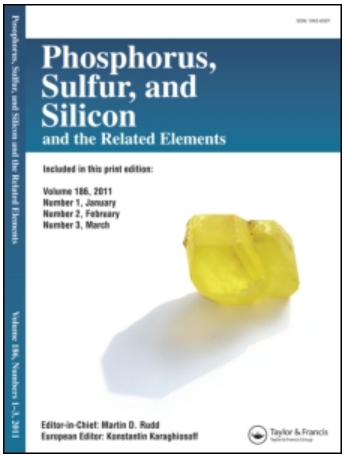

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CYCLISATION OF DIARYL COMPOUNDS WITH CHLOROSULFONIC ACID

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CYCLISATION OF DIARYL COMPOUNDS WITH CHLOROSULFONIC ACID

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Biphenyl(1) and other compounds of type PhXPh (X = O(19); S(30); NH(33); CH_2(40); $(CH_2)_2$(41); $(CH_2)_3$(51); $C(CH_3)_2$(55) were reacted with chlorosulfonic acid. Under forcing conditions (100–150°C), compounds 1, 19, 33, 40, 41, and 55 afforded the cyclic sulfones (2, 26, 27, 39, 43, 46, and 63). Cyclisation occurred most readily with diphenylethane (41) to give the 7-membered sulfone (46). On the other hand, diphenylsulfide (30) and diphenylpropane (51) failed to give cyclic products, while 2,2-diphenylpropane (55) afforded only a low yield of the cyclic compound (63) among a mixture of uncyclised products (57, 61, 62). With chlorosulfonic acid under milder conditions, the substrates afforded mono-, di, tri- and tetra-sulfonyl chlorides which have been converted into 32 sulfonamides for screening as candidate medicinals and pesticides. The spectroscopic properties of selected compounds are briefly discussed with special reference to the orientation of sulfonation.

Key words: Biphenyl; diphenyl compounds (PhXPh; X = 0, S, NH, $(CH_2)_n$, $C(CH_3)_2$); chlorosulfonation.

INTRODUCTION

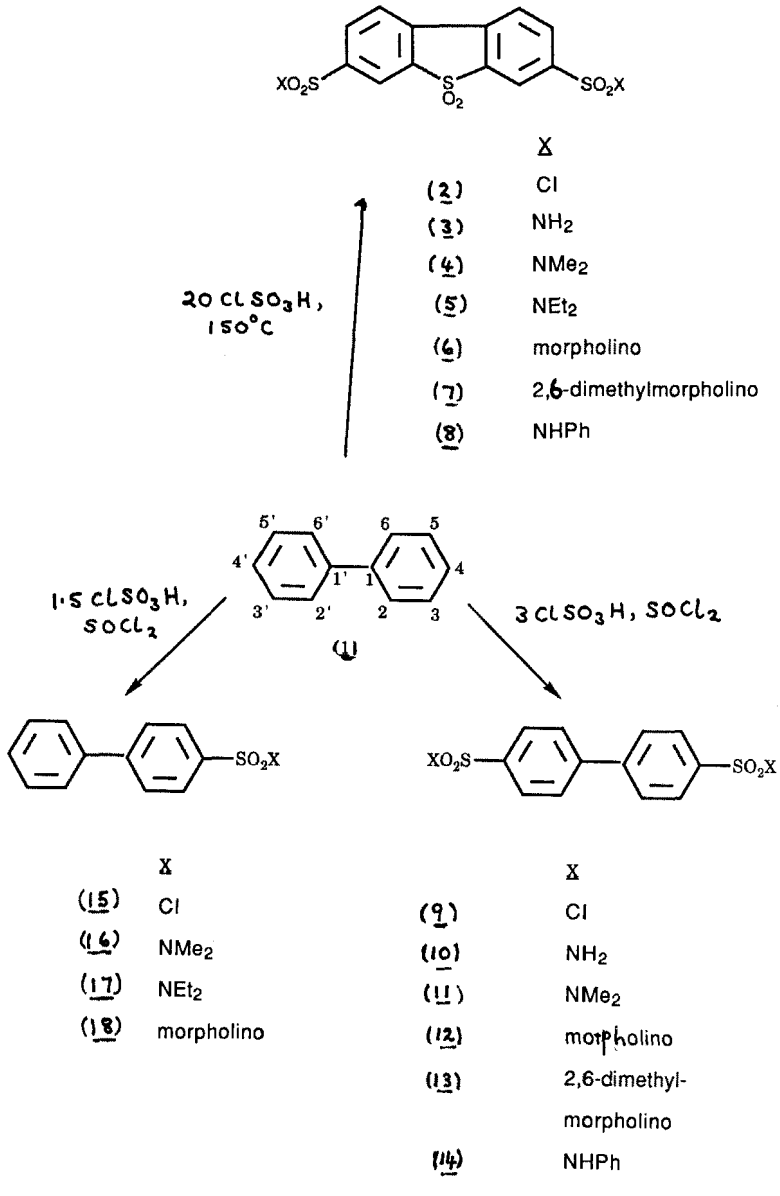
The work described in this paper forms part of our general programme concerned with the chemistry and biological activity of aromatic sulfonyl derivatives.[1–3] In the current study biphenyl and compounds of the general type PhXPh (x = 0, S, NH, CH_2, CH_2CH_2, —$(CH_2)_3$ and $C(CH_3)_2$), have been treated with excess quantities of chlorosulfonic acid. The initially formed sulfonyl chlorides were converted into stable derivatives by nucleophilic substitution, and the compounds identified by microanalytical and spectroscopic data. The reactivity and orientation of sulfonation are interpreted on the basis of the spectroscopic and other data.

DISCUSSION

Pollak *et al.*[4] claimed that the reaction of biphenyl (1) with chlorosulfonic acid (6 molar equivalents) at room temperature gave dibenzothiophene-5,5-dioxa-3,7-disulfonyl chloride (2). In the present work, repeated attempts to obtain (2) using the conditions reported by Pollak *et al.*[4] were unsuccessful. The reaction only gave biphenyl-4,4′-disulfonyl chloride (9) in a low yield (Chart 1). However, the cyclic sulfone (2) was prepared using more forcing conditions: treatment of biphenyl (1) with chlorosulfonic acid (20 molar equivalents) at 150°C resulted in the formation of (2) (72% yield). This product was also obtained (51%) by using less of the reagent (10 molar equivalents) in the presence of aluminum trichloride (1.5 molar equivalents) at 100°C. The latter experiment was successful on a small scale (bi-

CHART 1

Sulfonation of biphenyl (1)



phenyl 0.026 moles) but it was not reproducable on large scale. The cyclic sulfone disulfonyl chloride (2) was condensed with various amines to afford the sulfonamides (3–8) (Chart 1 and Table I). Reaction of biphenyl (1) with chlorosulfonic acid (3 and 1.5 molar equivalents) at room temperature afforded moderate yields 42% and 74% of the mono- and disulfonyl chlorides (15) and (9), respectively. An improved yield of compound (9) 89% was obtained by reacting (1) with a mixture

TABLE I

Sulfonyl derivatives of biphenyl (1) and diphenyl ether (19)

