), 28.2 (*C*H_2–CH_2–S); 42.8 (CH_2–*C*H_2–S); 44.3 (benzyl CH_2); 131.45 (quaternary C); 131.45 (CH); *m/z* (FAB for salt AB_2) 191 (100%, $A–S(CH_2)_4^+$), 289 (11, $AB–S(CH_2)_4^+$), 377 (31, AB cluster); (Found: C, 40.6; H, 5.5%. $C_{16}H_{26}O_8S_4$ requires: C, 40.5; H, 5.5%).

4.5.4. 1,1′-[(2,3,5,6-Tetrafluoro-1,4-phenylene) bis-(methylene)] bis-(tetrahydrothiophenium hydrogensulfate) (4d). This was prepared as above for **4c** from 98% sulfuric acid (10.0 g, 100 mmol), 1,4-(2,3,5,6-tetrafluoro)-benzenedimethanol (5.26 g, 50 mmol) and tetrahydrothiophene (30 cm^3). After work up, the resulting solid was triturated with hot ethanol, filtered and the solid was dried under high vacuum to give the title compound (**4d**) as an off-white, crystalline solid (6.31 g, 23%); mp 184–184.5°C; ν_{max} (KBr)/cm^{-1}, 3396, 2991, 2593, 1498, 1426, 1310, 1190, 1042, 998, 831, 584; δ_H (d_6-DMSO), 2.25 (m, 8H, C*H*$_2$–CH_2–S); 3.3–3.65 (m, 8H, CH_2–C*H*$_2$–S); 4.8 (s, 4H, benzyl CH_2); δ_C (100.6 MHz, d_6-DMSO), 28.0 (*C*H_2–CH_2–S); 32.6 (benzyl CH_2); 44.2 (CH_2–*C*H_2–S); 111.2 (t, $^2J_{CF}$=10 Hz, quaternary C); 145.3 (dt, $^1J_{CF}$=245 Hz, $^2J_{CF}$=11 Hz, CF); δ_F (376.5 MHz, d_6-DMSO), −139.3 (s); *m/z* (FAB for salt AB_2) 264 (3.7%, $A–S(CH_2)_4^+$), 361 (2.4, $AB^+–S(CH_2)_4^+$); (Found: C, 34.7; H, 4.3%. $C_{16}H_{22}F_4O_8S_4$ requires: C, 35.2; H, 4.1%).

4.5.5. 1,1′[(2,3,5,6-Tetrafluoro-1,4-phenylene) bis-(methylene)] bis-(tetrahydrothiophenium tetrafluoroborate) (4e) and 1-[2,3,5,6-tetrafluoro-4-hydroxymethyl) benzyl]tetrahydrothiophenium tetrafluoroborate (5). A 54% w/w solution of tetrafluoroboric acid in diethyl ether (2.76 cm^3, 3.25 g, equivalent to 1.76 g of acid, 20 mmol) was added to a stirred solution of 1,4-(2,3,5,6-tetrafluoro)-benzenedimethanol (2.10 g, 10 mmol) and tetrahydrothiophene (3.88 g, 44 mmol) in acetonitrile (20 cm^3) at 0°C. The mixture was allowed to warm to 20°C and stirred overnight. The solvents were evaporated under reduced pressure to give a viscous, yellow oil. Unreacted starting material (1.5 g) was removed from this oil by repeated sonication under diethyl ether (6×30 cm^3, 1 h). Finally, sonication under acetone (3×30 cm^3) left a greyish powder which was dried (0.1 Torr, 25°C) to give 1,1′-[(2,3,5,6-tetrafluoro-1,4-phenylene) bis-(methylene)] bis-(tetrahydrothiophenium tetrafluoroborate) (**4e**) as an off-white powder (140 mg, 2.5%) mp 250°C (dec.); ν_{max} (KBr)/cm^{-1}, 3424, 2952, 1497, 1305, 1032; δ_H (d_6-DMSO), 2.1–2.5 (m, 8H, C*H*$_2$–CH_2–S); 3.3–3.6 (m, 8H, CH_2–C*H*$_2$–S); 4.8 (s, 4H, benzyl CH_2); δ_C (100.6 MHz, d_6-DMSO), {^{1}H} 28.1 (*C*H_2–CH_2–S); 32.6 (benzyl CH_2); 44.3 (CH_2–*C*H_2–S); {^{19}F} 111.0 (quaternary C); 145.3 (CF); δ_F (376.5 MHz, d_6-DMSO), −148.80 (BF_4^-); −139.28 (s, CF); *m/z*(FAB for salt AB_2) 263 (100%, $A–S(CH_2)_4–ZH^+$), 439 (86, AB^+); (Found: C, 36.2; H, 3.8%. $C_{16}H_{20}B_2F_{12}S_2$ requires: C, 36.5; H, 3.8%).

