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N-ARYL SULFIMIDES[a]

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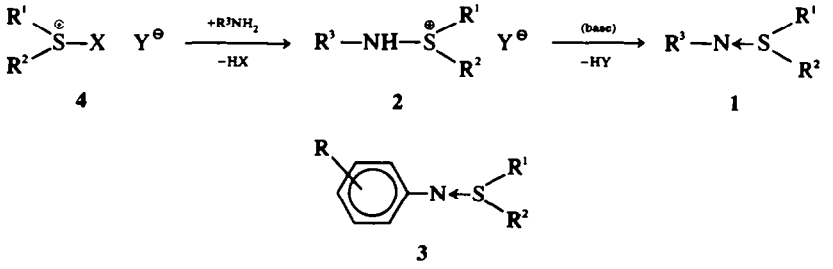
Abstract—N-Aryl sulfimides with various substituents at the aromatic ring and various alkyl or aryl groups at the S atom have been synthesised in high yields by applying three different procedures: reactions of anilines with sulfides and (A) N-chloro-succinimide, (B) *t*-butyl hypochlorite or (C) sulfuryl chloride. These reactions offer remarkable advantages compared to the known sulfoxide-P_4O_{10} method for preparation of N-aryl-sulfimides. Mechanistic considerations are discussed. N-Aryl-sulfoximides have been obtained by oxidation of N-aryl-sulfimides and by reaction of anilines with DMSO and *t*-butyl hypochlorite or sulfuryl chloride. Mass spectra of N-aryl-sulfimides are also discussed.

In recent years considerable interest has been given to the chemistry of sulfimides **1**,[1] in particular the N-tosyl-(**1**, R^3 = tosyl)[4], N-acyl-(R^3 = RCO)[5], N-halogeno-(R^3 = halogen)[6], N-cyano-(R^3 = CN)[7], N-alkyl-(R^3 = alkyl)[8] sulfimides or the parent compounds $R_2S{=}NH$[9] have been studied. The title compounds, N-aryl-sulfimides **3** (=**1** with R^3 = aryl) were unknown before 1968, and the only reference[10] claiming the preparation of **3**, namely N,S,S-triphenyl sulfimide (**1**, $R^1 = R^2 = R^3$ = phenyl), reported an impure compound which did not allow further characterisation.

Claus *et al.* reported the first preparation of N-aryl-sulfimides (**3**) by the reaction of anilines with sulfoxides in presence of P_4O_{10} and triethylamine.[2,11] The mechanism of this reaction is not fully understood, but it has been generally assumed that sulfoxides and P_4O_{10} form reactive intermediates of type **4**, which suffer nucleophilic attack by the amine. Though the reactions of anilines with dimethyl sulfoxide (DMSO) give fair yields of **2**, we looked for better methods of preparation of N-aryl sulfimides (**3**) which are of particular interest in view of their easy rearrangement.[2,12,13] The sulfoxide-P_4O_{10}-method presents difficulties arising during work-up and purification of the compounds (**3**), and is generally restricted to the use of DMSO as sulfoxide (though some other sulfoxides have been successfully used[11]).

DISCUSSION OF RESULTS

Sulfonium compounds (**4**) with a proper leaving group X could be useful intermediates for synthesis of sulfimides in general. In addition Claus and Rieder found that chloro - dimethyl - sulfonium - hexachloroantimonate (**4**, $R^1 = R^2$ = Me, X = Cl, Y = $SbCl_6$)[14] reacts (a) with anilines to give N-aryl-sulfimides[15] and (b) with phenols to give *o*- or *p*-hydroxyphenyl sulfonium chlorides (**4**, $R^1 = R^2$ = Me, X = 2- or 4-HO-aryl)[16] and not the expected phenoxy sulfonium salts (**4**, $R^1 = R^2$ = Me, X = O-aryl).[17] Vilsmaier *et al.*[18] prepared an interesting azasulfonium compound **4** ($R^1 = R^2$ = Me, X = N-succinimidyl, Y = Cl) by the reaction of dimethyl sulfide (DMS) with N-chloro-succinimide (NCS) and we found that mixtures of anilines and sulfides, dissolved in CH_2Cl_2, reacted with NCS to give sulfimides (**3**) in fair yields. Vilsmaier[8b] found that the azasulfonium compound mentioned[18] reacted with amines



4 **2** **1**

3

[a]Methylthiomethylation of Anilines and Phenols. Part 9. Part 8: see [12]. Parts of this paper have been presented at the VI International Symposium of Organic Sulfur Chemistry, July 1–5 1974, Bangor, Wales.