Comp No	Yield (%)	m.p. (°C)	molecular formula	microanalysis found (calc.) % C	H	N	MS (M+)
2	72	236-240	$C_{12}H_6Cl_2O_6S_3$				412
3	54	287-288	$C_{12}H_{10}N_2O_6S_3$	38.2 (38.5)	2.5 (2.7)	7.5 (7.5)	374
4	55	290-291	$C_{16}H_{18}N_2O_6S_3$	44.6 (44.7)	4.2 (4.2)	6.0 (6.5)	430
5	40	184-186	$C_{20}H_{26}N_2O_6S_3$	49.3 (49.4)	5.3 (5.3)	5.9 (5.8)	486
6	70	323	$C_{20}H_{22}N_2O_8S_3$	46.2 (46.7)	4.0 (4.3)	5.1 (5.1)	514
7	67	304	$C_{24}H_{30}N_2O_8S_3$	50.4 (50.2)	5.4 (5.3)	5.2 (4.9)	570
8	79	195-196	$C_{24}H_{18}N_2O_6S_3$	54.5 (54.8)	2.9 (3.4)	5.0 (5.3)	526
9	89	197-199	$C_{12}H_8Cl_2O_4S_2$				350
10	78	285-286	$C_{12}H_{12}N_2O_4S_2$	45.9 (46.2)	3.5 (3.8)	9.0 (9.0)	312
11	70	218-220	$C_{16}H_{20}N_2O_4S_2$	52.2 (52.2)	5.3 (5.4)	7.6 (7.6)	368
12	75	240-241	$C_{20}H_{24}N_2O_6S_2$	53.2 (53.1)	5.6 (5.3)	6.4 (6.2)	452
13	72	236-237	$C_{24}H_{32}N_2O_6S_2$	57.4 (56.7)	6.5 (6.3)	5.6 (5.5)	
14	82	205(s)*	$C_{24}H_{20}N_2O_4S_2$	62.4 (62.1)	4.5 (4.3)	6.1 (6.0)	464
15	42	116-118	$C_{12}H_9ClO_2S$				252
16	42	84-85	$C_{14}H_{15}NO_2S$	63.9 (64.4)	5.4 (5.7)	5.2 (5.4)	261
17	67	130-132	$C_{16}H_{19}NO_2S$	66.2 (66.4)	6.8 (6.6)	5.1 (4.8)	289
18	41	137-138	$C_{18}H_{21}NO_3S$	65.1 (65.3)	5.9 (6.3)	4.5 (4.2)	331
20	82	117(s)*					
21	47	168-169	$C_{18}H_{25}N_3O_7S_3$	44.5 (44.0)	5.2 (5.1)	8.5 (8.6)	491
22	68	145-146	$C_{27}H_{37}N_3O_7S_3$	53.5 (53.0)	6.3 (6.1)	7.4 (6.9)	611
23	86	210-211	$C_{24}H_{31}N_3O_{10}S_3$	46.3 (46.7)	5.0 (5.0)	6.7 (6.8)	617
24	75	191-192	$C_{30}H_{43}N_3O_{10}S_3$	51.4 (51.4)	5.8 (6.1)	6.2 (6.0)	
28	30	220-221	$C_{16}H_{18}N_2O_7S_3$	42.9 (43.0)	3.9 (4.0)	6.1 (6.3)	446
29	60	238-239	$C_{18}H_{23}N_3O_9S_4$	38.7 (39.1)	4.0 (4.2)	7.4 (7.6)	553

* represent melting with sublimation

of chlorosulfonic acid and thionyl chloride. The biphenyl sulfonyl chlorides (9) and (15) were condensed with various amines to yield the monosulfonamides (16–18) and disulfonamides (10–14), respectively (Chart 1 and Table I).

With diphenyl ether (19), sulfonation is known to occur in the positions *para* to the strongly electron-donating oxygen atom.[5–8] Attempts to produce the 4-substituted mono-sulfonyl chloride using chlorosulfonic acid were unsuccessful in agreement with previous work by Cremlyn[9]; the only isolated product was the 4,4′-disulfonyl chloride. To study possible further sulfonation of diphenyl ether (19),

TABLE II

Sulfonyl derivatives of diphenyl-amine (33), methane (40), ethane (41), propane (51), and 2,2-diphenylpropane (55)

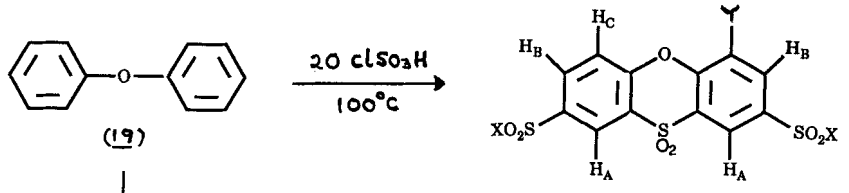
Comp No	Yield (%)	m.p. (°C)	molecular formula	microanalysis found (calc.) % C	H	N	MS (M^+)
34	77	152-153	$C_{12}H_7Cl_4NO_8S_4$	25.8 (25.6)	1.3 (1.1)	2.7 (2.5)	
35	60	283-285	$C_{20}H_{31}N_5O_8S_4$	40.2 (40.8)	5.2 (5.5)	11.7 (11.4)	597
36	75	212-214	$C_{28}H_{47}N_5O_8S_4$	47.4 (47.2)	6.6 (6.7)	9.9 (9.8)	
37	60	162-165	$C_{28}H_{39}N_5O_{12}S_4H_2O$	42.9 (42.9)	5.2 (5.2)	8.9 (8.9)	
38	35	224-226	$C_{36}H_{35}N_5O_{12}S_4$	49.3 (49.0)	6.3 (6.4)	8.0 (7.9)	
39	62	260(s)≠	$C_{20}H_{29}N_5O_{10}S_5$	36.4 (36.2)	4.4 (4.1)	10.6 (10.3)	659
46	90	190(s)≠	$C_{14}H_{10}Cl_2O_6S_3$				440
47	68	270-271	$C_{18}H_{22}N_2O_6S_3$	47.2 (47.5)	4.8 (4.9)	6.1 (5.9)	458
48	78	219-220	$C_{24}H_{30}N_2O_6S_3$	53.5 (53.5)	5.6 (5.6)	5.2 (5.1)	538
49	72	299	$C_{22}H_{26}N_2O_8S_3$	48.7 (48.5)	4.8 (4.7)	5.2 (5.2)	542
50	84	241-242	$C_{26}H_{34}N_2O_8S_3$	52.0 (52.2)	5.8 (5.7)	4.7 (4.7)	598
53	42	210-212°C	$C_{23}H_{36}N_4O_8S_4$	44.3 (44.2)	5.6 (5.8)	8.7 (9.0)	
54	75	194-196	$C_{31}H_{44}N_4O_{12}S_4$	47.3 (47.0)	5.2 (5.5)	6.2 (6.0)	
56	57	216	$C_{19}H_{26}N_2O_4S_2$	55.3 (55.6)	6.6 (6.5)	6.5 (6.8)	410
57	89	120(s)≠	$C_{15}H_{14}Cl_2O_4S_2$				392
58	80	190-192	$C_{15}H_{18}N_2O_4S_2$	50.9 (50.8)	5.3 (5.1)	6.6 (7.9)	354
59	86	110-111	$C_{23}H_{34}N_2O_4S_2$	59.3 (59.2)	7.2 (7.3)	5.6 (6.0)	466
60	79	215-217	$C_{27}H_{38}N_2O_6S_2$	58.7 (58.9)	7.0 (6.9)	4.9 (5.1)	550
62	-	246	$C_{21}H_{31}N_3O_6S_3$	49.0 (48.7)	6.1 (6.0)	7.7 (8.1)	517
63	-	185-186	$C_{19}H_{24}N_2O_6S_3$	48.6 (48.3)	5.2 (5.1)	5.3 (5.9)	472

≠ represent melting with sublimation

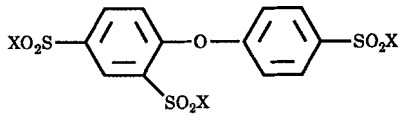
the reaction with a large excess of the reagent (20 molar equivalents) was investigated. After 4 weeks at room temperature, a low yield (15%) of the 2,4,4′-trisulfonyl chloride (20) was isolated. The trisulfonyl chloride (20) was characterized by condensation with amines to afford the sulfonamides (21–24) (Chart 2 and Table I). However, heating the above reaction mixture at 100°C resulted in an improved yield of (20) (82%) as the major product, with small amounts of the tetrasulfonyl chloride (25) and the cyclic sulfone (26). TLC of the mixture showed one major spot (R_F 0.58) and two faint spots (R_F 0.34, 0.27) which corresponded to (20), (25) and (26). Mass spectrometry showed the molecular ions for all three compounds, m/z 562, 464 and 428 (highest mass ion of the molecular ion cluster quoted in each case). The action of chlorosulfonic acid on diphenyl ether (19) under forcing conditions furnished a novel synthetic route to substituted phenoxathiin-10,10-dioxides.

