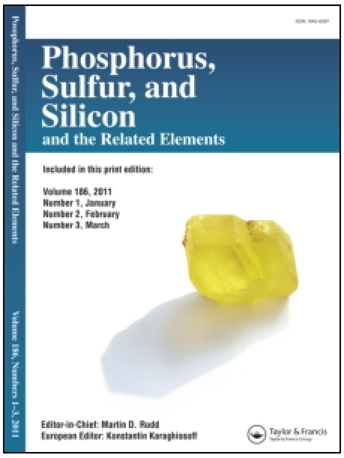

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CHLOROSULFONATION OF SOME DIPHENYL DERIVATIVES

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CHLOROSULFONATION OF SOME DIPHENYL DERIVATIVES

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Benzophenone (**1**), diphenyl sulfone, and 4-nitro-2′-chloro- and 4-nitro-2′,6′-dichloro-diphenyl ethers (**23,24**) have been chlorosulfonated. The direct yield of benzophenone-3,3′-disulfonyl chloride (**2**) was low, the majority of product was the disulfonic acid. Diphenyl sulfone (**11**) with a large amount of chlorosulfonic acid (8 mols) at 140° gave the 3,3′-disulfonyl chloride (**12**). With less reagent (6 mols) at 90° a mixture of the 3-sulfonyl chloride (**21**) and diphenyl sulfone was formed. Subsequent reaction with sodium azide gave the 3-sulfonyl azide (**22**). The diphenyl ether sulfonyl chlorides (**25,26**) were very susceptible to hydrolysis, especially (**26**) which probably accounts for the low yield obtained (31%). The various sulfonyl chlorides were characterized as amides, azides, hydrazides and hydrazones (Tables I–III) and their i.r., n.m.r., and mass spectral data are included.

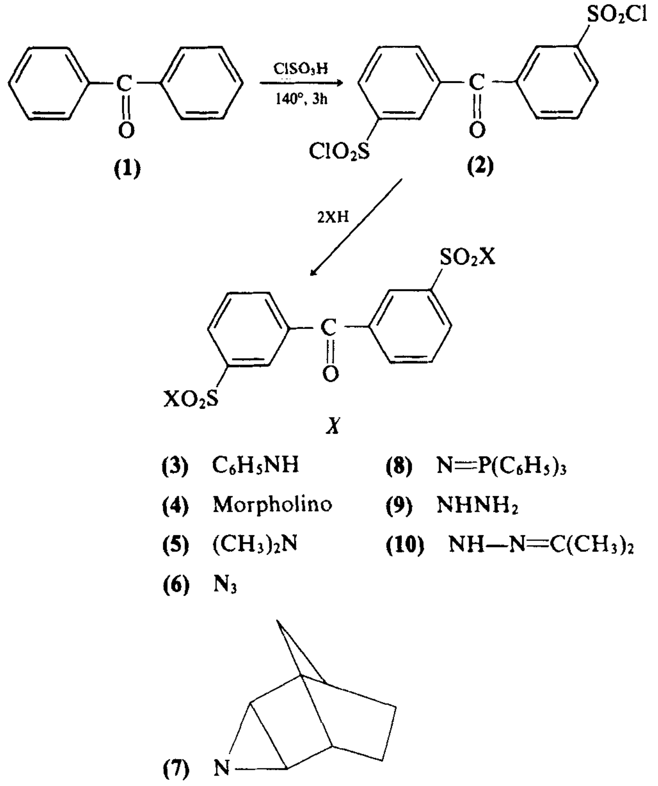
INTRODUCTION

The paper is a continuation of our program on the chemistry and biological activity of various aromatic sulfonyl compounds.[1,2] We have examined the chlorosulfonation of some diphenyl derivatives in a search for new pest control agents.

Several diphenyl sulfones are important acaricides[3] and so the synthesis of their sulfonyl derivatives appeared interesting for examination as potential acaricides. Nitrodiphenyl ethers are valuable herbicides, the best known example is nitrofen (2′,4′-dichlorophenyl-4-nitrodiphenyl ether) which is an excellent soil herbicide for preemergence weed control in brassica.[4] Previous studies[5] on diphenyl ether sulfonyl derivatives have been extended; this appeared a promising area since some of these compounds showed high algicidal activity.

DISCUSSION

Benzophenone was first converted to the 3,3′-disulfonic acid by Lapworth[6] using 15% fuming sulfuric acid. He claimed that benzophenone is scarcely affected by chlorosulfonic acid. We found that benzophenone (**1**) with excess chlorosulfonic acid (6 mols) gave a small amount of the disulfonyl chloride (**2**) (15%) (Scheme 1). However, most of the product was the disulfonic acid which was isolated as the dipotassium salt and was subsequently converted to the chloride (**2**) by reaction with thionyl chloride giving an overall yield of 95%. The chloride was converted into the amides (**3–5**) (Table I) as previously described.[7] These are claimed[7] to possess insecticidal activity against cotton leaf worm and so we have prepared other derivatives, including the azide (**6**), which with norbornene and triphenylphosphine gave the azidine (**7**) and the phosphinimine (**8**) respectively (Table I). With hydrazine, the chloride (**2**) gave the hydrazide (**9**) and this was characterized as the acetone derivative (**10**). In contrast, attempted preparation of the *p*-nitrobenzaldehyde