Table 1. N-aryl sulfimides 3

R	Product 3 R¹	R²	m.p.[a]	picrate m.p.[a]	yield[b] (%)	NMR (δ, ppm)[c]	Elemental analysis			
4-Cl	Me	Me	66–67	160–162	82[d](A) 92(B)	Ref 11	C calc.	51·19,	found	51·39
							H calc.	5·37,	found	5·34
							N calc.	7·46,	found	7·30
4-Cl	Me	Pr	oil	124–128	87[d](A) 90(B)	1·05(t), 1·77(m), 2·56(s), 2·5–3·15(m), 6·75–7·2(m)	picrate:			
							C calc.	43·20,	found	43·20
							H calc.	3·85,	found	3·93
							N calc.	12·59,	found	12·47
4-Cl	Me	Me_2CH	oil	140–142	76[d](A)	1·30(d), 2·48(s), 2·9(m), 6·7–7·15(m)	picrate:			
							C calc.	43·20,	found	43·16
							H calc.	3·85,	found	3·59
							N calc.	12·59,	found	12·67
4-Cl	Me	Ph	77–79	133–135	55[d](A)	2·86(s), 6·65–7·05(m) 7·4–7·8(m)	C calc.	62·52,	found	62·23
							H calc.	4·84,	found	4·81
							N calc.	5·61,	found	5·46
4-Cl	Me	4-$CH_3C_6H_4$	103–105	140–141	82[d](A)	2·41(s), 2·88(s), 6·7–7·7(m)	C calc.	63·75,	found	63·63
							H calc.	5·35,	found	5·33
							N calc.	5·31,	found	5·21
4-Cl	Me	$C_6H_5CH_2$	96–100	148–149	80[d](A) 88(B)	2·48(s), 3·89(d), 4·05(d), 6·65–7·2(m), 7·4(s)	C calc.	63·75,	found	63·73
							H calc.	5·35,	found	5·25
							N calc.	5·31,	found	5·13
4-Cl	4-$MeOC_6H_4$	4-$MeOC_6H_4$	oil	133–134	74[d](A)	3·77(s), 6·8–7·7(m)	picrate:			
							C calc.	51·96,	found	51·50
							H calc.	3·52,	found	3·59
							S calc.	5·34,	found	5·50
4-Cl	-$CH_2SCH_2CH_2CH_2$-		123–128	132–134	89[d](A) 91(B)	2·15–3·6(m), 3·59(d), 3·97(d), 6·7–7·25(m)	C calc.	48·87,	found	49·05
							H calc.	4·92,	found	4·92
							N calc.	5·70,	found	5·73
H	-$CH_2SCH_2CH_2CH_2$-		108–111		60(A)	2·25–3·4(m), 3·55(d), 3·98(d), 6·6–7·35(m)	C calc.	56·83,	found	56·62
							H calc.	6·20,	found	6·16
							N calc.	6·63,	found	6·55
4-CN	Me	Me	110–112	184–185	46[d](A) 57(B)	Ref 12	C calc.	60·64,	found	60·25
							H calc.	5·65,	found	5·61
							N calc.	15·72,	found	15·36
4-CN	Me	Pr	oil	133–137	65[d](A)	1·08(t), 1·80(m), 2·64(s), 2·92(t), 6·75–7·5(m)		—		
4-COOMe	Me	Me	80–82	178–182	83(A)	Ref 12	C calc.	56·85,	found	56·79
							H calc.	6·20,	found	6·14
							N calc.	6·63,	found	6·52
4-Me	Me	Me	52–55	163–167	69[d](C)	Ref 11		—		
2-Me	-$CH_2SCH_2CH_2CH_2$-		112–116	143–144	79[d](A)	2·23(s), 2·25–3·4(m), 3·6(d), 3·96(d), 6·55–7·2(m)	C calc.	58·62,	found	58·69
							H calc.	6·71,	found	6·75
							N calc.	6·21,	found	6·16
4-MeO	Me	Me	45–47	117–121	88[d](A) 75[d](C)	Ref 11		—		
4-COOR'[e]	Me	4-$CH_3C_6H_4$	oil	108–110	52[d](A)	0·78(d), 0·89(d), 0·7–2·4(m), 2·38(s), 2·87(s), 6·7–8·0(m)		—		
f	Me	Me	86–88[g]	—	63(A)	2·68(*s*), 6·35–6·8(*m*), 7·2–7·5(m), 8·05(m)	C calc.	54·51,	found	54·46
							H calc.	6·54,	found	6·69
							N calc.	18·16,	found	18·31
f	-$CH_2SCH_2CH_2CH_2$-		132–135	117–119	56(A)	2·1–3·6(m), 3·68(d), 4·5(d), 6·45–6·8(m), 7·25–7·55(m), 8·06(m)	C calc.	50·91,	found	50·84
							H calc.	5·70,	found	5·81
							N calc.	13·19,	found	13·27