CHART 2

Sulfonation of diphenyl ether (19)



	X	Y
(26)	Cl	H
(27)	Cl	SO_2Cl
(28)	NMe_2	H
(29)	NMe_2	SO_2NMe_2

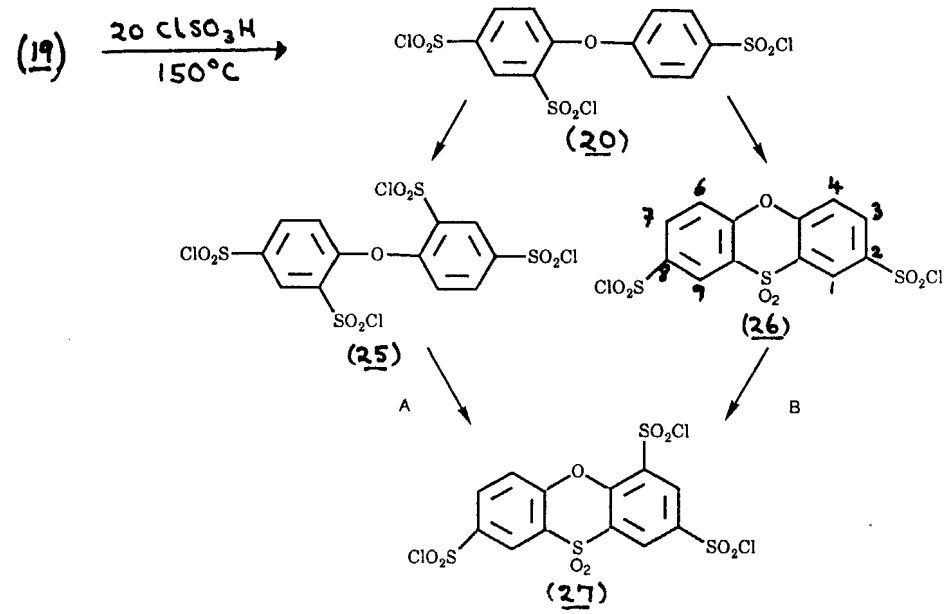


	X
(20)	Cl
(21)	NMe_2
(22)	piperidino
(23)	morpholino
(24)	2,6-dimethylmorpholino

Treatment of (19) with an excess of chlorosulfonic acid (20 molar equivalents) at 150°C gave a mixture of phenoxathiin-10,10-dioxa-2,8-disulfonyl chloride (26) and phenoxathiin-10,10-dioxa-2,4,8-trisulfonyl chloride (27) as the major products with trace amounts of the tetrasulfonyl chloride (25) (Scheme 1).

The reaction was monitored by TLC over a 5 hour interval period of time to investigate the formation of compounds (26) and (27). TLC evidence suggests that the majority of the trisulfonyl chloride (20) was rapidly converted into the symmetrical cyclic sulfone (26), which may possess aromatic character (14 π electron system). A small amount of (20) is probably converted into the bulky tetrasulfonyl chloride (25). The formation of the tri-sulfonyl chloride (27) therefore involves further sulfonation of compound (26), and possibly cyclisation of the tetrasulfonyl chloride (25). Thus, the formation of (27) could take place by routes A and B, with the latter as the predominant pathway (Scheme 1).

The sulfonyl chlorides (26) and (27) were identified by conversion into the corresponding dimethylsulfonamides (28) and (29) which were separated by fractional recrystallisation. In each case, their identities were confirmed by spectroscopic



SCHEME 1

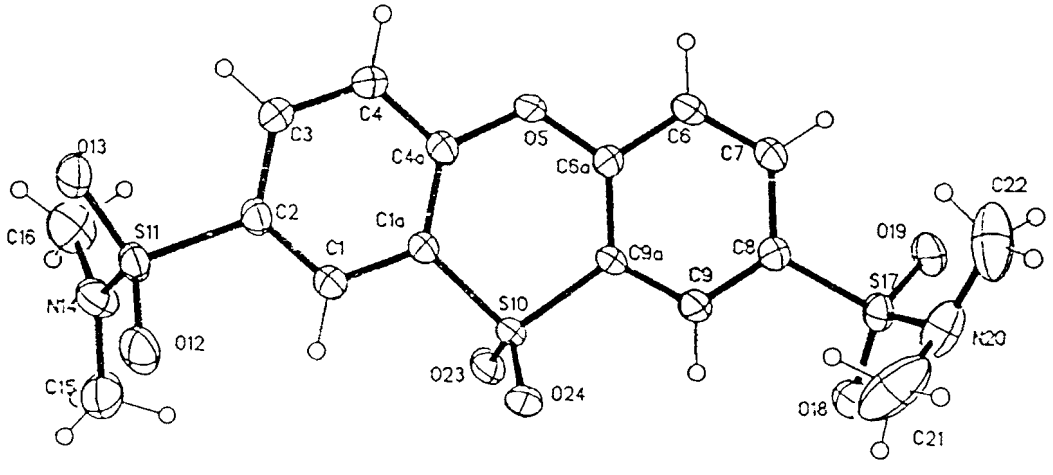


FIGURE 1 The structure of phenoxathiin-10,10-dioxa-2,8-di(*N*,*N*-dimethylsulfonamide) (28).

data. The aromatic region of the ^{1}H NMR spectrum of the bis-dimethylsulfonamide (28) showed total symmetry (ABC pattern) as expected. The aromatic proton H_A (J; 2.5 Hz and H_C (J; 8.5 Hz) appeared as doublets at (δ 8.5, 7.6, respectively, while proton H_B appeared as a doublet of doublets (δ 8.1) due to coupling with protons H_A and H_C. For the tris-dimethylsulfonamide (29), the aromatic proton resonances exhibited combined ABC and AB patterns which were consistent with further substitution. Mass spectrometry showed the highest mass ions at 553 and 446 for compounds (29) and (28), respectively. The structure of compound (28) was confirmed by X-ray crystallographic analysis (Figure 1).

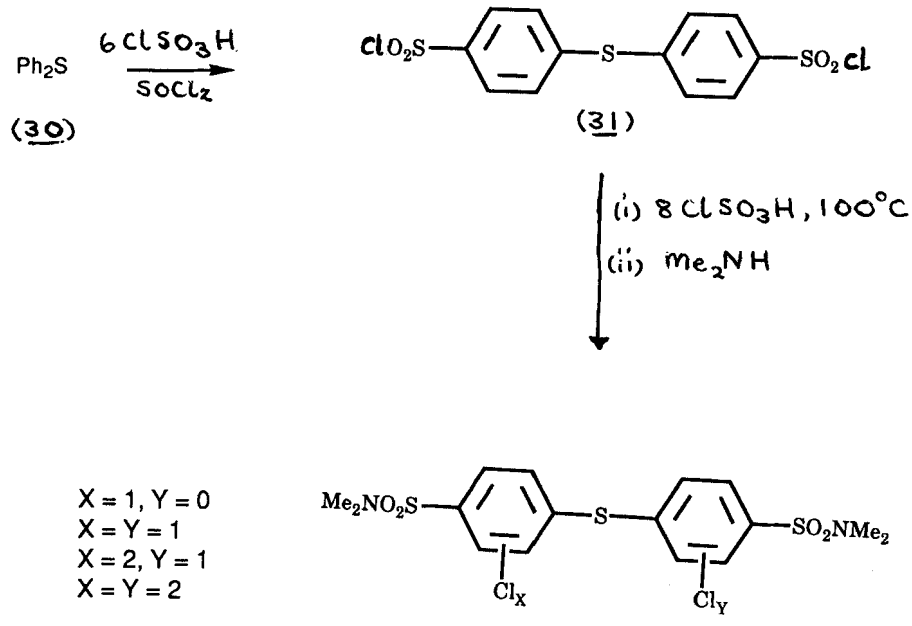
The action of chlorosulfonic acid on diphenyl sulfide (30) has been reported[10,11] to give the disulfonyl chloride (31). Preparation of the 4,4′-disulfonyl chloride (31) was repeated to investigate further chlorosulfonation of the disulfonyl chloride. Reaction of (31) with chlorosulfonic acid (8 molar equivalents) at 100°C produced a very fine white precipitate which was directly treated with dimethylamine to yield a mixture of highly chlorinated compounds (32) (5 spots on TLC) (Scheme 2).