(3)	C_6H_5NH	(8)	$N{=}P(C_6H_5)_3$
(4)	Morpholino	(9)	$NHNH_2$
(5)	$(CH_3)_2N$	(10)	$NH{-}N{=}C(CH_3)_2$
(6)	N_3		
(7)			

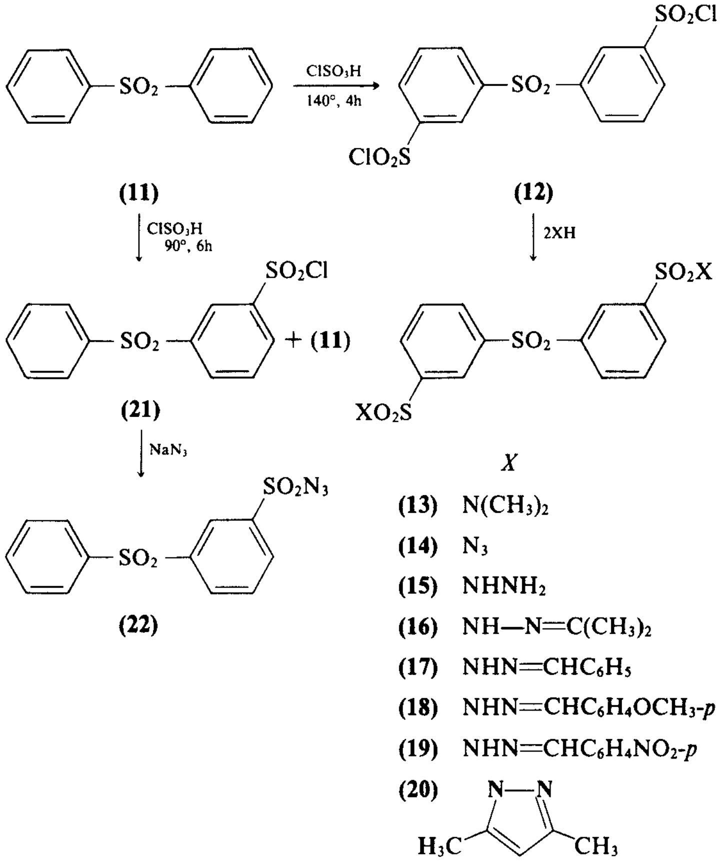
SCHEME 1

hydrazone gave *p*-nitrobenzaldehyde azine; this has been previously formed in the analogous reaction using 5-chlorosalicylic acid-3-sulfonohydrazide.[8]

Diphenyl sulfone (**11**) on treatment with chlorosulfonic acid (2 mols) was reported[9] to give the 3,3′-disulfonic acid which was subsequently converted to the disulfonyl chloride (**12**) by reaction with phosphorus pentachloride. We found that when diphenyl sulfone (**11**) was heated (140°) with chlorosulfonic acid (8 mols) a good yield (77%) of the dichloride (**12**) was obtained. This was significantly higher than was directly obtained with benzophenone under comparable conditions (15%), possibly because the more bulky sulfonyl group may reduce the mesomeric deactivation of the phenyl rings as cf. the smaller carbonyl group by an interaction of steric and electronic effects.

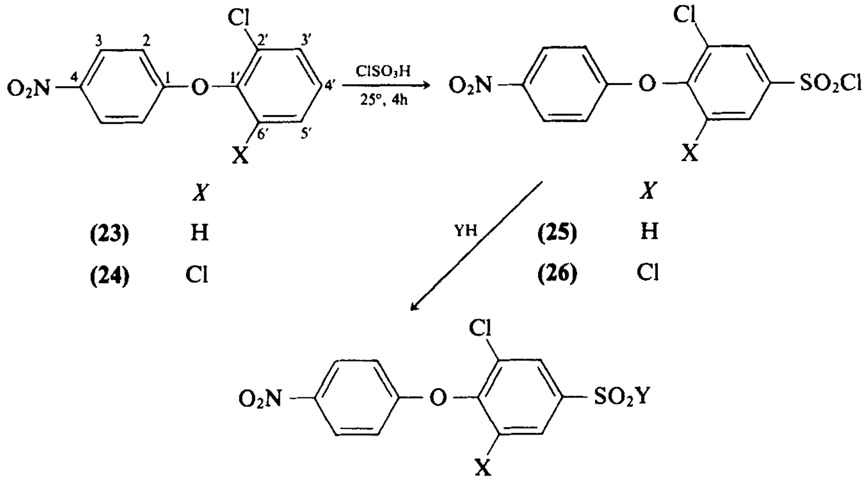
The dichloride (**12**) was converted to the dimethylamide (**13**), azide (**14**), hydrazide (**15**), hydrazones (**16–19**) and 3,5-dimethyl-pyrazole (**28**) (Scheme 2 and Table II).

The reaction of diphenyl sulfone with chlorosulfonic acid was examined further to see if the 3-sulfonyl chloride (**21**) could be prepared. This reaction needed prolonged treatment with chlorosulfonic acid (6 mols) at 90° (Scheme 2) but the product (**21**) was shown (t.l.c. and microanalysis) to be contaminated with diphenyl sulfone (ca. 50%). Temperatures >100° tended to give the dichloride (**12**) and the use of less chlorosulfonic acid gave larger amounts of unreacted diphenyl sulfone. Treatment of the crude chloride (**21**) with hydrazine did not give the pure hydrazide, but with sodium azide followed by recrystallization the azide (**22**) was isolated.