4.6. Reactions of (9-anthrylmethyl)dimethylsulfonium hydrogensulfate (1n)

The acetone extracts from above were evaporated under reduced pressure to afford 1-[(2,3,5,6-tetrafluoro-4-hydroxymethyl)benzyl] tetrahydrothiophenium tetrafluoroborate (**5**) as a brown oil (2.9 g, 79%); δ_H (d_6-DMSO), 2.1–2.35 (m, 4H, C*H*$_2$–CH_2–S); 3.3–3.6 (m, 4H, CH_2–C*H*$_2$–S); 4.5 (broad s, 1H, OH); 4.55, 4.75 (s, 4H, 2×benzyl CH_2); δ_C (100.6 MHz, C_2D_6SO), {^{1}H} 28.1 (*C*H_2–CH_2–S); 36.0 (benzyl CH_2–S); 42.3 (CH_2–*C*H_2–S); 51.1 (CH_2OH); {^{19}F} 108.7, 121.8 (2 quaternary C's); 144.6, 145.0 (CF); δ_F (376.5 MHz, d_6-DMSO), −148.80 (s, BF_4^-); −146.04 (s); −144.33 (q, *J*=11 Hz); −140.96 (q, *J*=11 Hz); −139.28 (s); *m/z* (FAB for salt AB) 117 (100%); 193 (6.7, $A–S(CH_2)_4^+$), 281 (26, A^+), 649 (0.43, A_2B^+ cluster). This compound could not be obtained analytically pure.

4.6.1. Reactions of (9-anthrylmethyl)dimethylsulfonium hydrogensulfate (1n) with d^6-dimethyl sulfoxide. (9-Anthrylmethyl)dimethylsulfonium hydrogensulfate (**1n**) (70 mg, 0.2 mmol) was added to d^6-DMSO (0.7 cm^3) in an NMR tube. The proton and carbon-13 spectra showed the

presence of **1n**, **6a** and dimethyl sulfide. δ_H (d_6-DMSO), 2.0 [s, $(CH_3)_2S$]; 2.95 [s, $(CH_3)_2S^+$]; 5.75 [s, CH_2–O); 5.8 (s, CH_2–S^+); 7.5–8.9 (two sets of overlapping aromatic protons corresponding to the correct integral for the two salts **1n** and **6a**). δ_C (d_6-DMSO), 17.7 [$(CH_3)_2S$]; 24.8 [$(CH_3)_2S^+$]; 39.9 (CH_2–S^+); 60.7 (CH_2–O); 124.5, 124.8, 125.6, 126.0, 126.7,128.0, 128.5, 129.2, 129.9, 130.9 (10×CH, 5 for each of **1n** and **6a**); 119.9, 128.1, 131.3, (2 unresolved peaks), 131.4, 131.5 (6 quaternary C's, 3 for each of **1n** and **6a**).

4.6.2. Reactions of (9-anthrylmethyl)dimethylsulfonium hydrogensulfate (1n) with d^7-*N*,*N*-dimethylformamide. (9-Anthrylmethyl)dimethylsulfonium hydrogensulfate (**1n**) (70 mg, 0.2 mmol) was added to d^7-DMF (0.7 cm^3) in an NMR tube. The proton and carbon-13 spectra showed that the presence of **1n**, **6b** and dimethyl sulfide. δ_H (400 MHz, d_7-DMF), 2.1 [s, $(CH_3)_2S$]; 3.25 [s, $(CH_3)_2S^+$]; 5.95 (s, CH_2–O); 6.05 (s, CH_2–S^+); 7.5–8.9 (two sets of overlapping aromatic H's corresponding to the correct integral for the two salts **1n** and **6b** combined). δ_C (100.6 MHz, d_7-DMF), 16.6 [$(CH_3)_2S$]; 24.0 [$(CH_3)_2S^+$]; 39.3 (CH_2–S^+); 60.1 (CH_2–O); 123.8, 124.3, 124.6, 125.2, 125.8,127.3, 127.7, 128.4, 129.1, 130.3 (10×CH, 5 for each of **1n** and **6b**); 119.1, 128.1, 130.6, (2 unresolved peaks), 131.0, 131.2 (6 quaternary C's, 3 for each of **1n** and **6b**).

4.6.3. Reactions of (9-anthrylmethyl)dimethylsulfonium hydrogensulfate (1n) with water. (9-Anthrylmethyl)dimethylsulfonium hydrogensulfate (**1n**) (35 mg, 0.1 mmol) was warmed (~40°C) with water (2 cm^3) for 5 min. The product was extracted with dichloromethane (2 cm^3) and the extract was evaporated under reduced pressure to give 9-anthracenemethanol (**6c**) as a yellow, crystalline solid (20 mg, 96%) mp 160–163°C (lit. 29 162–164°C) which was identical (ir, NMR) to an authentic sample.

4.6.4. Reactions of (9-anthrylmethyl)dimethylsulfonium hydrogensulfate (1n) with alcohols. (9-Anthrylmethyl)dimethylsulfonium hydrogensulfate (**1n**) (350 mg, 1 mmol) was added to the appropriate alcohol (25 cm^3) and the mixture was stirred at 50°C until dissolution occurred. The product was partitioned between chloroform (20 cm^3) and water (40 cm^3), the organic layer was separated and the aqueous layer extracted with chloroform (2×10 cm^3). The combined organic layer was washed with saturated brine, dried ($MgSO_4$) and then evaporated under reduced pressure to give, separately: 9-methoxymethyl anthracene (**6d**) (206 mg, 93%); mp 89–90.5°C (lit. 30 90–91°C); and 9-ethoxymethyl anthracene (**6e**) (230 mg, 97%); mp 74–75.5°C (lit. 31 74–75°C) as yellow crystalline solids.