The infrared spectrum of the mixture (32) showed the stretching frequencies for the sulfonyl group at 1150, and 1350 cm^{-1}, and the C—Cl stretch at 710 cm^{-1}. Presence of chlorine was also confirmed by a positive Beilstein test.

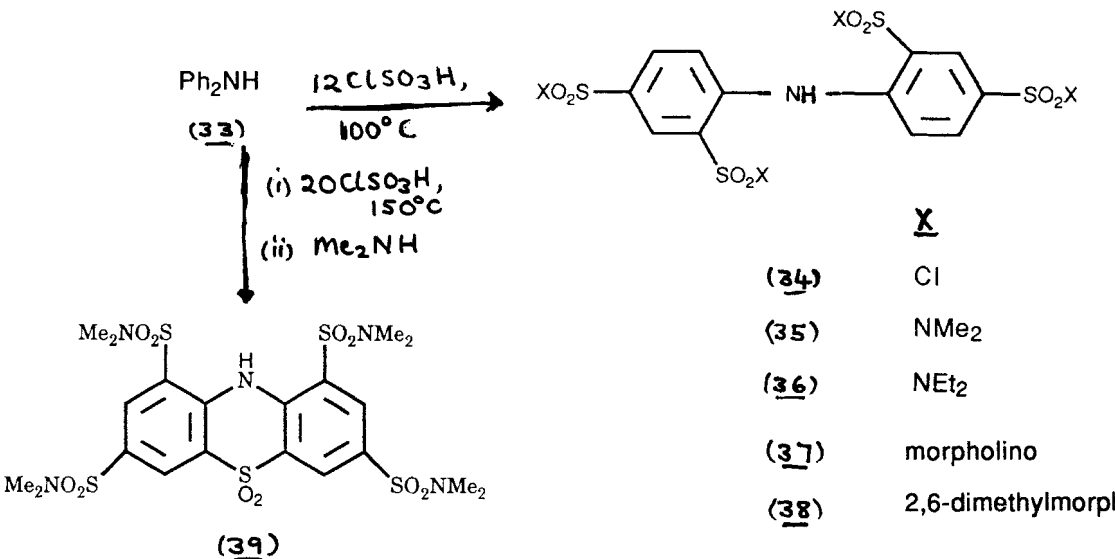
Sulfonation of diphenylamine (33) with chlorosulfonic acid has been reported[12,13] to give the 4,4′-disulfonic acid. However, attempts to produce the 4,4′-disulfonyl chloride by reaction of (33) with chlorosulfonic acid were unsuccessful. For example, treatment of diphenylamine (33) with chlorosulfonic acid (5 molar equivalents) in thionyl chloride gave a complex mixture of polychloro derivatives of phenothiazine (4 spots on TLC). This result was not surprising as 1,3,7,9-tetrachlorophenothiazine has been isolated from the reaction of diphenylamine (33) with thionyl chloride.[14–16] On the other hand, (33) with chlorosulfonic acid (12 molar equivalents) at 100°C for 1 hour afforded a good yield (72%) of the 2,2′,4,4′-tetrasulfonyl chloride[17] (34) (Scheme 3).

The sulfonyl chloride (34) was characterized by conversion to a range of sulfonamides (35–38) (Scheme 3 and Table II).

The above reaction was repeated at 100°C over a longer period of time (3, 5, 10 hours) in an attempt to obtain an alternative route to the chlorosulfonyl phe-



(SCHEME 2)



X	
(34)	Cl
(35)	NMe_2
(36)	NEt_2
(37)	morpholino
(38)	2,6-dimethylmorpholino

SCHEME 3

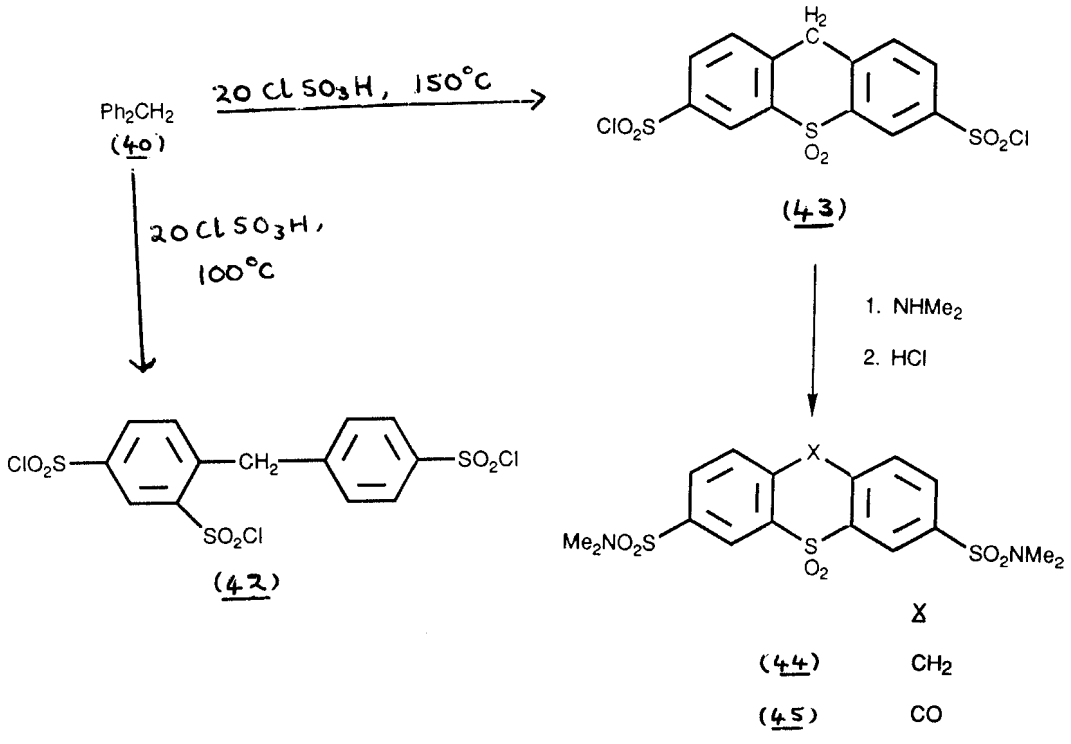
nothiazine-5,5-dioxide, as the introduction of the sulfonyl groups into the 3- and 7-positions of phenothiazine and the 5,5-dioxide had been previously observed.[18,19] This reaction failed to give the cyclised product. However, reaction of diphenylamine (33) with chlorosulfonic acid (20 molar equivalents) at 150°C gave an unworkable gum which was directly treated with dimethylamine to give the *N,N*-dimethylsulfonamide (39) (Scheme 3). The ^{1}H NMR spectrum of compound (39) showed an AB splitting pattern in the aromatic region (δ 8.5–8.7). The aromatic protons resonated as doublets (δ 8.7, δ 8.5) with a coupling constant (J, 2.9 Hz) consistent with *meta* coupling in the benzene ring. Two distinct methyl peaks for the *N,N*-dimethylsulfomoyl groups were observed (δ 2.8, 2.9) with the NH group appearing as a broad singlet (δ 11.7) which diminished after D_2O addition.