SCHEME 2

The condensation of *p*-chloronitrobenzene with *o*-chlorophenol and 2,6-dichlorophenol in *N,N*-dimethylacetamide-potassium hydroxide initially gave only low yields of the corresponding 4-nitrodiphenyl ethers (**23,24**), although good yields were previously reported.^{5,10,11} In the literature only 0.85 mol of potassium hydroxide was used, but efforts to increase the efficiency of the reaction by using more potassium hydroxide (1 mol), or by varying the temperature, rates of addition or the reaction time had little effect on the yields of products (ca. 20%). However, when potassium hydroxide pellets were finely powdered immediately before addition to the reaction mixture, the yield of the diphenyl ether (**23**) was increased to 70%, although the yield of (**24**) remained low (37%). The chlorosulfonation of the 4-nitrodiphenyl ethers (**23,24**) initially afforded very poor yields of the sulfonyl chlorides (**25,26**). (Scheme 3 and Table III). The sulfonyl chlorides apparently are very susceptible to hydrolysis due to the electron-withdrawing chloro- and *p*-nitrophenoxy-groups, similar facile hydrolysis has been reported^{12} with 2,4-dichlorobenzenesulfonyl chloride. Repetition of chlorosulfonation, in which the crude product was stirred with an ethyl acetate-ice-water mixture, gave a good yield (72%) of the sulfonyl chloride (**25**), but the yield of (**26**) remained poor. The chlorides (**25,26**) were converted into the derivatives (**27–38**). (Scheme 3 and Table III). Condensation of the chlorides with hydrazine hydrate gave low yields of the hydrazides (**30,35**). On the other hand, with anhydrous hydrazine the yields were much higher (Table III) again reflecting the ease of hydrolysis of the sulfonyl chlorides. The n.m.r. spectra of the diphenyl ether sulfonyl derivatives in deuterated dimethylsulfoxide were first-order AB type spectra permitting identification of all the aromatic protons (Table III). The most deshielded protons (H_A) are *ortho* to the nitro group, followed by the protons (H_D and H_E) *ortho* to the SO_2Y group, and finally the proton H_C. The signals for the protons H_A, H_B, H_C showed *ortho* spin-spin coupling (J ≏ 10 Hz) and protons H_D, H_E showed *meta* coupling (J ≏ 2 Hz).



	X
(23)	H
(24)	Cl

	X
(25)	H
(26)	Cl

	X	*Y*
(27)	H	N_3
(28)	H	$N(CH_3)_2$
(29)	H	Morpholino
(30)	H	$NHNH_2$
(31)	H	$NHN{=}C(CH_3)_2$
(32)	H	$NHN{=}CHC_6H_5$
(33)	H	$NHN{=}CHC_6H_4NO_2$-*p*
(34)	H	$NHN{=}CHC_6H_4OCH_3$-*p*
(35)	Cl	$NHNH_2$
(36)	Cl	$NHN{=}C(CH_3)_2$
(37)	Cl	$NHN{=}CHC_6H_5$
(38)	Cl	$NHN{=}CHC_6H_4NO_2$-*p*

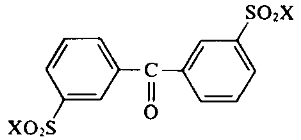
SCHEME 3

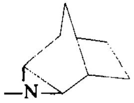
EXPERIMENTAL

I.r. spectra were recorded as Nujol mulls using a Perkin-Elmer 237 spectrophotometer. N.m.r. spectra were determined with a Varian HA 100 spectrometer using tetramethylsilane as internal standard. In the Tables solvents used are indicated as follows: (a) $(CD_3)_2SO$; (b) $CDCl_3$; (c) $(CD_3)_2CO$. Mass spectra were

TABLE I

Benzophenone-3,3′-disulfonyl derivatives



No.	X	Yield (%)	m.p.	Formula	Found (%) C	Found (%) H	Found (%) N	Found (%) S	Required (%) C	Required (%) H	Required (%) N	Required (%) S
2	Cl	95	132–135°[6]	$C_{13}H_8Cl_2O_5S_2$	40.8	2.2	—	16.7	41.1	2.1	—	16.9
3	C_6H_5NH	90	172–174°[7]	$C_{25}H_{20}N_2O_5S_2$	60.75	3.9	5.4	—	60.8	4.1	5.7	—
4	morpholino	83	192–194°[7]	$C_{21}H_{24}N_2O_7S_2$	52.2	4.8	5.9	13.4	52.5	5.0	5.8	13.3
5	$(CH_3)_2N$	76	164–166°	$C_{17}H_{20}N_2O_5S_2$	51.2	5.2	6.8	—	51.5	5.1	7.1	—
6	N_3	92	106–108°	$C_{13}H_8N_6O_5S_2$	39.6	2.2	21.1	16.5	39.8	2.1	21.4	16.3
7		67	178–180°	$C_{27}H_{28}N_2O_5S_2$	60.0	5.9	5.5	—	60.0	5.6	5.6	—
8	$N{=}P(C_6H_5)_3$	63	110°	$C_{49}H_{33}N_2O_5P_2S_2$	68.6	4.7	3.4	7.4	68.4	4.45	3.25	7.45
9	$NHNH_2$	52	150°	$C_{13}H_{14}N_4O_5S_2$	42.4	4.1	15.3	—	42.15	3.8	15.3	—
10	$NHN{=}C(CH_3)_2$	63	140–143°	$C_{19}H_{22}N_4O_5S_2$	50.9	5.2	12.7	—	50.65	4.9	12.4	—