4.6.5. Reactions of (9-anthrylmethyl)dimethylsulfonium hydrogensulfate (1n) with ethanol in DMSO. (9-Anthrylmethyl)dimethylsulfonium hydrogensulfate (**1n**) (700 mg, 2 mmol) was added to DMSO (20 cm^3) and the mixture was warmed until dissolution of the salt was complete. Ethanol (460 mg, 10 mmol) was added and the mixture was placed in a sonic bath overnight at 30°C. The DMSO was evaporated under reduced pressure and the residue was partitioned between water (30 cm^3) and dichloromethane (30 cm^3). The organic layer was separated, washed with 2 M aqueous sodium hydroxide then water and finally saturated brine. The extract was dried ($MgSO_4$), filtered and evaporated under reduced pressure to give 9-anthraldehyde as a crystalline, yellow solid (354 mg, 86%) mp 102–103°C (THF/hexane) (lit. 32 103–104°C).

4.7. Reaction of (9-anthrylmethyl)dimethylsulfonium hydrogensulfate (1n) with nucleophiles in DMF: general procedure

(9-Anthrylmethyl)dimethylsulfonium hydrogensulfate (**1n**) (700 mg, 2 mmol) was added to DMF (20 cm^3) and the mixture was warmed until dissolution of the salt was complete. The nucleophile (6 mmol, 3 mol equiv.) was added and the mixture was placed in a sonic bath overnight at 30°C. The DMF was evaporated under reduced pressure and the residue partitioned between water (100 cm^3) and dichloromethane (50 cm^3). After filtration through celite, the organic layer was separated, washed with 2 M aqueous sodium hydroxide, then water and finally saturated brine before being separated, dried ($MgSO_4$) and filtered. The solvents were evaporated under reduced pressure to give the crude products, which were purified as detailed below.

4.7.1. Ethanol. The crude product was a yellow powder which was recrystallized to give pure 9-ethoxymethyl anthracene (**6e**) as a yellow, crystalline solid (330 mg, 70%); This compound was identical (mp, ^1H NMR) to that described above.

4.7.2. Potassium cyanide. The crude product was a yellow powder which was recrystallized to give pure (9-anthryl)-acetonitrile (**6f**) as a crystalline, yellow solid (330 mg, 76%) mp 161.5–163°C (Et_2O/hexane) (lit. 33 161–163°C); ν_{max} (KBr)/cm^{-1}, 3052, 2241, 1622, 1403, 1345, 1155, 900, 885, 789, 735; δ_H (200 MHz, $CDCl_3$), 4.5 (s, 2H, CH_2); 7.4–7.7 (m, 4H, Ar–H); 8.0 (d, J=8 Hz, 2H, Ar–H); 8.1 (d, J=8 Hz, 2H, Ar–H); 8.45 (s, 1H, Ar–H); δ_C ($CDCl_3$), 16.1 (CH_2); 122.8, 125.2, 127.2, 128.8, 129.4 (5×CH); 117.7, 120.6, 129.6, 131.3 (4 quaternary C's); *m/z* (FAB), 217 (100%, M^+) 191 (39, M^+-CN).

4.7.3. Potassium thiocyanate. The crude product was a yellow powder which was recrystallized to give pure 9-(thiocyanatomethyl)anthracene (**6g**) as a crystalline, yellow solid (400 mg, 80%) mp 143.5–144°C (THF/Et_2O); ν_{max} (KBr)/cm^{-1}, 3050, 2145, 1446, 1217, 896, 851, 794, 732; δ_H ($CDCl_3$), 5.3 (s, 2H, CH_2); 7.45–7.7 (m, 4H, Ar–H); 8.0 (d, J=8.5 Hz, 2H, Ar–H); 8.2 (d, J=8.5 Hz, 2H, Ar–H); 8.5 (s, 1H, Ar–H); δ_C ($CDCl_3$), 31.7 (CH_2); 112.2 (SCN); 122.8, 125.4, 127.4, 129.5, 129.8 (5×CH); 123.3, 130.1, 131.2 (3 aromatic quaternary C's); *m/z* (FAB), 249 (13%, M^+) 191 (100, M^+-SCN),; (Found: C, 76.9; H, 4.3; N, 5.45%. $C_{16}H_{11}NS$ requires: C, 77.1; H, 4.45; N, 5.6%).

4.7.4. Sodium acetate. The crude product was a yellow powder which was recrystallized to give pure (9-anthryl)-methyl acetate (**6h**) as a crystalline, yellow solid (254 mg, 78%) mp 110–111°C (THF/hexane) (lit. 34 111–112°C); δ_H ($CDCl_3$), 2.1 (s, 3H, CH_3); 6.15 (s, 2H, CH_2); 7.5–7.65 (m, 4H, Ar–H); 8.0 (d, J=8 Hz, 2H, Ar–H); 8.3 (d, J=8 Hz, 2H, Ar–H); 8.5 (s, 1H, Ar–H).

4.7.5. Potassium benzaldoximate (prepared as below). The crude product was a yellow oil which was purified by flash column chromatography on silica gel, [petroleum ether (bp 60–80°C)/ethyl acetate, 10:1 eluant] to give a yellow powder. This was recrystallized to give pure benzaldehyde oxime *O*-(9-anthryl)methyl ether (**6i**) as a crystalline, yellow solid (150 mg, 24%) mp 134–135°C [petroleum ether (bp 60–80°C)]; ν_{max} (KBr)/cm^{-1}, 3060, 2942, 1444, 1329, 1206, 1162, 1053, 1015, 940, 883, 858, 756, 725; δ_H ($CDCl_3$), 6.2 (s, 2H, CH_2); 7.3–7.6 (m, 9H, Ar–H); 8.0 (d, *J*=8 Hz, 2H, Ar–H); 8.1 (s, 1H, CH=N); 8.45 (s, 1H, Ar–H); 8.48 (d, *J*=8 Hz, 2H, Ar–H); δ_C ($CDCl_3$), 68.6 (CH_2); 124.4, 125.0, 126.3, 127.0, 128.6, 128.8, 128.9, 129.8 (8×CH); 127.3, 131.2, 131.4, 132.1 (4 aromatic quaternary C's); 149.0 (CH=N); *m/z* (FAB), 311 (13%, M^+); 191 (100, M^+-SCN), (Found: C, 84.8; H, 5.4; N, 4.5%. $C_{22}H_{17}NO$ requires: C, 84.9; H, 5.5; N, 4.5%).