The action of chlorosulfonic acid on diphenylmethane (40) and 1,2-diphenylethane (41) has been reported[20,21] to give the 4,4′-disulfonyl chloride. The reaction of these substrates with chlorosulfonic acid were investigated under more forcing conditions. Diphenylmethane (40) with chlorosulfonic acid (20 molar equivalents) at 100°C afforded the trisulfonyl chloride (42) in a moderate yield (67%). Attempts to characterize the sulfonyl chloride (42) by reaction with various amines (dimethylamine, piperidine and morpholine) gave ill-defined products. The mass spectra of the derivatives each showed the molecular ion for the corresponding trisulfonamides. However, the aromatic proton resonances of the derivatives were complex, and definite structures could not be assigned. When diphenylmethane (40) was refluxed with chlorosulfonic acid (20 molar equivalents) for 4 hours a poor yield (45%) of the cyclic sulfone disulfonyl chloride (43) was isolated. The mass spectrum of (43) showed the molecular ion cluster (m/z 426, 428, 430) and the ^{1}H NMR spectrum displayed a clearly-defined ABC splitting pattern in the aromatic region (δ 7.2–8.9). Characterization of the cyclic sulfone disulfonyl chloride (43) with various amines proved difficult. When (43) was reacted with dimethylamine a deep red solution was obtained. Addition of cold water followed by neutralisation with dilute hydrochloric acid afforded a low yield of the dimethylsulfonamides (44) and (45) (Scheme 4).

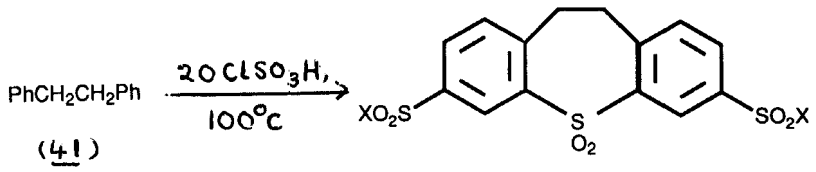
The mass spectrum of the product showed the expected molecular ion (m/z 444) for compound (44), and an additional mass ion (m/z 458) corresponding to (45). TLC of the product showed two spots (R_F 0.23 and 0.11). Further evidence from microanalytical data and the ^{1}H NMR spectrum was in agreement with a mixture of compounds (44) and (45) in a ratio of approximately 1:9. The infrared spectrum of the sulfone-disulfonyl chloride (43) showed no absorption band for the carbonyl group. This evidence suggests that oxidation of the methylene group occurs at the derivative formation stage. This observation finds some support from previous work by Sprinzak[22] who reported the oxidation of fluorene to fluorenone in basic media *via* a carbanion intermediate. Similar oxidations involving aromatic substrates containing active methylenic groups have been claimed.[23–25]

The action of chlorosulfonic acid (20 molar equivalents) on 1,2-diphenylethane (41) at 100°C afforded 10,11-dihydro[b.f]dibenzo-thiepin-5,5-dioxa-3,7-disulfonyl chloride (46) in an excellent yield (90%). The disulfonyl chloride (46) was condensed with various amines, and after repeated recrystallisation afforded the sulfonamides (47–50) (Scheme 5 and Table II).

Comparison of the reaction of chlorosulfonic acid with diphenylmethane (40) and 1,2-diphenylethane (41) indicates that cyclisation of (41) to the seven-mem-



SCHEME 4



(46) Cl
(47) NMe_2
(48) piperidino
(49) morpholino
(50) 2,6-dimethylmorpholino

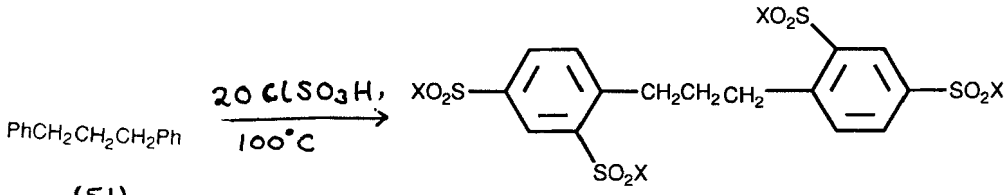
SCHEME 5

bered ring was more readily achieved. The relative ease of formation of the seven-membered ring seems rather surprising as the two phenyl rings in 1,2-diphenylethane (41) are further apart. However, examination of molecular models indicated that the methylene carbon in the six-membered sulfone (43) appeared to be strained due to distortion of the normal sp^3 bond angle. In the analogous seven-membered sulfone (46), the ethylene carbon atoms appeared to be more tetrahedral, and consequently somewhat less sterically strained.

The reaction of 1,3-diphenylpropane (51) with chlorosulfonic acid was investigated in an attempt to obtain the eight-membered cyclic sulfone. However, reaction of (51) with the reagent (20 molar equivalents) at 100°C and 150°C afforded the tetrasulfonyl chloride (52) as the sole isolated product. The tetrasulfonyl chloride (52) was condensed with amines to give the sulfonamides (53–54) (Scheme 6 and Table II).

2,2-Diphenylpropane (55) was reacted with chlorosulfonic acid in an attempt to synthesise the cyclic sulfone analogous to the compound (43). The major reason for this study was to examine the effect of replacing the methylene protons by methyl groups to remove the possibility of oxidation. Treatment of 2,2-diphenylpropane (55) with chlorosulfonic acid (10 molar equivalents) gave a uncrystallisable gum, which was directly condensed with dimethylamine to yield the bis-*N*,*N*-dimethylsulfonamide (56) (Scheme 7). However, later work showed that chlorosulfonic acid (3 molar equivalents) in excess thionyl chloride afforded the 4,4′-disulfonyl chloride (57) in excellent yield (89%). The disulfonyl chloride (57) was characterized as the bis-*N*,*N*-dimethylsulfonamide (56), and was also condensed with other amine to yield the sulfonamides (58–60) (Scheme 7 and Table II).