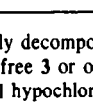
[a] Frequently decomposition occurs on melting.

[b] Yield of free 3 or of 3-picrates, crude materials (at least 90% pure). Method of preparation in parenthesis (A: sulfide-NCS, B: sulfide-*t*-butyl hypochlorite, C: sulfide-SO_2Cl_2).

[c] $CDCl_3$, 60 MHz (s = singlet, d = doublet, t = triplet, m = multiplet).

[d] Yield of picrate (for isolation of free 3 from 3-picrates see Ref 12).

[e] R' = *L*-menthyl.

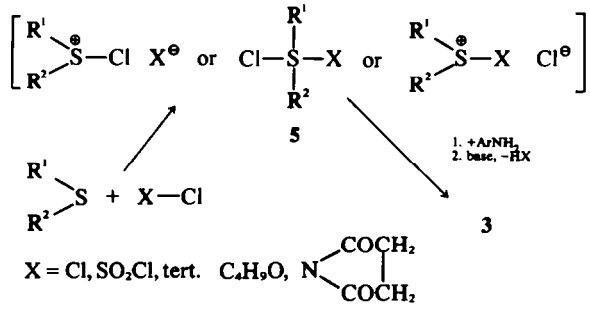
[f] R-C_6H_4 =  (starting material: 2-amino pyridine).

[g] Preparation reported also by Gassman[23] (no NMR and analytical data were given).

and other nucleophiles by displacement of the succinimidyl group, and also reported the isolation of a number of N-aryl-azasulfonium compounds (4, $R^1 = R^2 =$ Me, X = NH-aryl, Y = Cl). The simple reaction of anilines with sulfides and NCS followed by treatment with base provides good yields of N-aryl-sulfimides (3) with a wide range of substituents on the aromatic ring and on the S atom.[19] Table 1 lists the sulfimides (3) which we prepared by applying this reaction and two other methods. Anilines carrying electron-withdrawing substituents on the aromatic ring are preferred because of the higher stability of derived sulfimides (3), but anilines with electron-donating substituents react as well. Some of the sulfimides (3) mentioned in Table 1 did not crystallize and were characterized by NMR data and the corresponding picrates. Most N-aryl-sulfimides proved to be thermally unstable, at least on prolonged storage at room temperature, and should be stored at temperatures below 0° or as the corresponding picrates.