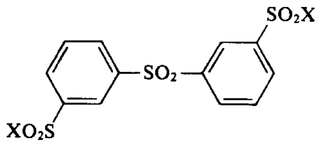
	I.r. data (ν_{max}, cm^{-1})	N.m.r. data (δ ppm)
2	1670 (CO), 1600, 1575 (arom C=C), 1380, 11.80 (SO_2)	8.10–7.55, m, (8 ArH)[a]
3	3240 (NH), 1650 (CO), 1580 (arom C=C), 1350, 1150 (SO_2)	10.4, brS, 2H(2 NH); 8.1–7.7, m, 8H(2 × C_6H_4); 7.4–7.0, m, 10H(2 × C_6H_5)[a]
4	1670 (CO), 1360, 1180 (SO_2), 1120 (C—O—C)	8.4–7.6, m, (8 ArH); 4.1–3.4, t, 8H($O{<}^{CH_2}_{CH_2}$ × 2); 3.4–2.7, t, 8H($N{<}^{CH_2}_{CH_2}$ × 2)[b]
5	1680 (CO), 1600 (arom C=C), 1350, 1165 (SO_2)	8.20–7.55, m, (8 ArH); 2.7, S, 12H(4 × CH_3)[a]
6	2140 (N_3), 1660 (CO), 1590 (arom C=C), 1380, 1170 (SO_2)	8.40–7.80, m, (8 ArH)[c]
7	3000–2860 (alip C—H), 1655 (CO), 1325, 1150 (SO_2)	8.40–7.55, m, (8 ArH); 3.10–0.5, m, 20H(norbornyl H's)[b]
8	1660 (CO), 1595 (arom C=C), 1360, 1150 (SO_2)	7.90–7.30, m, (38 ArH)[c]
9	3300, 3260 (NH), 1640 br(CO), 1590 (arom C=C), 1380, 1170 (SO_2)	9.20, brs, 2H(2 NH); 8.1–7.0, m, (8 ArH); 4.0 brs, 4H(2 NH_2)[a]
10	3250 (NH), 1645 br(CO), 1600 (arom C=C), 1360, 1165 (SO_2)	9.30, brs, 2H(2 NH); 8.25–7.4, m, (8 ArH); 1.83, s, 2H(4 CH_3)[a]

M.s. data

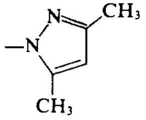
2 378 (M^+), 343 (M—Cl), 279 (M—SO_2Cl), 215, 205, 203, 180, 152, 104, 76 (base peak), 51
5 396 (M^+), 353 (M—NMl_2), 289 (base peak), 225, 212, 180, 152, 108, 76, 44
6 392 (M^+), 350 (M—N_3, base peak), 210, 194, 180, 166, 152, 139, 104, 90, 76
9 No M^+ ion at 370; highest ion .279 (electron impact) or 246 (chemical ionization)
(2) lit.[6] 137–138° (3) lit.[7] 173° (4) lit.[7] 192°

TABLE II

Diphenyl Sulfone-3,3′-disulfonyl derivatives



No.	X	Yield (%)	m.p.	Formula	Found (%)				Required (%)			
					C	H	N	S	C	H	N	S
12	Cl	77	156°[9]	$C_{12}H_8Cl_2O_6S_3$	34.8	2.1	—	22.7	34.7	1.9	—	23.1
13	$(CH_3)_2N$	45	170°	$C_{16}H_{20}N_2O_6S_3$	44.2	4.6	6.2	—	44.4	4.6	6.5	—
14	N_3	81	147°	$C_{12}H_8N_6O_6S_3$	44.3	4.5	6.3	—	44.2	4.6	6.5	—
15	NH NH_2	76	153°	$C_{12}H_{14}N_4O_6S_3$	35.3	3.6	14.1	23.3	35.5	3.4	13.8	23.6
16	$NHN{=}C(CH_3)_2$	57	194–196°	$C_{18}H_{22}N_4O_6S_3$	44.2	4.5	11.2	—	44.4	4.5	11.5	—
17	$NHN{=}CHC_6H_5$	78	215°	$C_{26}H_{22}N_4O_6S_3$	53.8	3.8	9.7	—	53.6	3.7	9.6	—
18	$NHN{=}CHC_6H_4OCH_3$-*p*	76	192°	$C_{28}H_{26}N_4O_8S_3$	52.1	3.8	8.8	—	52.3	4.05	8.7	—
19	$NHN{=}CHC_6H_4NO_2$-*p*	55	164°	$C_{26}H_{20}N_6O_{10}S_3$	46.6	3.2	12.3	14.1	46.4	3.0	12.5	14.3