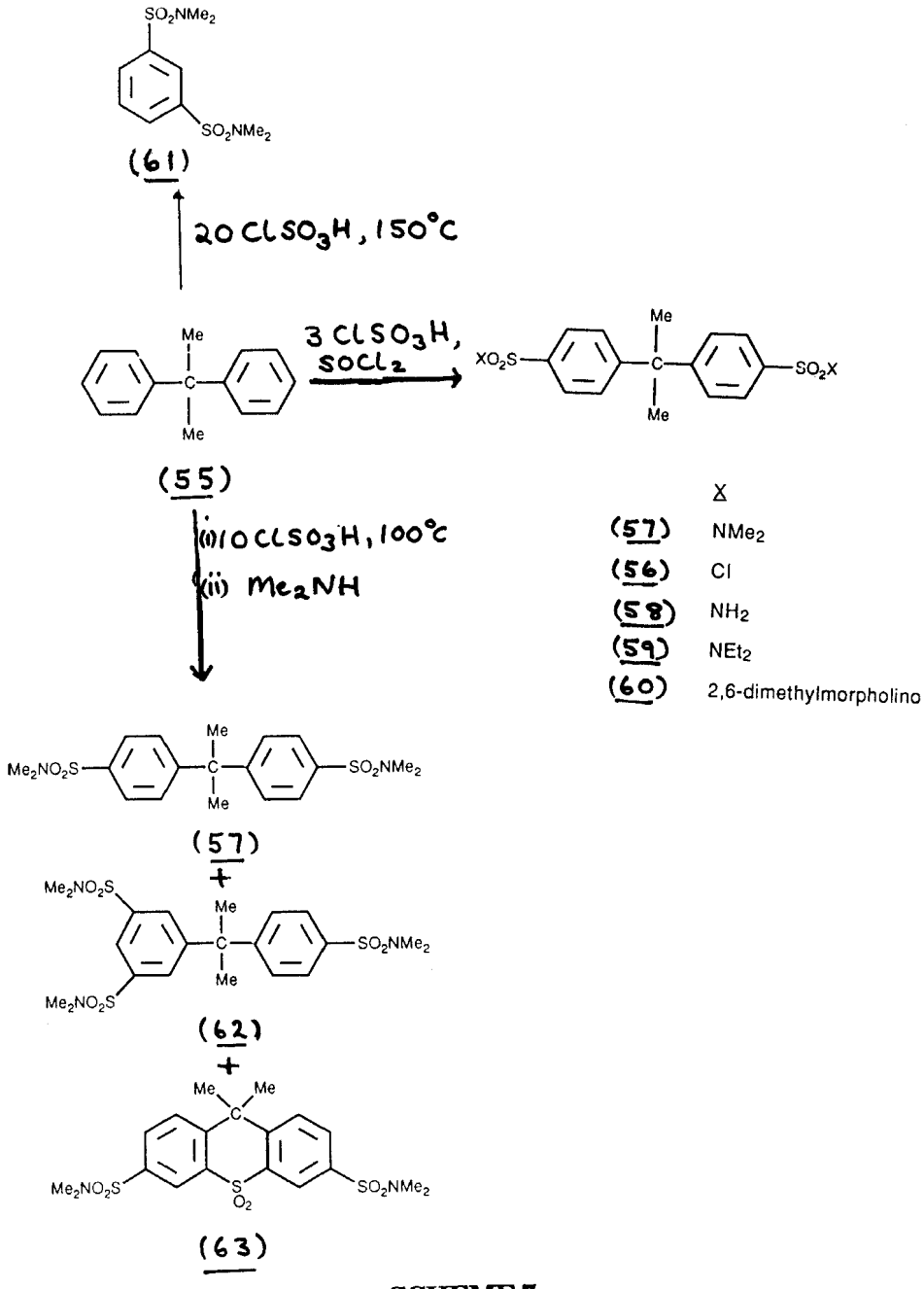
2,2-Diphenylpropane (55) with a large excess of chlorosulfonic acid (20 molar equivalents) at 150°C gave a gum which was extracted with ether. The resultant red solution was reacted with aqueous dimethylamine and unexpectedly gave benzene-1,3-bis(*N*,*N*-dimethylsulfonamide) (61) as the sole isolated product in a low yield. The observed melting point (140–141°C) was in good agreement with the literature value (139–141°C) for this compound.[26] The transformation of 2,2-diphenylpropane (55) to compound (61) may involve dealkylation, since this has been reported[27–29] to occur with *t*-butylbenzene in highly acidic sulfonating media. On



(51)

	X
(52)	Cl
(53)	NMe_2
(54)	morpholino

SCHEME 6



SCHEME 7

the other hand, repetition of the above reaction conditions again resulted in a gum which was this time reacted directly with dimethylamine to give a mixture of three dimethylsulfonamides (56), (62) and (63). The three compounds were separated by column chromatography. For compound (62), the highest mass ion at m/z 517

was observed in the mass spectrum. The ^1H NMR indicated AA'BB' and AB_2 splitting patterns in the aromatic region (δ 7.3–8.0) consistent with structure (62). Two distinct methyl peaks (δ 2.70, 2.75) in a 1:2 ratio were observed for the dimethylamine protons, and a singlet (δ 1.8) for the C-methyl protons. The ^1H NMR spectrum of compound (63) showed a clearly defined ABC splitting pattern for the aromatic protons (δ 8.1–8.4), and a singlet for the dimethylamino protons (δ 2.8) together with a singlet corresponding to the C-methyl protons (δ 1.3).

EXPERIMENTAL

Melting points were determined using a Gallenkamp electric apparatus and are uncorrected. NMR spectra were recorded with a Bruker AC250 spectrometer using tetramethysilane as internal standard and deuterochloroform as solvent unless otherwise stated. Resonances indicated by an asterisk were removed by D_2O treatment. IR spectra were recorded as KBr discs using a Perkin-Elmer 237 spectrophotometer. Mass spectra were determined with a VG Micromass V15 spectrometer operating at 70 ev. TLC was carried out using Camlab silica gel plates sensitized to UV 254 nm using ethyl acetate-cyclohexane (1:2) for the sulfonyl chlorides and petroleum ether-ethylacetate (2:3) as eluants for the derivatives unless otherwise stated.

Dibenzothiophene-5,5-dioxa-3,7-disulfonyl chloride (2)
Biphenyl (10 g, 0.065 mole) was gradually added to chlorosulfonic acid (150.6 g, 1.3 moles) at 0°C. The mixture was heated under reflux for 4 hours, cooled and poured onto crushed ice. The resultant precipitate was filtered off, washed and dried in a vacuum desiccator to give (2) (19.3, g 72%), m.p. 236–240°C (lit.[4], 236°C). IR ν_{max} 1600 (Ar C=C), 1370, 1160 (SO_2) cm^{-1}. MS: 412, 414, 416 (M^+), 377, 379 (M^+-Cl), 313, 315 (M^+-SO_2Cl), 214 (M^+-$(SO_2Cl)_2$.

Biphenyl-4,4'-disulfonyl chloride (9)

Method 1
Biphenyl (20 g, 0.13 mol) was gradually added to chlorosulfonic acid (90 g, 0.78 mole) at 0°C. The mixture was left at room temperature for 72 hours. The solution was poured onto crushed ice and the resultant precipitate filtered off under suction, washed with water and dried to give (9) (35.5 g, 74%), m.p. 196–198°C (lit.[4], 200–202°C).

Method 2
Biphenyl (15.4 g, 0.1 mole) was added to a mixture of chlorosulfonic acid (34.8 g, 0.3 moles) in thionyl chloride (30 ml) at 0°C. The mixture was left at room temperature for one week to give (9) (31.2 g, 89%), m.p. 197–199°C (lit.[4], 200–202°C).

Biphenyl-4-sulfonyl chloride (15)
Biphenyl (15.2 g, 0.1 mol) was added to chlorosulfonic acid (12.8 g, 0.15 mole) in thionyl chloride (20 ml) at 0°C with occasional stirring. The mixture was left at room temperature for a week and poured onto crused ice to give a pale green precipitate which was filtered off, washed with water and dried to give (15) (10.2 g, 43%) m.p. 116–118°C (lit.[4], 115–116°C).

2,4,4'-Oxy-tri[benzenesulfonyl chloride] (20)
Diphenyl ether (10 g, 0.059 moles) was gradually added to chlorosulfonic acid (136 g, 1.18 moles) at room temperature. The mixture was heated at 100°C for 4 hours, allowed to cool to room temperature and poured onto crushed ice producing a white precipitate which was filtered, washed with water and dried to give (20) (22.3 g, 82%), m.p. 117°C (sublimed).

Phenoxathiin-10,10-dioxa-2,8-disulfonyl chloride (25) *and phenoxathiin-10,10-dioxa-2,4,8-trisulfonyl chloride* (26)
Diphenyl ether (10 g, 0.059 moles) was added to chlorosulfonic acid (136 g, 1.18 moles). The mixture heated under reflux for 4 hours and allowed to cool to room temperature. The solution was poured onto crushed ice to give a mixture of (25) and (26) (10.2 g), m.p. 170–175°C. TLC showed 2 spots (R_F 0.27, 0.45). The sulfonyl chlorides (4 g) were reacted with dimethylamine to give a mixture of compounds (27) and (28) which were separated by recrystallization from ethanol.

Compound (27). TLC showed 1 spot, R_F 0.29. IR: ν_{max} 1580 (Ar C=C), 1350, 1150 (SO_2) cm^{-1}. ^1H NMR: δ 8.6–7.6 (m, 6H, ABC, Ar-H), 2.8 (s, 12H, CH_3). MS: 446 (M^+), 402 (M^+-$N(CH_3)_2$), 338 (M^+-$SO_2N(CH_3)_2$), 230 (M^+-$(SO_2N(CH_3)_2)_2$).