Recently Corey *et al.*[20] reported a new method for the oxidation of aliphatic alcohols using the "complexes" of DMS with either Cl_2 or NCS. Vilsmaier[18] postulated on basis of IR and NMR data an ionic structure for the isolated complex DMS-NCS, though a structure of type 5 with tetracovalent sulfur (as it has been discussed for complexes formed by reaction of sulfides with *t*-butyl hypochlorite[21,22]) cannot be excluded. Similar structural questions remain for sufide-Cl_2 "complexes".[23] Following but not with free amides or anilines.[24] Recently Gassman *et al.*[25] reported on the formation of a sulfimide (3) by reaction of 2-amino-pyridine with DMS and *t*-butyl hypochlorite, and it is obvious that the reactions reported in the related work[26] proceed via hydrochlorides of N-aryl-sulfimides (3). According to Gassman anilines will react with *t*-butyl hypochlorite to give N-chloro-anilines in one step. Though usually we added *t*-butyl hypochlorite or SO_2Cl_2 to mixtures of the aniline and the sulfide, N-aryl-sulfimides could be prepared with similar success also by treatment of sulfide with SO_2Cl_2 in one step and subsequent addition of aniline. In case of reaction with *t*-butyl hypochlorite this latter procedure resulted in considerably lower yields of sulfimides (3) compared with the yields after applying the usual procedure. Whether a reaction of formed N-chloro-aniline with sulfide, a reaction of formed chloro sulfonium intermediate of type 5 with aniline or an equilibrium between different species with tetravalent sulfur is operating, is still open to discussion. A similar formation of azasulfonium compounds has been reported also by Johnson *et al.*[22] The sulfide-SO_2Cl_2 procedure used for preparation of N-aryl-sulfimides (3) is mechanistically related to the oxidation of sulfides to sulfoxides with SO_2Cl_2.[27]

Other methods for preparations of N-aryl-sulfimides (3) have been reported recently,[28-31] but are—with the exception of the procedures reported by Swern[28]—of limited application.

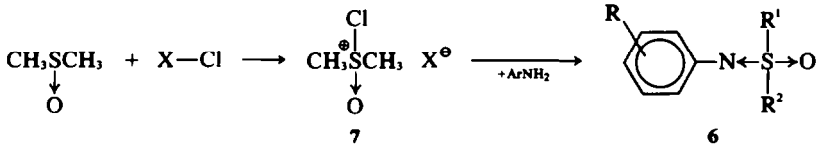


our first results on reactions of anilines with chloro sulfonium compounds,[15] we found reactions of anilines with sulfides and *t*-butyl hypochlorite or SO_2Cl_2 to offer valuable methods for preparation of N-aryl-sulfimides 3 (Table 1). Sulfide-*t*-butyl hypochlorite mixtures have been reported to react with amide anions (yielding N-tosyl- and N-acyl sulfimides 1 with R^3 = tosyl and acyl, respectively)

*For examples of oxidations of other sulfimides 1 see Ref 32.

Oxidation of N-*aryl-sulfimides* 3

N-Aryl-sulfimides (3) may be oxidized with $KMnO_4$ to give high yields of hitherto unknown N-aryl-sulfoximides (6) except when electron-donating substituents are present (Table 2).* N-Aryl-sulfoximides (6) can be obtained also by reaction of anilines with DMSO and *t*-butyl hypochlorite or sulfuryl chloride. This reaction is assumed to proceed via intermediates 7 and is mechanistically related to the oxidations of aliphatic alcohols with DMS-Cl_2.[33]



X = Cl, SO_2Cl or *t*-C_4H_9O

Table 2. N-aryl-sulfoximides (6)