20		80	196–197°	$C_{22}H_{22}N_4O_6S_3$	49.3	4.3	10.4	—	49.6	4.1	10.5	—

	I.r. data (ν_{max} cm^{-1})	N.m.r. data (δ ppm)
12	1600 (arom C═C), 1390, 1355, 1180, 1160 (SO_2)	
13	1595 (arom C═C), 1380, 1365, 1185, 1155 (SO_2)	8.4–7.6, m, (8 ArH); 2.77, 12H,(2 × $N(CH_3)_2$[b]
14	2130 (N_3), 1590 (arom C═C), 1380, 1340, 1170 (SO_2)	
15	3310 br (NH), 1600 (arom C═C), 1340, 1165 (SO_2)	
16	3305 (NH), 1595 (arom C═C), 1370, 1330, 1180, 1155 (SO_2)	10.1, brS, (2 NH); 8.6–7.6, m, (8 ArH); 1.8, S, 12H(2 × N═$C(CH_3)_2$)[c]
17	3210 (NH), 1600 (arom C═C), 1340, 1180, 1150 (SO_2)	11.1 brS, 2H(2 NH); 8.4–6.7, m, 18H(16 ArH, 2N═CH)[c]
18	3220 (NH), 1600 (arom C═C), 1370, 1330, 1180 (SO_2)	11.5, brS, 2H(2 NH); 8.5–6.8, m, 18H(16 ArH, 2N═CH); 3.8, S, 6H(2 × OCH_3)[c]
19	3210 (NH), 1610 (arom C═C), 1520 (NO_2), 1180, 1140 (SO_2)	
20	3320 br (NH), 1580 (arom C═C), 1350, 1180, 1160 (SO_2)	

	M.s. data
12	414 (M^+), 379 (M—Cl), 251, 239, 223, 175
13	432 (M^+), 389 (M—$N(CH_3)_2$, 325 (M—$SO_2N(CH_3)_2$, 261, 216
16	no M^+ ion at 486 (highest ion at 97)
17	no M^+ ion at 582; ions at 208, 119, 77
18	no M^+ ion at 642; ions at 359, 268, 219, 161
19	no M^+ ion at 672; highest ion at 448
20	534 (M^+), 439 (M-pyrazole ring), 375, 312, 216, 189, 170, 95

(12) lit.[9] 175–176°

determined with an AEI MS9 spectrometer at 70 eV. T.l.c. was carried out using silica gel G plates developed with iodine vapor. Microanalyses by I.C.I. Ltd. (Pharmaceuticals Division), Alderley Park, Cheshire, England. Melting points were determined with a Kofler hot-stage apparatus and are uncorrected.

Benzophenone-3,3′-disulfonyl chloride (*Table I*) (**2**)

Benzophenone (**1**) (18.2 g) was heated with chlorosulfonic acid (40 ml; 6 mols) at 140° for 3 h. The yellow solution was poured onto ice-water (400 ml). The gummy solid was extracted with ether (2 × 500 ml), washed with water, dried ($MgSO_4$) and evaporated. Trituration with acetone-ether and crystallization ($CHCl_3$) gave the chloride. The combined aqueous phase was treated with barium carbonate until it was alkaline; the suspension was heated to 90°, and filtered. The cold filtrate (25°) was treated with potassium sulfate until precipitation was complete; the suspension was heated (80°) for $\frac{1}{2}$ h and filtered. Evaporation gave benzophenone-3,3′-dipotassium-disulfate (25.1 g; 60%).

This was refluxed with thionyl chloride (75 ml) and dimethylformamide (10 drops) for 2 h. Cooling and filtration gave a solid which was dissolved in dichloromethane. The solution was washed with water, dried ($MgSO_4$) and concentrated to give the chloride (**2**) (18.2 g; 80% from the dipotassium salt).

Benzophenone-3,3′-disulfonyl Azide (**6**)

The chloride (**2**) (0.5 g) was reacted with sodium azide (0.35 g; 4 mols) in aqueous acetone (20 ml of 1:1) for 3 h. The precipitate was collected, washed with water and recrystallized (aqueous acetone) to give the *azide*.

Derivatives of the Azide (**6**)

(*a*) *With norbornene* The azide (1 g) was refluxed with norbornene (1 g; 4 mols) in benzene (150 ml) until evolution of nitrogen ceased (5 h). Cooling gave a solid which was triturated with methanol to give the *aziridine* (**7**).

(*b*) *With triphenylphosphine* The azide (1 g) was refluxed with triphenylphosphine (1.6 g; 2.2 mols) in ether-tetrahydrofuran (50 ml of 1:1) for 1 h. Evaporation gave a solid which was crystallized (ether) to give the *triphenylphosphinimine* (**8**).