4.7.6. Potassium *syn*-benzaldoximate. Potassium hydroxide (2.78 g, 49.5 mmol) was added in portions to a stirred solution of *syn*-benzaldoxime (6.05 g, 0.05 mol) in water (25 cm^3) and ethanol (25 cm^3). After stirring overnight at ambient temperature the solvents were removed by evaporation under reduced pressure and the crude product was partitioned between water (20 cm^3) and diethyl ether (10 cm^3). The aqueous layer was separated and evaporated to dryness under reduced pressure to give potassium *syn*-benzaldoximate as an off-white powder (7.0 g, 90%) mp 245–250°C (dec.); δ_C (C_2D_6SO), 123.6, 124.5, 128.4 (3×CH); 139.7 (quaternary C); 142.3 (CH=N). *m/z* (FAB for salt KB), 357 (0.57%, $K_3B_2^+$ cluster) 198(12, K_2B^+ cluster), 39 (100, K^+).

4.7.7. Reaction of (9-anthrylmethyl)dimethylsulfonium hydrogensulfate (1n) with acetonitrile. (9-Anthrylmethyl)dimethylsulfonium hydrogensulfate (**1n**) (3.50 g, 10 mmol) was suspended in dry acetonitrile (20 cm^3). DMF (0.8 cm^3, 10 mmol) was added and the mixture was heated under reflux overnight. The solvents were evaporated under reduced pressure and the residue was partitioned between water (20 cm^3) and chloroform (20 cm^3). The organic layer was separated and washed consecutively with water, saturated sodium bicarbonate solution, water and finally saturated brine. The solution was dried ($MgSO_4$), filtered, and the solvents were by evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel, [2% methanol in dichloromethane, eluant] to give a brown powder. This product was recrystallized to give [*N*-(9-anthrylmethyl)]-acetamide (**6j**) as a crystalline, orange solid (370 mg, 15%) mp 253–256.5°C (THF/hexane); ν_{max} (KBr)/cm^{-1}, 3232, 3056, 1629, 1548, 1373, 1286, 886, 729; δ_H (d_6-DMSO), 1.8 (s, 3H, CH_3); 5.25 (d, *J*=5 Hz, 2H, CH_2); 7.5–7.65 (m, 4H, Ar–H); 8.1 (d, *J*=8.5 Hz, 2H, Ar–H); 8.35 (t, *J*=5 Hz, 1H, NH); 8.4 (d, *J*=8.5 Hz, 2H, Ar–H); 8.6 (s, 1H, Ar–H); δ_C (d_6-DMSO), 22.8 (CH_3); 35.3 (CH_2); 125.0, 125.7, 126.7, 127.7, 129.3 (5×CH); 130.4, 130.5, 131.5 (3 aromatic quaternary C's); 169.3 (C=O); *m/z* (FAB), 249 (70%, M^+); 43 (100, $CONH^+$), [Found (EI, 15 eV) 249.11489, $C_{17}H_{15}NO$ requires: 249.11537]; (Found: C, 81.7; H, 5.9; N, 5.1%. $C_{17}H_{15}NO$ requires: C, 81.9; H, 6.1; N, 5.6%).

4.8. Oligomerization in nitromethane

(9-Anthrylmethyl)dimethylsulfonium hydrogensulfate (**1n**) (3.50 g, 10 mmol) was suspended in dry nitromethane (20 cm^3). DMF (8 cm^3, 10 mmol) was added and the mixture was heated under reflux overnight. The solvents were evaporated under reduced pressure and the residue was partitioned between water (20 cm^3) and chloroform (20 cm^3). The organic layer was separated and washed consecutively with water, saturated sodium bicarbonate solution, water, and finally saturated brine. The solution was dried ($MgSO_4$), filtered, and the solvents were evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel [petroleum ether (bp 60–80°C)/ethyl acetate, 1:1 eluant] to give a dark red powder believed to be poly-[9(10)-anthrylenemethylene] (7) (1.50 g, 79%); ν_{max} (KBr)/cm^{-1},; δ_H ($CDCl_3$), 4.0–4.6 (broad s, CH_2); 6.3–8.7 (broad m, Ar–H); δ_C ($CDCl_3$), 49 (broadened peak, CH_2); 124–140 (many aromatic peaks); *m/z* (FAB), 571 [4.3, (anthryl-CH_2)$_3$+H^+]; 381 [25, (anthryl-CH_2)$_2$+H^+]; 191 [100, (anthryl-CH_2)+H^+],; (Found: C, 91.6; H, 5.40%. $(C_{15}H_{10})_n$ requires C, 94.7; H, 5.3%).