Products 6 R	R¹	R²	m.p.[a]	Yield[b] (%)	NMR(δ, ppm)[c]	Elemental analysis			
H	Me	Me	58–60	25[d]	3·06(s), 6·9–7·3(m)		—		
4-Cl	Me	Me	62–63	96	3·10(s), 6·9-7·3(m)	C calc.	47·17,	found	46·63
						H calc.	4·95,	found	4·96
						N calc.	6·88,	found	7·01
4-Br	Me	Me	81–83	69	3·1(s), 6·85–7·4(m)	C calc.	38·72,	found	38·85
						H calc.	4·06,	found	4·06
						N calc.	5·64,	found	5·71
4-CH_3	Me	Me	77–80	14[d]	3·07(s), 6·96(s)		—		
4-COOMe	Me	Me	95–97	88	3·2(s), 7·05–8·0(m)		—		
4-CN	Me	Me	111–112	95	3·22(s), 7·0–7·6(m)		—		
4-NO_2	Me	Me	160–162	99	3·24(s), 7·05–8·2(m)	C calc.	44·85,	found	45·20
						H calc.	4·70,	found	5·17
						N calc.	13·08,	found	13·24
3-Cl	Me	Me	38–39	76	3·1(s), 6·7–7·3(m)	C calc.	47·17,	found	47·35
						H calc.	4·95,	found	4·94
						N calc.	6·88,	found	6·84
3-NO_2	Me	Me	105–107	80	3·2(s), 7·25–8·05(m)	C calc.	44·85,	found	44·64
						H calc.	4·70,	found	4·92
						N calc.	13·08,	found	12·80
4-Cl	Me	Ph	87–89	68	3·23(s), 6·85–8·15(m)	C calc.	58·75,	found	58·83
						H calc.	4·55,	found	4·62
						N calc.	5·27,	found	5·22
4-Cl	Me	4-$CH_3C_6H_4$	75–77	89	2·37(s), 3·18(s),	C calc.	60·10,	found	60·24
					6·8–7·9(m)	H calc.	5·04,	found	5·27
						N calc.	5·01,	found	5·17
4-CN	Me	Pr	90–92	85	1·07(t), 1·6–2·25(m),	C calc.	59·43,	found	59·20
					3·08(s), 3·1–3·4(m),	H calc.	6·35,	found	6·24
					7·05–7·55(m)	N calc.	12·60,	found	12·57

[a] M.p. of pure compounds 6.
[b] Yield of crude materials.
[c] $CDCl_3$, 60 MHz (s = singlet, d = doublet, t = triplet, m = multiplet).
[d] Isolated by preparative TLC.

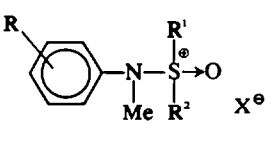
N-Aryl-sulfoximides with powerful electron-donating substituents could not be obtained by applying either of the two procedures. Sulfoximides 6 could be methylated with methyl fluorosulfonate ("magic methyl") to yield (after anion exchange) N-aryl-N-methyl-azasulfoxonium chlorides (8).

Mass spectra of N-*aryl-sulfimides* (3)

Spectral data (UV, IR, NMR) of N-aryl-sulfimides (3) have been reported[11] and some mass spectra data 3 are given.

The spectra show the molecular peaks of 3 ($R^1 = R^2 =$ Me) with high intensities (50–90% of the intensity of the basis peak). The basis peak invariably occurs at $m/e = M - 15$, corresponding to the loss of $CH_3^{\cdot}$; this fragmentation is also indicated by corresponding metastable peaks. The next step of fragmentation is the loss of a second $CH_3^{\cdot}$ ($m/e = M - 30$, 50–60%) as shown by high resolution mass spectrometry. On fragmentation of N-4-methoxyphenyl sulfimide (3, $R^1 = R^2 =$ Me, R = 4-MeO) and of N-4-carbethoxyphenyl sulfimide ($R^1 = R^2 =$ Me, R = 4-COOMe) the loss of CH_2O is of minor importance as compared to the loss of two $CH_3^{\cdot}$ radicals (less than 0·5%, respectively, about 5% of importance of the latter pathway). On fragmentation of N-4-nitrophenyl-sulfimide (3, $R^1 = R^2 =$ Me, R = 4-NO_2) the peak intensity at $m/e = M - NO$ is 60% of the peak intensity at $m/e = M - 2\,CH_3^{\cdot}$. Other peaks of fair intensity are observed in all mass spectra of S,S-dimethyl-sulfimides 3 ($R^1 = R^2 =$ Me) at $m/e = M - 61$ (formal loss of $CH_3SCH_2^{\cdot}$), $M - 62$ (formal loss of CH_3SCH_3) and $M - 76$ (formal loss of $(CH_3)_2SN^{\cdot}$). Peaks at $m/e = M - 47$ correspond to the loss of $CH_3S^{\cdot}$; a rearrangement by migration of one Me group from S to N might explain this pathway of fragmentation. Characteristic peaks at the low mass region are observed at $m/e = 61$ ($CH_3SCH_2^+$) and 62 ($CH_3{}^{\cdot}{}^+SCH_3$).