Benzophenone-3,3′-disulfonohydrazide (**9**)

The chloride (**2**) (0.5 g) dissolved in tetrahydrofuran (10 ml) was gradually added to a stirred solution of hydrazine hydrate (0.66 g of 98%; 5 mols) in tetrahydrofuran (20 ml). The suspension was stirred for 2 h, concentrated under reduced pressure, and poured onto ice-water (100 ml). Dilute hydrochloric acid was added to pH6; the precipitate was filtered off, washed with water and triturated (ether-petroleum ether 40–60° 1:1) to give the *hydrazide* (**9**), which with boiling acetone (0.5 h) gave the *acetone hydrazone* (**10**).

p-*Nitrobenzaldehyde Azine*

The hydrazide (**9**) (1.5 g) was refluxed with *p*-nitrobenzaldehyde (3 mols) in methanol (25 ml) for 2 h. Cooling gave the azine as golden plates (2 g), m.p. 298–299° (dimethylformamide) (lit.[13] 300°). (Found C, 56.6; H, 3.0; N, 18.7. $C_{14}H_{10}N_4O_4$ requires C, 56.4; H, 3.35; N, 18.8%). Ms. (chemical ionization) showed ions at 199 (M + 1), 176, 154, 152, 149.

Diphenyl Sulfone-3,3′-disulfonyl chloride (**12**) (*Table II*)

Diphenyl sulfone (**11**) was heated with chlorosulfonic acid (29 ml; 8 mols) at 140° for 4 h. The solution was poured onto ice-water with stirring to give the chloride (**12**) (15.9 g). T.l.c. (EtOAc-cyclohexane 1:1) showed one spot, R_F 0.49. When less chlorosulfonic acid (6 mols) was used, the product was contaminated with diphenyl sulfone. T.l.c. (EtOAc-cyclohexane 1:1) showed 2 spots R_F 0.72 (diphenyl sulfone) and 0.49.

Diphenyl Sulfone-3,3′-disulfonohydrazide (**15**)

The chloride (**12**) (10 g) was reacted with hydrazine hydrate (5 ml of 98%; 4 mols) in methanol (40 ml) at 0°. After 1 h at room temperature, addition of ice-water (150 ml) gave a white precipitate. Filtration, and trituration with methanol and ether gave the ***hydrazide*** (76%). When tetrahydrofuran was used as solvent the yield of the hydrazide was reduced to 65%.

The hydrazide (**15**) was characterized as the hydrazones (**16–19**) (Table II).

Reaction of the hydrazide (**15**) *with Acetylacetone*

The hydrazide (0.8 g) was refluxed with acetylacetone (0.39 g; 2 mols) in methanol (30 ml) for 6 h. The precipitate was recrystallized (methanol) to give the *3,5-dimethylpyrazole* (**20**). T.l.c. (EtOAc-cyclohexane 1:1) showed one spot, R_F 0.52.

Diphenyl Sulfone-3-sulfonyl chloride (**21**)

Diphenyl sulfone (10.9 g) was heated with chlorosulfonic acid (22 ml; 6 mols) at 90° for 6 h to give a mixture of the ***chloride*** (**21**) and diphenyl sulfone (5.9 g), m.p. 59–64° (Found: C, 54.4; H, 3.7; S, 17.7. The chloride, $C_{12}H_9ClO_4S_2$ requires C, 45.5; H, 2.8; S, 20.3%) (This result suggests the product is an approximately 1:1 mixture of (**21**) with diphenyl sulfone which requires C, 53.9; H, 3.5; S, 17.9%). T.l.c. (EtOAc-cyclohexane 1:1) showed two spots, R_F 0.72 (diphenyl sulfone) and R_F 0.65. Ms. showed the molecular ion for (**21**), M^+, 316 fragment ions at 281 (M—Cl), 218 (Ph_2SO_2), 217 (M—SO_2Cl), 125, 77.

Repetition of chlorosulfonation at higher temperatures (125° and 100°) gave mixtures of the disulfonyl chloride (**12**) with some diphenyl sulfone.

Diphenyl sulfone-3-sulfonyl Azide (**22**)

The crude chloride (**21**) (1 g) was reacted with sodium azide (2 mols) in aqueous acetone (20 mls of 1:1) for 2 h. The white solid was filtered off, washed with water and recrystallized twice from aqueous acetone to give the ***azide*** (0.4 g), m.p. 87–88° (Found: C, 44.7; H, 3.0; N, 12.7. $C_{12}H_9N_3O_4S_2$ requires C, 44.6; H, 2.8; N, 13.0%). T.l.c. (EtOAc-cyclohexane 1:1) showed one spot, R_F 0.52. ν_{max} 2130 (N_3), 1600 (arom C=C), 1380, 1160 (SO_2) cm^{-1}. Ms. showed the molecular ion (M^+, 323) and fragment ions at 281 (M—N_3), 217 (M—SO_2N_3), 125.

2′-Chloro-4-Nitrodiphenyl Ether (**23**)

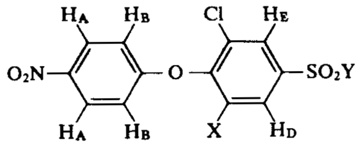
1-Chloro-4-nitrobenzene (30.6 g) was added to a stirred solution of *o*-chlorophenol (25 g; 1 mol) and freshly powdered potassium hydroxide (10.9 g; 1 mol) in *N,N*-dimethylacetamide (125 ml) at 50°, then the mixture was heated at 160° for 6 h. The cold mixture was treated with 2M-sodium hydroxide (250 ml) and extracted with toluene (3 × 100 ml). The combined extracts were washed with 1M-hydrochloric acid (2 × 50 ml), water (2 × 50 ml), dried ($MgSO_4$) and evaporated *in vacuo*. Recrystallization of the residue from cyclohexane gave the diphenyl ether (**23**) (35 g; 70%), m.p. 78–80° (lit.[5] 46–47°, lit.[11] 74–76°). ν_{max} 1600 (arom C=C), 1530 (NO_2), 1360, 1170 (SO_2), 1060 (C—O—C), 690 (C—Cl) cm^{-1}. T.l.c. (cyclohexane) showed one spot, R_F 0.20. Ms. showed the molecular ion (M^+, 249) and fragment ions at 219 (M—NO), 168, 111.