Compound (28). TLC showed 1 spot, R_F 0.51. IR: ν_{max} 1600 (Ar C=C), 1360, 1140 (SO_2) cm^{-1}. ^1H NMR: δ 8.7–7.7 (m, 5H, Ar-H), 3.08 (s, 6H, CH_3), 2.85 (s, 6H, CH_3), 2.8 (s, 6H, CH_3). MS: 553 (M^+), 509 (M^+-$N(CH_3)_2$), 445 (M^+-$SO_2N(CH_3)_2$), 338 (M^+-$(SO_2N(CH_3)_2)_2$), 230 (M^+-$(SO_2N(CH_3)_2)_3$).

Diphenylamine-2,2',4,4'-tetrasulfonyl chloride (34)
Diphenylamine (20 g, 0.12 moles) was added portionwise to chlorosulfonic acid (170 g, 1.4 moles) with rapid swirling. The exothermic reaction was allowed to proceed and when addition was complete, the solution was heated on a steam bath for one hour at 80°C, cooled and poured onto ice. The green precipitate was filtered off and dried in a vacuum desiccator over P_2O_5 to give (34). (52 g, 77%), TLC showed 1 spot, R_F 0.85.

Compound (39). Diphenylamine (5 g, 0.03 mole) was gradually added to chlorosulfonic acid (68.6 g, 0.6 mole) at 0°C. The solution was refluxed for 2 hours and allowed to cool to room temperature. The solution was poured onto crushed ice and the resultant gummy precipitate was reacted with excess dimethylamine. The crude product was recrystallised from ethanol to give the *N,N*-dimethylsulfonamide (39). TLC showed 1 spot, R_F 0.30. IR: ν_{max} 3250 (NH), 1600 (Ar C=C), 1360, 1150 (SO_2) cm^{-1}. ^1H NMR: δ 11.7 (s, 1H, *NH), 8.7–8.5 (2d, 4H, AB, Ar-H) 2.9 (s, 12H, CH_3), 2.8 (s, 12H, CH_3). MS: 659 (M^+), 551 (M^+-$SO_2N(CH_3)_2$), 444 (M^+-$(SO_2N(CH_3)_2)_2$), 336 (M^+-$(SO_2N(CH_3)_2)_3$), 228 (M^+-$(SO_2)N(CH_3)_2)_4$).

10-H-Dibenzo[b,e]thiin-5,5-dioxa-3,7-disulfonyl chloride (43)
Diphenylmethane (5 g, 0.029 mole) was gradually added to chlorosulfonic acid (68.2 g, 0.58 mole) at 0°C. The mixture was heated at 150°C for 4 hours under a nitrogen atmosphere. The dark black solution was poured into crushed ice producing a grey precipitate which was filtered off, washed with water and dried to give (43) (5.7 g, 45%). TLC showed 1 spot, R_F 0.57, IR: ν_{max} 1590 (Ar C=C), 1340, 1160 (SO_2) cm^{-1}. ^1H NMR: δ 8.9–7.2 (m, 6H, ABC, Ar-H), 4.6 (s, 2H, CH_2). MS: 426 (M^+), 327 (M^+-SO_2Cl).

10,11-Dihydro[b,f]dibenzothiepin-5,5-dioxa-3,7-disulfonyl chloride (46)
1,2-Diphenylethane (5 g, 0.027 mole) was added portionwise to chlorosulfonic acid (63.7 g, 0.55 mole) with cooling and rapid stirring. The solution was heated at 100°C for 4 hours. The cooled solution was poured onto crushed ice and the precipitate filtered off under suction, washed with water and dried to yield (46) (10.9 g, 90%), m.p. at 190°C (sublimed). TLC showed 1 spot, R_F 0.24.

1,3-Diphenylpropane-2,2',4,4'-tetrasulfonyl chloride (52)
1,3-Diphenylpropane (5 g, 0.026 mole) was gradually added to chlorosulfonic acid (59.2 g, 0.51 mole) at 0°C. The mixture was heated at 100°C for 4 hours. The cooled solution was poured into crushed ice to yield a gummy white precipitate which was directly treated with amines.

The dimethylsulfonamide (53). TLC showed 1 spot, R_F 0.32, IR: ν_{max} 1610 (Ar C=C), 1350, 1140 (SO_2) cm^{-1}. MS: no M^+ ion observed at m/z 624; the highest ion at m/z 516 (M^+-$SO_2N(CH_3)_2$).

The morpholidate (54). TLC showed 1 spot, R_F 0.56, IR: ν_{max} 1600 (Ar C=C), 1360, 1140 (SO_2) cm^{-1}. MS: no M^+ ion at m/z 792, the highest ion at m/z 643 (M^+-$SO_2NC_4H_8O$).

2,2-Diphenylpropane-4,4'-disulfonyl chloride (57)
2,2-Diphenylpropane (5 g, 0.026 mole) was added to chlorosulfonic acid (9.0 g, 0.078 mole) dissolved in thionyl chloride (20 ml) at 0°C. The mixture was left at room temperature for 7 days and poured onto crushed ice. The resultant precipitate was filtered off under suction, washed with water and dried to give (57) (8.9 g, 89%). TLC showed 1 spot, R_F 0.50, IR: ν_{max} 1600 (Ar C=C), 1350, 1160 (SO_2) cm^{-1}. ^1H NMR: δ 7.9–7.3 (q, 8H, AA'BB', Ar-H), 1.8 (s, 6H, CH_3). MS: 392, 394, 396 (M^+), 357, 359 (M^+-Cl), 293, 295 (M^+-SO_2Cl).

The dimethylsulfonamide derivatives (56, 61 and 62)
2,2-Diphenylpropane (5 g, 0.026 mole) was gradually added to chlorosulfonic acid (60.7 g, 0.52 moles) at room temperature. The solution was refluxed for 4 hours and allowed to stand overnight at room temperature and poured onto crushed ice. The resultant gummy precipitate was reacted with dimethylamine. The crude product was recrystallised from methanol to give a mixture of (56), (62) and (63). The three compounds were separated by column chromatography on silica gel using cyclohexane-ethylacetate (3:2) as the eluant.

Compound (56). TLC showed 1 spot, R_F 0.77, IR: ν_{max} 1620 (Ar C=C), 1350, 1140 (SO_2) cm^{-1}. ^1H NMR: δ 8.0–7.4 (q, 8H, Ar-H, AA'BB'), 3.8 (s, 12H, NCH_3), 1.9 (s, 6H, CH_3). MS: 410 (M^+), 395 (M^+-CH_3), 302 (M^+-$SO_2N(CH_3)_2$).

Compound (62). TLC showed 1 spot, R_F 0.53, IR: ν_{max} 1590 (Ar C=C), 1360, 1150 (SO_2) cm^{-1}. ^1H NMR: δ 8.1–7.3 (m, 7H, Ar-H), 2.75–2.70 (2xs, 18H, NCH_3), 1.8 (s, 6H, CH_3). MS: 517 (M^+), 410 (M^+-$SO_2N(CH_3)_2$), 366 (M^+-$SO_2(N(CH_3)_2)_2$), 301 (M^+-$(SO_2N(CH_3)_2)_2$).

Compound (63). TLC showed 1 spot, R_F 0.20, IR: ν_{max} 1160 (Ar C=C), 1360, 1150 (SO_2) cm^{-1}. ^1H NMR (Acetone-D_6): δ 8.5–8.1 (m, 6H, ABC, Ar-H), 2.7 (s, 12H, NCH_3), 1.9 (s, 6H, CH_3). MS: 472 (M^+), 364 (M^+-$SO_2N(CH_3)_2$), 320 (M^+-$SO_2(N(CH_3)_2)_3$).

General procedure for the synthesis of sulfonamides
The amine (2 molar equivalents) was gradually added to the sulfonyl chloride (2 g) in ethanol or methanol (20 ml) at 0°C. The mixture was stirred for 24 hours and poured onto an ice-water mixture. The resultant precipitate was filtered off, washed (water) and dried. The crude sulfonamide was recrystallised from ethanol or methanol unless otherwise stated.