4.9. Reactions of (9-anthrylmethyl)dimethylsulfonium hydrogensulfate (1n) with phenol in nitromethane

(9-Anthrylmethyl)dimethylsulfonium hydrogensulfate (**1n**) (1.75 g, 5 mmol) and phenol (471 mg, 5 mmol) were heated under reflux in nitromethane (20 cm^3) for three days. The solvents were evaporated under reduced pressure and the residue was partitioned between water (20 cm^3) and chloroform (20 cm^3). The organic layer was separated and washed consecutively with water, 6 M aqueous sodium hydroxide, saturated aqueous ammonium chloride, water and saturated brine. The solution was dried ($MgSO_4$) and filtered, and the solvent was evaporated under reduced pressure. The residual yellow oil was purified by flash column chromatography on silica gel [petroleum ether (bp 60–80°C)/ethyl acetate, 5:1 eluant] to give 9-anthraldehyde as a crystalline, yellow solid (470 mg, 46%); This was identical (mp, ^{1}H NMR) to the compound prepared previously (see above—'reaction with EtOH in DMSO'). Further elution gave 9-(4-hydroxybenzyl)anthracene (**6k**) as a crystalline, yellow solid (280 mg, 20%); mp 185–187°C (toluene/hexane) (lit. 35 187–188°C); δ_H ($CDCl_3$), 4.9 (s, 2H, CH_2); 6.15 (s, 1H, OH, lost on deuteration); 6.7 (d, *J*=8.5 Hz, 2H, Ar–H); 7.0 (d, *J*=8.5 Hz, 2H, Ar–H); 7.45 (m, 4H, Ar–H); 8.0–8.1 (m, 2H, Ar–H); 8.2–8.3 (m, 2H, Ar–H); 8.45 (s, 1H, Ar–H); δ_C ($CDCl_3$), 67.7 (CH_2); 106.2, 115.4, 124.8, 124.9, 125.8, 126.4, 129.1 (7×CH); 130.4, 131.6, 132.4, 132.6, 154.1 (5 quaternary C's); *m/z* (FAB), 284 (3.2%, M^+); 71 (100).

4.10. General procedure for benzylation of phenol and thiophenol with sulfonium salts

A mixture of the appropriate sulfonium salt (see Discussion) (10.5 mmol), phenol or thiophenol (10 mmol) and sodium carbonate (25 mmol) in water (25 cm^3) and toluene (25 cm^3) was heated to 60°C until all the phenol or thiophenol was consumed (gc analysis). The toluene layer was separated and the aqueous phase was extracted with toluene (2×10 cm^3). The combined toluene phase was dried

($MgSO_4$), filtered, and evaporated under reduced pressure to afford the crude products, which were purified as shown below.

4.10.1. 2-Chlorobenzyl phenyl ether (8a). Purified by distillation to afford a colorless liquid (96%), bp 118–122°C/0.1 Torr (lit. 36 140–145°C/2.5 Torr); ν_{max} (KBr)/cm^{-1}, 3063, 2921, 1598, 1495, 1445, 1380, 1304, 1241, 1172, 1036, 881, 752, 691; δ_H ($CDCl_3$), 5.2 (s, 2H, CH_2); 6.95–7.05 (m, 3H, Ar–H); 7.15–7.4 (m, 5H, Ar–H); 7.5–7.6 (m, 1H, Ar–H); δ_C ($CDCl_3$), 67.0 (CH_2); 114.8, 121.1, 126.9, 128.7, 128.9, 129.3, 129.5, (7×CH); 132.5, 134.7, 158.4 (3 quaternary C's); *m/z* (FAB), 218, 220 (21%, 8.2% M^+); 125, 127 (100, 49, $M^+ - OC_6H_5$) (Found (EI), 218.04705, $C_{13}H_{11}{}^{35}ClO$ requires: 218.04984).

This compound (**8a**) was also formed (97%) from phenol and 2-chlorobenzyldimethylsulfonium tetrafluoroborate (**1t**) using the method described above.

4.10.2. 2,6-Dichlorobenzyl phenyl ether (8b). Purified by recrystallization to afford a colorless crystalline solid (95%), mp 49–50°C (hexane); ν_{max} (KBr)/cm^{-1}, 3073, 2955, 1583, 1493, 1437, 1381, 1291, 1233, 1086, 1011, 866, 756, 690; δ_H ($CDCl_3$), 5.25 (s, 2H, CH_2); 6.95–7.05 (m, 3H, Ar–H); 7.15–7.4 (m, 5H, Ar–H); δ_C ($CDCl_3$), 65.1 (CH_2); 114.9, 121.3, 128.4, 129.5, 130.4, (5×CH); 132.1, 137.0, 158.8 (3 quaternary C's); *m/z* (FAB), 252, 254, 256 (27%, 20%, 3.6%, M^+); 159, 161, 163 (100, 61, 11, $M^+ - OC_6H_5$), (Found: C, 61.7; H, 3.9%. $C_{13}H_{10}Cl_2O$ requires: C, 61.7; H, 4.0%).