2′,6′-Dichloro-4-Nitrodiphenyl Ether (**24**)

Reaction of 2,6-dichlorophenol (25 g; 1 mol) with potassium hydroxide (8.8 g; 1 mol) and 1-chloro-4-nitrobenzene (24 g; 1 mol) under similar conditions afforded the diphenyl ether (**24**) (16 g; 37%), m.p. 116–118° (lit.[5,11] 115–117°). ν_{max} 1600 (arom C=C), 1520 (NO_2), 1370, 1175 (SO_2), 1100 (C—O—C), 695 (C—Cl) cm^{-1}. Ms. showed the molecular ion (M^+, 283) and fragment ions at 253 (M—NO), 251, 139. T.l.c. (cyclohexane) showed one spot, R_F 0.63.

TABLE III

4-Nitro-2′-chloro and 2′,6′-dichloro-diphenylether 4′-sulfonyl derivatives



No.	X	Y	Yield (%)	m.p.	Formula	Found (%) C	H	N	S	Required (%) C	H	N	S
25	H	Cl	72	103–105°[5]	$C_{12}H_7Cl_2NO_5S$	41.0	2.2	3.8	—	41.3	2.0	4.0	—
26	Cl	Cl	31	72–74°[5]	$C_{12}H_6Cl_3NO_5S$	37.3	1.8	3.8	—	37.6	1.6	3.7	—
27	H_C	N_3	59	102–104°[5]	$C_{12}H_7ClN_4O_5S$	40.8	1.9	16.1	8.7	40.6	2.0	15.8	9.0
28	H_C	$N(CH_3)_2$	26	92–94°	$C_{14}H_{13}ClN_2O_5S$	47.4	3.3	7.6	—	47.1	3.65	7.85	—
29	H_C	morpholino	35	125–127°	$C_{16}H_{15}ClN_2O_6S$	47.9	4.0	7.2	—	48.1	3.8	7.0	—
30	H_C	$NHNH_2$	76	112–114°	$C_{12}H_{10}ClN_3O_5S$	41.7	3.1	12.0	8.9	41.9	2.9	12.2	9.3
31	H_C	$NHN{=}C(CH_3)_2$	20	129–130°	$C_{15}H_{14}ClN_3O_5S$	46.8	3.4	11.1	8.5	46.9	3.65	10.95	8.3
32	H_C	$NHN{=}CHC_6H_5$	15	79–80°	$C_{19}H_{14}ClN_3O_5S$	52.5	2.7	9.8	—	52.8	2.9	9.7	—
33	H_C	$NHN{=}CHC_6H_4NO_2$-*p*	15	125–128°	$C_{19}H_{13}ClN_4O_7S$	48.1	2.5	11.5	6.9	47.85	2.7	11.75	6.7
34	H_C	$NHN{=}CHC_6H_4OCH_3$-*p*	22	120–122°	$C_{20}H_{16}ClN_3O_6S$	51.7	3.8	9.3	—	52.0	3.5	9.1	—
35	Cl	$NHNH_2$	51	131–133°	$C_{12}H_9Cl_2N_3O_5S$	38.3	2.6	11.0	8.6	38.1	2.4	11.1	8.5
36	Cl	$NHN{=}C(CH_3)_2$	18	163–165°	$C_{15}H_{13}Cl_2N_3O_5S$	43.4	3.1	9.7	—	43.1	3.1	10.05	—
37	Cl	$NHN{=}CHC_6H_5$	16	99–100°	$C_{19}H_{13}Cl_2N_3O_5S$	48.7	3.0	8.8	7.1	48.9	2.8	9.0	6.9
38	Cl	$NHN{=}CHC_6H_4NO_2$-*p*	15	145–147°	$C_{19}H_{12}Cl_2N_4O_7S$	44.8	2.4	11.1	6.3	44.6	2.35	10.95	6.3

	I.r. data (ν_{max}, cm^{-1})	N.m.r. data (δ, ppm) in a
25	1600 (arom C=C), 1520 (NO_2), 1380, 1180 (SO_2), 1160 (C—O—C), 680 (C—Cl)	8.34, d, $2H_A$; 8.1, d, H_E; 7.9, dd, H_D; 7.47, d, $2H_B$; 7.25, d, H_C
26	1595 (arom C=C), 1520 (NO_2), 1380, 1175 (SO_2), 1170 (C—O—C), 680 (C—Cl)	8.38, d, $2H_A$, 8.1, d, H_E; 7.95, dd, H_D; 7.35, d, $2H_B$
27	2125 (N_3), 1600 (arom C=C), 1510 (NO_2), 1370, 1190 (SO_2), 1150 (C—O—C), 650 (C—Cl)	8.35, d, $2H_A$; 8.07, d, H_E; 7.91, dd, H_D; 7.30, d, $2H_B$; 7.20, d, H_C