Compound (3). TLC showed 1 spot, R_F 0.11, IR: ν_{max} 3330 (NH_2), 1600 (Ar C=C), 1350, 1160 (SO_2) cm^{-1}. ^1H NMR (DMSO-d_6): δ 8.6–8.1 (m, 6H, ABC, Ar-H), 7.5 (s, 4H, NH_2).

Compound (4). TLC showed 1 spot, R_F 0.72, IR: ν_{max} 1610 (Ar C=C), 1350, 1170 (SO_2) cm^{-1}. ^1H NMR (DMSO-d_6): δ 8.7–8.2 (m, 6H, ABC, ArH), 2.8 (s, 12H, CH_3).

Compound (6). TLC showed 1 spot, R_F 0.42, IR: ν_{max} 1580 (Ar C=C), 1340, 1160 (SO_2) cm^{-1}. ^1H NMR: (DMSO-d_6): δ 8.8–8.1 (m, 6H, ABC, Ar-H), 3.9–2.8 (m, 16H, Alkyl CH).

Compound (10). TLC showed 1 spot, R_F 0.21, IR: ν_{max} 3300, 3250 (NH_2), 1600 (Ar C=C), 1360, 1140 (SO_2) cm^{-1}. ^1H NMR: δ 8.1–7.2 (m, 8H, AA'BB', Ar-H), 6.5* (s, 4H, NH_2). MS: 312 (M^+), 232 (M^+-SO_2NH_2), 152 (M^+-$(SO_2NH_2)_2$).

Compound (11). TLC showed 1 spot, R_F 0.82, IR: ν_{max} 1600 (Ar C=C), 1350, 1140 (SO_2) cm^{-1}. ^1H NMR: (DMSO-d_6) δ 8.3–7.5 (m, 8H, AA'BB', ArH), 2.7 (s, 12H, CH_3). MS: 368 (M^+), 324 (M^+-$N(CH_3)_2$).

Compound (12). TLC showed 1 spot, R_F 0.63, IR: ν_{max} 1610 (Ar C=C), 1360, 1140 (SO_2) cm^{-1}. ^1H NMR (DMSO-d_6): δ 8.4–7.8 (m, 8H, AA'BB', Ar-H), 3.8–2.5 (m, 16H, Alkyl CH).

Compound (16). TLC showed 1 spot, R_F 0.62, IR: ν_{max} 1595 (Ar C=C), 1350, 1160 (SO_2) cm^{-1}. ^1H NMR: δ 8.3–7.6 (m, 9H, Ar-H), 2.9 (s, 6H, CH_3). MS: 261 (M^+), 217 (M^+-$N(CH_3)_2$), 153 (M^+-$SO_2N(CH_3)_2$).

Compound (17). TLC showed 1 spot, R_F 0.32, ^1H NMR: δ 8.1–7.1 (m, 9H, ArH), 3.3–3.1 (q, 4H, CH_2), 1.2–1.0 (t, 6H, CH_3). MS: 289 (M^+), 215 (M^+-$N(CH_2CH_3)_2$), 153 (M^+-$SO_2N(CH_2CH_3)_2$).

Compound (21). TLC showed 1 spot, R_F 0.36, IR: ν_{max} 1590 (Ar C=C), 1340, 1150 (SO_2) cm^{-1}. ^1H NMR: δ 8.5–7.1 (m, 7H, Ar-H), 3.0–2.7 (t, 18H, CH_3).

Compound (22). TLC showed 1 spot, R_F 0.86, ^1H NMR: δ 8.4–7.0 (m, 7H, Ar-H), 3.3–1.5 (m, 30H, Alkyl CH). MS: 611 (M^+), 463 (M^+-$SO_2NC_5H_{10}$), 315 (M^+-$(SO_2NC_5H_{10})_2$).

Compound (23). TLC showed 1 spot, R_F 0.11, IR: ν_{max} 1600 (Ar C=C), 1350, 1160 (SO_2) cm^{-1}. ^1H NMR: δ 8.4–7.0 (m, 7H, Ar-H), 3.8–2.9 (m, 24H, Alkyl CH).

Compound (35). TLC showed 1 spot, R_F 0.40, IR: ν_{max} 3200 (NH), 3050–2970 (C—H), 1600 (Ar C=C), 1360, 1160 (SO_2) cm^{-1}. ^1H NMR δ 9.6 (s, 1H, NH*), 8.3–7.5 (m, 6H, ABC, ArH), 2.8 (s, 12H, CH_3), 2.7 (s, 12H, CH_3). MS: 597 (M^+), 490 (M^+-$SO_2N(CH_3)_2$), 382 (M^+-$(SO_2N(CH_3)_2)_2$).

Compound (37). TLC showed 1 spot, R_F 0.30, IR: ν_{max} 3200 (NH), 1600 (Ar C=C), 1350, 1150 (SO_2) cm^{-1}. ^1H NMR: δ 9.5 (s, 1H, NH*), 8.3–7.5 (m, 6H, ABC, Ar-H), 3.9–3.6 (m, 16H, CH_2O), 3.3–3.0 (m, 16H, CH_2N).

Compound (47). TLC showed 1 spot, R_F 0.11, IR: ν_{max} 1610 (Ar C=C), 1350, 1160 (SO_2) cm^{-1}. ^1H NMR: δ 8.5–7.5 (m, 6H, ABC, Ar-H), 3.7 (s, 4H, CH_2), 2.8 (s, 12H, NCH_3). MS: 458 (M^+), 443 (M^+-CH_3), 414 (M^+-$N(CH_3)_2$), 350 (M^+-$SO_2N(CH_3)_2$), 242 (M^+-$(SO_2N(CH_3)_2)_2$).

Compound (48). Recrystallised from acetonitrile, TLC showed 1 spot, R_F 0.62, IR: ν_{max} 1600 (Ar C=C), 1340, 1150 (SO_2) cm^{-1}. ^1H NMR: δ 8.5–7.5 (m, 6H, ABC, Ar-H), 3.7 (s, 4H, CH_2), 3.0–1.7 (m, 20H, Alkyl CH). MS: 538 (M^+), 454 (M^+-NC_5H_{10}), 390 (M^+-$SO_2NC_5H_{10}$).

Compound (49). Recrystallised from acetone, TLC showed 1 spot, R_F 0.38, IR: ν_{max} 1610 (Ar C=C), 1350, 1150 (SO_2) cm^{-1}. ^1H NMR (DMSO-d_6): δ 8.3–7.8 (m, 6H, ABC, Ar-H), 3.7 (s, 4H, CH_2), 3.6–2.6 (m, 16H, Alkyl CH). MS: 542 (M^+), 498 (M^+-C_2H_4O), 456 (M^+-NC_4H_8O), 242 (M^+-$SO_2NC_4H_8O)_2$).

Compound (50). TLC showed 1 spot, R_F 0.22, IR: ν_{max} 1600 (Ar C=C), 1350, 1140 (SO_2) cm^{-1}. ^1H NMR (DMSO-d_6): δ 8.5–7.5 (m, 6H, ABC, Ar-H), 3.8 (s, 4H, CH_2), 3.7–1.3 (m, 24H, Alkyl CH).

Compound (56). TLC showed 1 spot, R_F 0.77, IR: ν_{max} 1620 (Ar C=C), 1350, 1140 (SO_2) cm^{-1}. ^1H NMR: δ 8.0–7.4 (q, 8H, AA'BB', Ar-H), 3.8 (s, 12H, NCH_3), 1.9 (s, 6H, CH_3). MS: 410 (M^+), 395 (M^+-CH_3), 302 (M^+-$SO_2N(CH_3)_2$), 287 (M^+-$SO_2N(CH_3)_3$).

Compound (59). Recrystallised from acetonitrile, TLC showed 1 spot, R_F 0.93, ^1H NMR (Acetone-D6): δ 7.8–7.5 (q, 8H, AA'BB', Ar-H), 3.3–3.1 (q, 8H, CH_2), 1.8 (s, 6H, CH_3), 1.1–1.0 (t, 12H, $CH_2\underline{CH_3}$).

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