The fragmentation pattern of sulfimide 9[11] is similar to that of N - aryl - S,S - dimethyl - sulfimides; loss of the



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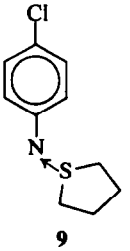

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carbon chain on sulfur (m/e = M − 56, 38%), loss of the total heterocyclic part (m/e = M − 88, 44%), formation of obviously rearranged fragments (m/e = M − 74, 43%) and formation of the low mass fragments $C_4H_7S^+$ (m/e = 87, 59%) and $C_4H_8S^{\cdot+}$ (m/e = 88, 29%) are the most important pathways of fragmentation.

EXPERIMENTAL

Reagents (commercially available or prepared according to known procedures) were purified if necessary before use by distillation or crystallisation. Solvents were Merck grades. CH_2Cl_2 (Merck p.a.) was carefully dried by stirring with P_4O_{10} and fractionated subsequently. M.ps (uncorrected) were obtained using a Kofler Mikroheiztisch. Tlc was conducted on Merck silicagel HF_{254} or on tlc cards SIF from Riedel-de Haen (solvent: $CHCl_3$ or $CHCl_3/(C_2H_5)_3N$ = 50:1). Column chromatography was performed on silicagel (Merck), using $CHCl_3$ as solvent. Frl. H. Martinek obtained the NMR spectra on a Varian model A-60 (TMS as internal standard). Mass spectra were obtained on Varian models MAT CH 7 and MAT SM 1B, respectively. Elemental analyses were done by Dr. J. Zak (Institute of Physical Chemistry, University of Vienna and H. Bieler (Institute of Organic Chemistry).

Preparation of N-*aryl-sulfimides* **3** (Table 1)

(A) *Sulfide-*N*-chloro-succinimide method.* Equimolar amounts (usually 5 mmoles each) of aniline and sulfide were dissolved in dry CH_2Cl_2 (10 ml). The mixture was cooled to −20° in a round-bottomed flask with an addition funnel with drying tube and pressure compensation, and stirred magnetically while equimolar amounts (5 mmoles) of N-chloro-succinimide, dissolved in 25 ml CH_2Cl_2, were added dropwise within 15–30 min. Stirring was continued for further 60 min (in case of reactions with anilines carrying powerful electron-withdrawing substitutents the mixture was left over night at −20°). The mixture was extracted with 5% NaOH aq (30 ml), dried over $NaSO_4$ and evaporated. Further purification of the residue depended on the results of TLC analysis and on the thermal stability of **3**. More stable sulfimides **3** may be crystallized from ether or ether-hexane (cooling to −20°). Less stable, less pure and oily compds were dissolved in ether and precipitated as picrates by addition of a saturated soln of picric acid in ether. Rather pure picrates of **3** are usually obtained, but may be recrystallized from acetone or acetone-ether. Free sulfimides **3** were obtained from corresponding picrates by treatment with excess KOH in aqueous ether,[12] and finally purified by recrystallisation from ether or ether-hexane.