4.10.3. 1-Naphthylmethyl phenyl ether (8c). Purified by recrystallization to give an off-white, crystalline solid (93%), mp 73–75°C (hexane) (lit. 37 76–77°C); ν_{max} (KBr)/cm^{-1}, 3046, 2919, 1596, 1486, 1468, 1387, 1293, 1229, 1173, 1005, 887, 792, 757, 696; δ_H ($CDCl_3$), 5.55 (s, 2H, CH_2); 7.1–7.7 (m, 9H, Ar–H); 7.9–8.0 (m, 2H, Ar–H); 8.1–8.2 (m, 1H, Ar–H); δ_C ($CDCl_3$), 68.6 (CH_2); 114.9, 121.1, 123.7, 125.4, 125.9, 126.5, 126.6, 128.7, 129.0, 129.5, (10×CH); 131.6, 132.4, 133.8, 158.9 (4 quaternary C's); *m/z* (FAB), 234, (4.8%, M^+); 141 (100, $M^+ - OC_6H_5$), (Found: C, 87.1; H, 6.0%. $C_{17}H_{14}O$ requires: C, 87.15; H, 6.4%).

4.10.4. Benzyl phenyl ether (8d). Colorless crystalline solid [(3.61 g, 98% from **1s**; 96% from **1r**), mp 39–40°C (lit. 38 39–39.5°C); δ_H ($CDCl_3$), 5.2 (s, 2H, CH_2); 7.05–7.15 (m, 3H, Ar–H); 7.4–7.6 (m, 7H, Ar–H); δ_C ($CDCl_3$), 69.9 (CH_2); 114.9, 121.0, 127.6, 128.0, 128.7, 129.6, (6×CH); 137.2 (*C*-CH_2), 158.9 (C–O).

4.10.5. 4-Methoxybenzyl phenyl ether (8e). Purified chromatographically [silica gel, petroleum ether (bp 60–80°C), ethyl acetate (15:1) eluant] to afford a colorless, crystalline solid (70%), mp 93–93.5°C (lit. 39 92–92.5°C); ν_{max} (KBr)/cm^{-1}, 2933, 1585, 1513, 1385, 1234, 1170, 1031, 869, 808, 752, 692; δ_H ($CDCl_3$), 3.8 (s, 3H, OMe); 4.95 (s, 2H, CH_2); 6.85–7.0 (m, 5H, Ar–H); 7.2–7.4 (m, 4H, Ar–H); δ_C ($CDCl_3$), 55.2 (CH_3); 69.6 (CH_2); 113.9, 114.8, 120.8, 129.2, 129.4, (5×CH); 129.0, 158.8, 159.4 (3 quaternary C's); *m/z* (FAB), 214 (2.1%, M^+); 121 (100, $M^+ - OC_6H_5$), (Found: C, 78.5; H, 6.6%. $C_{14}H_{14}O_2$ requires C, 78.5; H, 6.6%); after further elution, 4-methoxybenzyl alcohol was obtained as a colorless, crystalline solid (0.39 g, 28%) mp 22–25°C (lit. 40 23–25°C).

4.10.6. 1,4-Bis(phenoxymethyl)benzene (8f). Purified by recrystallization to give a colorless, crystalline solid (1.19 g, 82%), mp 141–142°C (THF/hexane), (lit. 41 140–141.5°C); ν_{max} (KBr)/cm^{-1}, 2912, 1599, 1496, 1247, 1171, 1010, 873, 803, 747, 689; δ_H ($CDCl_3$), 5.05 (s, 4H, CH_2); 6.9–7.0 (m, 6H, Ar–H); 7.25–7.35 (m, 4H, Ar–H); 7.45 (s, 4H, Ar–H, central ring); δ_C ($CDCl_3$), 69.5 (CH_2); 114.8, 120.9, 127.6, 129.4, (4×CH); 136.8 (*C*–CH_2); 158.7 (C–O); *m/z* (FAB), 290 (9.9%, M^+), 197 (100, $M^+ - OC_6H_5$).

4.10.7. 2,6-Dichlorobenzyl phenyl sulfide (8g). Colorless, crystalline solid (99%), mp 39–40°C (lit. 42 39–40°C); δ_H ($CDCl_3$), 4.4 (s, 2H, CH_2); 7.05–7.3 (m, 6H, Ar–H); 7.35–7.45 (m, 2H, Ar–H); δ_C ($CDCl_3$), 30.9 (CH_2); 122.6, 123.6, 124.0, 124.1, 127.4, (5×CH); 129.2, 130.6, 131.1 (3 quaternary C's); *m/z* (FAB), 268, 270, 272 (47, 36, 7.7%, M^+), 159, 161, 163 (100, 61, 12, $M-OC_6H_5$).