28	1620 (arom C=C), 1510 (NO_2), 1385, 1160 (SO_2), 1120 (C—O—C), 680 (C—Cl)	8.40, d, $2H_A$; 8.07, d, H_E; 7.85, d, H_D; 7.35, d, $2H_B$; 7.2, d, H_C; 2.8, s, 6H(NMe_2)
29	1600 (arom C=C), 1520 (NO_2), 1380, 1180, 1120 (C—O—C), 670 (C—Cl)	8.36–7.20, m, 7H(H_A—H_E), 4.20–2.72, m, 8H(morpholino Hs)
30	3220 (NH), 1575 (arom C=C), 1370, 1175 (SO_2), 1125 (C—O—C), 680 (C—Cl)	8.6, brS, NH; 8.34–7.25, m, 7H(H_A—H_E); 3.8, brS, NH_2
31	3210 (NH), 1600 (arom C=C), 1565 (NO_2), 1350, 1175 (SO_2), 1110 (C—O—C), 690 (C—Cl)	8.9, brS, NH; 8.37–7.27, m, 7H(H_A—H_E); 2.30, s, 6H(N=CMe_2)
32	3200 (NH), 1590 (arom C=C), 1520 (NO_2), 1370, 1180 (SO_2), 1150 (C—O—C), 695 (C—Cl)	
33	3200 (NH), 1600 (arom C=C), 1520 (NO_2), 1380, 1150 (SO_2), 1080 (C—O—C), 690 (C—Cl)	
34	3200 (NH), 1590 (arom C=C), 1520 (NO_2), 1375, 1170 (SO_2), 1060 (C—O—C), 670 (C—Cl)	9.0, brS, NH; 8.50–7.0, m, 11 ArH; 3.75, 3H(OMe)
35	3260 (NH), 1600 (arom C=C), 1520 (NO_2), 1375, 1165 (SO_2), 1140 (C—O—C), 680 (C—Cl)	8.82 brS, NH; 8.35–7.20, m, 6H(H_A—H_E); 3.75 brS, NH_2
36	3200 (NH), 1590 (arom C=C), 1570 (NO_2), 1370, 1170 (SO_2), 1150 (C—O—C), 680 (C—Cl)	8.85 brS, NH, 8.38–7.25 m, 6H(H_A—H_E); 3.8 brS, NH_2; 2.35, 6H(N=CMe_2)
37	3150 (NH), 1600 (arom C=C), 1540 (NO_2), 1380, 1180 (SO_2), 1080 (C—O—C), 690 (C—Cl)	
38	3200 (NH), 1600 (arom C=C), 1510 (NO_2), 1380, 1170 (SO_2), 1130 (C—O—C), 690 (C—Cl)	

M.s. data

25	347 (M^+), 312 (M—Cl), 248 (M—SO_2Cl), 218, 201, 75
27	354 (M^+), 312 (M—N_3), 248 (M—SO_2N^3), 201, 157
28	356 (M^+), 312 (M—NMl_2), 248 (M—SO_2NMl_2), 201, 157, 75
29	397 (M—H), 312 (M—morpholino), 201, 138, 86 (morpholino)
30	343 (M^+), 312 (M—$NHNH_2$), 253, 201, 157, 138
31	384 (M^+), 312 (M—NHN=CMe_2), 250, 201, 168
34	no M^+ ion at 461, ions at 268, 134
36	417 (M^+), 284 (M—SO_2NHN=CMe_2), 202, 173, 97, 71
37	466 (M^+), 284 (M—SO_2NH—N=CHPh), 119, 91
38	no M^+ ion at 512, ions at 284 (M—SO_2NH—N=$CHC_6H_4NO_2$), 202, 180, 152, 95

(25) lit.[5] 89–90° (26) lit.[5] 87–88° (27) lit.[5] 108–109°

2'-Chloro-4-Nitrodiphenyl Ether 4'-Sulfonyl Chloride (**25**) (*Table III*)

The diphenyl ether (**23**) (10 g) was reacted with chlorosulfonic acid (23.2 g; 5 mols) at room temperature for 4 h. The solution was gradually added to a stirred mixture of ethyl acetate (100 ml) and ice-water (200 ml). The ethyl acetate layer was washed with water (2 × 50 ml), dried ($MgSO_4$) and evaporated to give the *chloride.* T.l.c. (cyclohexane) showed one spot, R_F 0.30.

2',6'-Dichloro-4-Nitrodiphenyl Ether 4'-Sulfonyl Chloride (**26**) (*Table III*)

The diphenyl ether (**24**) was similarly reacted with chlorosulfonic acid (5 mols) to give the chloride (**26**).

2'-Chloro-4-Nitrodiphenyl Ether-4'-Sulfonyl Derivatives

The chloride (**25**) was converted, by standard methods, to the compounds (**27–34**) (Table III).

2',6'-Dichloro-4-Nitrodiphenyl Ether-4'-Sulfonyl Derivatives

The chloride (**26**) was converted to the derivatives (**35–38**) (Table III).

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