(B) *Sulfide-t.-butyl hypochlorite method.* Equimolar amounts (5 mmoles) of aniline and sulfide were dissolved in dry CH_2Cl_2 and cooled to −65° (apparature as described above). A soln of equimolar amounts (5 mmoles) of t-butyl hypochlorite[14] in dry CH_2Cl_2 was added dropwise (magnetical stirring). Reaction periods were chosen as described above (method A). Reactions may be monitored by TLC. The mixture was extracted with calculated amounts (slight excess) of NaOH aq and products were isolated as described. Alternatively, the hydrochlorides of **3** (=**2**, R^3 = aryl) may be isolated by partial evaporation of the mixture before extraction with NaOH, addition of ether-THF and filtration of the white ppts. Hydrochlorides of **3** are also less soluble in aceto-nitrile which may be used as solvent instead of CH_2Cl_2. Isolated crude products (**3**) were pure in many cases as shown by TLC, and were frequently used for further reactions (particularly rearrangements[12,13]) without additional purification.

(C) *Sulfide-sulfuryl chloride method.* 5 mmoles of sulfide were dissolved in 20 ml dry CH_2Cl_2 and cooled to −60°. A soln of 5 mmoles SO_2Cl_2 in 15 ml dry CH_2Cl_2 and subsequently a soln of 10 mmoles of aniline in 15 ml CH_2Cl_2 were added dropwise with stirring (a double amount of aniline is used for neutralisation of arising HCl). The mixture was stirred until the temp. had risen to 20° (about 5–6 hr). After extraction with 5% NaOH aq products were isolated via the corresponding picrates.

Oxidation of N-*aryl-sulfimides* (**3**)

Oxidations were performed at room temps (oxidation of N-phenyl- and N - 4 - methylphenyl - S,S-dimethyl - sulfimide at 0°), using a double-fold excess of $KMnO_4$. Typical procedure: 1·00 g of **3** ($R^1 = R^2$ = Me, R = 4-CN; 5·6 mmoles) was dissolved in 100 ml dioxane. 45 ml of a 0·25 molar $KMnO_4$ aq were added, and the mixture was stirred at room temp for 8 hr. Then 200 ml water was added, and the mixture extracted with 4 times 100 ml $CHCl_3$. The $CHCl_3$ layers were washed with water, dried over Na_2SO_4 and evaporated to dryness. The residue was recrystallized from ether-n-hexane (nitro derivatives from dioxane or dioxane-n-hexane).

Direct synthesis of N-*aryl-sulfoximides* **6** *from anilines and DMSO*

(a) N-*4-Chlorophenyl-*S,S-*dimethyl sulfoximide* (**6**, $R^1 = R^2$ = Me, R = 4-Cl). 8 mmoles t-butyl hypochlorite, dissolved in 5 ml CH_2Cl_2, and 10 mmoles 4-chloro-aniline, dissolved in 10 ml CH_2Cl_2, were added successively and dropwise to a stirred soln of 50 mmoles DMSO in 10 ml CH_2Cl_2 at −50°. After complete addition, the mixture was kept at −70° for 2 hr. Extraction with 0·1 N NaOH aq, drying over Na_2SO_4 and column chromatography (silicagel, $CHCl_3$) yielded 50% crude **6**, m.p. 45–52°.

Analogous reaction of 5 mmoles SO_2Cl_2, 10 mmoles 4-chloro-aniline and 5 mmoles DMSO (dissolved in 20 ml CH_2Cl_2 each) at −65° yielded 33% crude **6**, m.p. 54–62°.

(b) N-*Phenyl-*S,S-*dimethyl-sulfoximide* (**6**, $R^1 = R^2$ = Me, R = H): 8 mmoles *t*-butyl hypochlorite, dissolved in 5 ml CH_2Cl_2, were added to a soln of 5 ml DMSO and 8 mmoles aniline in 10 ml CH_2Cl_2 at −65°.

Extraction with 0·1 N NaOH, column chromatography and distillation (Kugelrohr, 0·1 Torr, bath temp 100–130°) yielded 40% crude **6** (oil; NMR indicated a purity of at least 90%). Crystallisation from ether: white needles, m.p. 58–60°.