4.11. Reaction of *syn*-benzaldoxime with 2-chlorobenzylsulfonium hydrogen sulfate (1b)

2-Chlorobenzyldimethylsulfonium hydrogensulfate (**1b**) (2.99 g, 10.5 mmol) was added to a solution of *syn*-benzaldoxime (1.21 g, 10 mmol) in a mixture of toluene (20 cm^3) and water (20 cm^3). After the solution was heated to 80°C, a solution of potassium hydroxide (1.18 g, 21 mmol) in water (5 cm^3) was added dropwise. The mixture was stirred at 80°C for 3 days. The toluene layer was separated, and the aqueous layer extracted with toluene (2×20 cm^3). The organic layers were combined and evaporated under reduced pressure. The crude product was dissolved in chloroform (20 cm^3) and this solution was washed with water (10 cm^3), then saturated brine (10 cm^3) and then dried ($MgSO_4$). The mixture was filtered and the solvent evaporated under reduced pressure to leave an oil that was purified chromatographically (silica gel, [petroleum ether (bp 60–80°C)/ethyl acetate, 10:1 eluant]) to give *syn*-benzaldoxime *O*-2-chlorobenzyl ether (**9**) as a colorless oil (after distillation), (1.40 g, 57%), bp 218°C/40 Torr; ν_{max} (KBr)/cm^{-1}, 3062, 2953, 1574, 1473, 1446, 1361, 1121, 1071, 1036, 1017, 947, 906, 754; δ_H (d_6-DMSO), 5.2 (s, 2H, CH_2); 7.3–7.7 (m, 9H, Ar–H); 8.4 (s, 1H, CH); δ_C (d_6-DMSO), 73.1 (CH_2); 127.4, 127.7, 129.2, 129.7, 130.1, 130.5, 131.0, (7×CH); 132.1, 133.1, 135.5 (3 quaternary C's); 150.1 (CH); *m/z* (EI), 245, 247 (11%, 3.7%, M^+); 125, 127 (100, 31, $M^+ - C_7H_6NO$). (Found: 245.06111. $C_{14}H_{12}{}^{35}ClNO$ requires: 245.06074). After further elution, *N*-benzylidene-(2-chlorobenzyl)amine *N*-oxide (**10**) was obtained as a white powder (130 mg, 5%), mp 76–77°C (lit. 43 75–77°C); δ_H ($CDCl_3$), 5.2 (s, 2H, CH_2); 7.2–7.6 (m, 8H, Ar–H); 8.2 (m, 2H, CH═N+Ar–H); δ_C ($CDCl_3$), 68.0 (CH_2), 127.3, 128.4, 128.7, 129.7, 130.3, 130.5, 131.8 (7×CH), 130.25, 130.9, 134.3 (3 quaternary Cs), 135.1 (*C*H═N). *m/z* (FAB), 246, 248 (83%, 25%, M+H^+) 125, 127 (100, 32, $M^+ - C_7H_6NO$).

4.12. Preparation and benzylation of *anti*-benzaldoxime

Dry hydrogen chloride gas was bubbled through a solution of *syn*-benzaldoxime (5.0 g, 43 mmol) in anhydrous diethyl ether (150 cm^3) via a wide delivery tube. The colorless crystals of *anti*-benzaldoxime hydrochloride which precipitated from the solution were filtered and washed with anhydrous diethyl ether (2×50 cm^3). This solid was added, in portions, to a vigorously stirred, large excess of a mixture of saturated aqueous sodium bicarbonate solution and dichloromethane stirring rapidly together in a beaker. When effervescence had ceased, the dichloromethane layer was separated and the aqueous layer was extracted with dichloromethane (2×50 cm^3). The combined organic layer was washed with saturated brine and then dried ($MgSO_4$). The mixture was filtered and the solvents were evaporated under reduced pressure to give the crude product which was recrystallized twice to give *anti*-benzaldoxime (3.55 g, 71%); mp 131–131.5°C (H_2O/EtOH) (lit. 44 132°C); δ_H (C_2D_6SO), 7.4 (m, 4H, Ar–H); 7.9–8.0 (m, 2H, Ar–H); 11.6 (s, 1H, OH). This compound was allowed to react with the sulfonium salt (**1b**) in the manner described above to afford a mixture of **9** (50%) and **10** (7%).

4.13. Procedure for the reaction of cyclohexanone oxime with sulfonium salts (1b, 1d)

A solution of potassium hydroxide (1.18 g, 21 mmol) in water (10 cm^{-3}) was added to a solution of cyclohexanone oxime (1.13 g, 10 mmol) and either **1b** or **1d** (10.5 mmol) in water (20 cm^3) over ca. 15 min. The mixture was stirred at 70°C for two days. Dichloromethane (30 cm^3) was added, the layers separated, and the aqueous layer was extracted with dichloromethane (2×20 cm^3). The combined organic layer was washed with saturated brine, then dried ($MgSO_4$), and filtered. The solvent was evaporated under reduced pressure to give the crude products as yellow oils that were purified chromatographically (silica gel [petroleum ether (bp 60–80°C)/ethyl acetate 10:1 eluant]). The following were isolated.

4.13.1. Cyclohexanone oxime *O*-2-chlorobenzyl ether (11a). As a pale yellow oil (0.90 g, 38%); δ_H ($CDCl_3$), 1.5 (m, 6H, CH_2); 2.2 (t, 2H, J=6 Hz, CH_2); 2.55 (t, 2H, J=6 Hz, CH_2); 5.15 (s, 2H, CH_2O); 7.1–7.4 (m, 4H, Ar–H); δ_C ($CDCl_3$), 25.4, 25.8, 25.8, 27.0, 32.1 (ring CH_2); 72.1 (CH_2); 126.5, 128.4, 128.9, 129.1 (4×CH); 132.8,136.1 (2 quaternary C's); 161.2 (C═N); *m/z* (FAB), 238, 240 (100%, 28%, $M+H^+$);202 (19, M^+-Cl). (Found (EI): 237.0916, $C_{13}H_{16}{}^{35}ClNO$ requires: 237.0920).