Methylation of N-*aryl-sulfoximides* (**6**)

Sulfoximide **6** (2·5 mmoles) with $R^1 = R^2$ = Me was treated with 1 g FSO_3CH_3 with exclusion of moisture (exothermic reaction). The mixture was heated at 60° for 3 hr. After evaporation the residue was dissolved in 40 ml H_2O and extracted with 3 times 20 ml ether (removal of unreacted sulfoximide **6**). The aqueous soln was subjected to anion exchange chromatography (100 ml Lewatit M 500, basic form). The effluents were neutralized with 0·1 N HCl, evaporated to give a volume of approx 20 ml and extracted with 3 times 20 ml $CHCl_3$. The aqueous soln was evaporated to dryness and carefully dried at 0·01 Torr, yielding **8** with $R^1 = R^2$ = Me.

R = H: 71% yield, m.p. (dec): 133–135°. NMR (δ, ppm, 60 MHz, solvent D_2O, DSS as internal standard): 3·61 (s), 3·97 (s), 7·70 (s). R = 4-CH_3: 68% yield, m.p. (dec): 130–132°; NMR 2·45 (s), 3·60 (s), 3·95 (s), 7·53 (s). R = 4-Cl: 85% yield, m.p. (dec): 105–108°; NMR: 3·65 (s), 4·00 (s), 7·68 (s). R = 4-NO_2: 50% yield, m.p. (dec): 109–115°; NMR: 3·77 (s), 4·10 (s), 7·85–8·65 (m).

Mass spectra of N-*aryl-sulfimides* (**3**) m/e (intensity in % of basis peak); 70 (°: 75) eV. $R^1 = R^2$ = Me, R = 4-CH_3O: M^+ 183 (62%, $C_9H_{13}NOS$), 168 (100), 153 (64), 138 (7), 136 (20), 123 (5), 122 (12), 121 (57), 106 (36), 62 (34), 61 (11).

$R^1 = R^2$ = Me, R = 4-Me°: M^+ 167 (62%, $C_9H_{13}NOS$), 152 (100), 137 (64), 120 (15), 106 (18), 105 (27), 91 (15), 79 (12), 78 (26), 77 (19), 62 (22), 61 (9).

$R^1 = R^2$ = Me, R = 2-Cl°: M^+ 187 (62%, $C_8H_{10}ClNS$), 172 (100), 157 (57), 140 (13), 126 (11), 125 (21), 111 (13), 90 (38), 64 (23), 63 (31), 62 (35), 61 (29).

$R^1 = R^2 = Me$, R = 4-Cl[a]: M^+ 187 (51%, $C_8H_{10}ClNS$), 172 (100), 157 (55), 140 (5), 126 (7), 125 (24), 111 (7), 90 (27), 64 (11), 63 (25), 62 (11), 61 (13).

$R^1 = R^2 = Me$, R = 4-COOMe: M^+ 211 (67%, $C_{10}H_{13}NO_2S$), 196 (100), 181 (40), 180 (19), 165 (14), 164 (9), 150 (10), 137 (9), 122 (10), 120 (6), 90 (17), 64 (13), 63 (23), 62 (30), 61 (10).

$R^1 = R^2 = Me$, R = 4-CN: M^+ 178 (72%, $C_9H_{10}N_2S$), 163 (100), 148 (61), 131 (8), 117 (8), 116 (19), 102 (14), 90 (5), 89 (17), 64 (11), 63 (14), 62 (50), 61 (17).

$R^1 = R^2 = Me$, R = 4-NO_2[a]: M^+ 198 (89%, $C_8H_{10}N_2O_2S$), 183 (100), 168 (8), 153 (31), 151 (11), 138 (29), 137 (24), 136 (7), 122 (18), 90 (25), 64 (19), 63 (40), 62 (65), 61 (29).

$R^1 = R^2 = -(CH_2)_4-$, R = 4-Cl[a]: M^+ 213 (100%, $C_{10}H_{12}ClNS$), 157 (38), 139 (43), 126 (16), 125 (44), 122 (8), 111 (15), 90 (31), 88 (29), 87 (59), 64 (12), 63 (23).

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