4.13.2. Cyclohexanone oxime *O*-2,6-dichlorobenzyl ether (11b). As a colorless, crystalline solid (2.04 g, 75%); ν_{max} (KBr)/cm^{-1}, 3254, 2932, 1564, 1436, 1195, 1092, 1037, 992, 933, 890, 780; δ^1H ($CDCl_3$), 1.5–1.6 (m, 6H, CH_2); 2.2 (t, J=6 Hz, 2H, CH_2); 2.4 (t, J=6.5 Hz, 2H, CH_2); 5.3 (s, 2H, CH_2O); 7.2 (m, 3H, Ar–H); $\delta^{13}C$ ($CDCl_3$), 25.1, 25.7, 25.7, 26.9, 32.1 (ring CH_2); 69.4 (CH_2); 128.1, 129.7 (2×CH); 132.9, 137.0 (2 quaternary C's); 161.2 (C═N); *m/z* (FAB), 272, 274, 276 (100, 66 11%, $M+H^+$ 236, 238 (25, 9.9, M^+-Cl); (Found (EI): 271.0547, $C_{13}H_{15}{}^{35}Cl_2NO$ requires: 271.0531).

4.13.3. Procedure for the reaction of benzimidazole with sulfonium salts (1a, b). A solution of potassium hydroxide (1.18 g, 21 mmol) in water (10 ml) was added to a solution of benzimidazole (1.18 g, 10 mmol) and either **1a** or **1b** (10.5 mmol) in water (20 cm^3), ethanol (5 cm^3) and toluene (30 cm^3). The mixture was stirred at 70°C overnight and the solvents were then evaporated under reduced pressure and the residue partitioned between dichloromethane (30 cm^3). and distilled water (30 cm^3). The aqueous layer was extracted with dichloromethane (2×20 cm^3) and the combined organic layer was washed with saturated brine, dried over ($MgSO_4$), filtered, and the solvent evaporated under reduced pressure to give the crude products as brown oils. The mixtures were purified chromatographically (silica gel [2% methanol in DCM, eluant]), to give the following.

4.13.4. 1-benzylbenzimidazole (12a). As a colorless crystalline solid (8.66 g, 59%) mp 113–115°C [THF/petroleum ether (60/80)] (lit. 45 115–115.5°C).

4.13.5. 1-(2-chlorobenzyl)benzimidazole (12b). As a colorless crystalline solid (1.20 g, 50%) mp 93–93.5°C [THF/petroleum ether (60/80)]; ν_{max} (KBr)/cm^{-1}, 3082, 1614, 1493, 1427, 1351, 1264, 1204, 1179, 1038, 967, 885, 750; δ_H ($CDCl_3$), 5.4 (s, 2H, CH_2); 6.8 (d, J=7.5 Hz, 1H, Ar–H); 7.0–7.4 (m, 6H, Ar–H); 7.8 (m, 1H, Ar–H); 7.9 (s, 1H, CH═N); δ_C ($CDCl_3$), 46.2 (CH_2); 109.9, 120.4, 122.3, 123.1, 127.3, 128.5, 129.5, 129.8 (8×CH); 132.9, 133.0, 133.7, 143.7 (4 quaternary C's); 143.4 (CH═N); *m/z* (FAB), 243, 245 (84%, 28%, $M+H^+$); 125, 127 (100, 29, M^+-benzimidazolyl); (Found: C, 69.2; H, 4.5%. $C_{14}H_{11}N_2Cl$ requires: C, 69.3; H, 4.6%).

4.14. Reaction of benzimidazole with 1-methyltetrahydrothiophenium hydrogen sulfate (2c)

A stirred mixture of potassium hydroxide (1.18 g, 21 mmol), benzimidazole (2.03 g, 17.1 mmol), 1-methyltetrahydrothiophenium hydrogensulfate (**2c**) [3.43 g, 17.1 mmol)], water (25 cm^3), ethanol (5 cm^3) and toluene (25 cm^3) was heated under reflux overnight. The solvents were evaporated under reduced pressure and the residue was partitioned between dichloromethane (30 cm^3) and distilled water (30 cm^3). The aqueous layer was separated and extracted with dichloromethane (2×20 cm^3). The combined organic layer was washed with saturated brine, dried ($MgSO_4$) and filtered. The solvents were evaporated under reduced pressure to give a yellow oil which was purified by flash column chromatography on silica gel [petroleum ether (bp 60–80°C)/ethyl acetate 10:1, eluant], to give 1-[(4-methylthio)butyl]benzimidazole (**12c**) as a yellow oil (1.92 g, 51%) which charred upon attempted distillation; ν_{max} (KBr)/cm^{-1}, 3393, 3086, 2916, 1614, 1495, 1459, 1366, 1286, 1201, 1155, 1007, 893, 746; δ_H ($CDCl_3$), 1.6 (m, 2H, CH_2); 1.95 (m, 2H, CH_2); 2.0, (s, 3H, CH_3); 2.45 (t, J=7 Hz, 2H, CH_2S); 4.2 (t, J=7 Hz, 2H, CH_2N); 7.2–7.4 (m, 3H, Ar–H); 7.8 (m, 1H, Ar–H); 7.85 (s, 1H, CH═N); δ_C ($CDCl_3$), 15.3 (CH_3); 25.9, 28.6, 33.4, 44.5 (4×CH_2); 109.6, 120.2, 121.9, 122.7 (4×CH); 133.6, 143.7 (2 quaternary C's); 142.8 (CH═N); *m/z* (FAB), 221 (96%, $M+H^+$); 103 (100, M^+-benzimidazolyl); 221 (96%, $M+H^+$); [Found (EI): 220.10250, $C_{12}H_{16}N_2S$ requires: 220.10342];

after further elution, 1-methylbenzimidazole (**12d**) was obtained as a white powder (700 mg, 31%), mp 60–62.5°C (lit. 46 59–62°C).

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