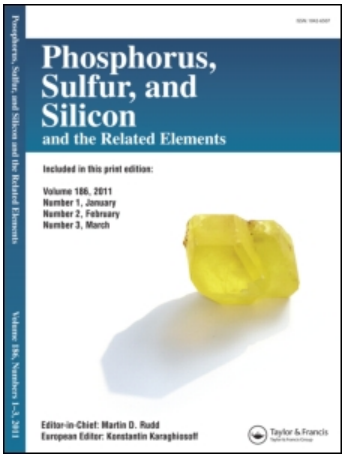

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CHLOROSULFONATION OF SOME COMPOUNDS CONTAINING TWO PHENYL RINGS

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CHLOROSULFONATION OF SOME COMPOUNDS CONTAINING TWO PHENYL RINGS

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Diphenylmethane (**1**) and dibenzyl (**17**) reacted with chlorosulphonic acid to give the corresponding *p,p'*-disulphonyl chlorides (**2, 18**). However, attempted chlorosulfonations of α-chloro-, αα'-dichlorodiphenylmethane, stilbene and 1,4-diphenylbutadiene were unsuccessful.

Diphenylacetic acid reacted with chlorosulfonic acid to give a mixture of 4,4'-dichlorosulfonylbenzophenone (**40**) and α-chlorodiphenylmethane-4,4'-disulfonyl chloride (**39**). Benzilic acid (**41**) afforded 9-chlorofluorene-2,7-disulfonyl chloride (**42**), which with amines gave 3 different products according to the reaction conditions. Fluorene (**53**) and the 9-carboxylic acid (**43**) have been treated with chlorosulfonic acid. The various sulfonyl chlorides were converted into 43 derivatives for biocidal evaluation. Mechanistic interpretations for the reactions are included.

Key words: Chlorosulfonation; diphenylmethane-4,4'-disulfonyl chloride; 4,4'-dichlorosulfonylbenzophenone; 9-chlorofluorene-2,7-disulfonyl chloride; 1,2-diphenylethane-4,4'-disulfonyl chloride.

INTRODUCTION

The work reported here forms part of our general programme concerned with the chemistry and biocidal properties of arylsulfonyl derivatives.[1–3] In the current study, a number of compounds containing two phenyl rings, of the general type PhXPh, have been treated with excess quantities of chlorosulfonic acid. Several of these reactions have not previously reported and the results obtained are of particular interest from a synthetic standpoint. The sulfonyl chloride intermediates have been characterized with the aid of spectroscopic methods and by reaction with various nucleophilic reagents, e.g. amines, azide ion and hydrazine, to provide novel sulfonyl derivatives for evaluation as potential pest control agents.

DISCUSSION

The chlorosulfonation of diphenylmethane (**1**) was reported by Bordwell and Crosby.[4] Repetition of their procedure gave a gum which proved difficult to extract into an organic solvent and the yield of the disulfonyl chloride (**2**) was only 45%. Increasing the amount of reagent from 4.2 to 8 equivalents decreased the yield of **2**. The optimum yield (70%) was realised by using 4.5 equivalents of chlorosulfonic acid for 48 hours and direct filtration of the crude product from the reaction mixture *before* addition to ice. This procedure avoided gum formation

and gave a higher yield of pure product. The disulfonyl chloride (**2**), by condensation with ammonia and amines, gave the compounds (**3–11**) (Chart 1 and Table I). Reaction with hydrazine hydrate afforded the hydrazide (**12**), which was characterized as the hydrazones (**15**, **a–d**). Treatment with sodium azide gave the azide (**13**), characterized as the triethoxy phosphinimine (**14**) by reaction with triethyl phosphite. Condensation of the hydrazide (**12**) with pentane-2,4-dione afforded the 3,5-dimethylpyrazole (**16**).

As benzophenone on direct chlorosulfonation yields the corresponding 3,3′-disulfonyl chloride,[5] it was of considerable interest to attempt the oxidation of the methylene group in some of the disulfonamides (**3**, **4**, **7**, **8**). Treatment of the disulfonamide (**3**) with chromic anhydride-glacial acetic acid, as previously reported,[4] gave the 4,4′-disulfonamide of benzophenone (**3a**). The conversion was confirmed by the IR spectrum which showed the presence of the carbonyl group (1650 cm^{-1}) and the ^1H NMR spectrum which indicated the absence of the methylene protons (no signal at δ 4.2). This approach therefore appeared to present a potentially valuable route to 4,4′-disulfonamides of benzophenone. Unfortunately, repeated attempts to extend the oxidation to the sulfonamides (**4**), (**7**), and (**8**) did not yield pure products. Under mild conditions, TLC, spectroscopic and analytical data indicated formation of the desired benzophenone derivative contaminated with the starting material. Under more

CHART 1

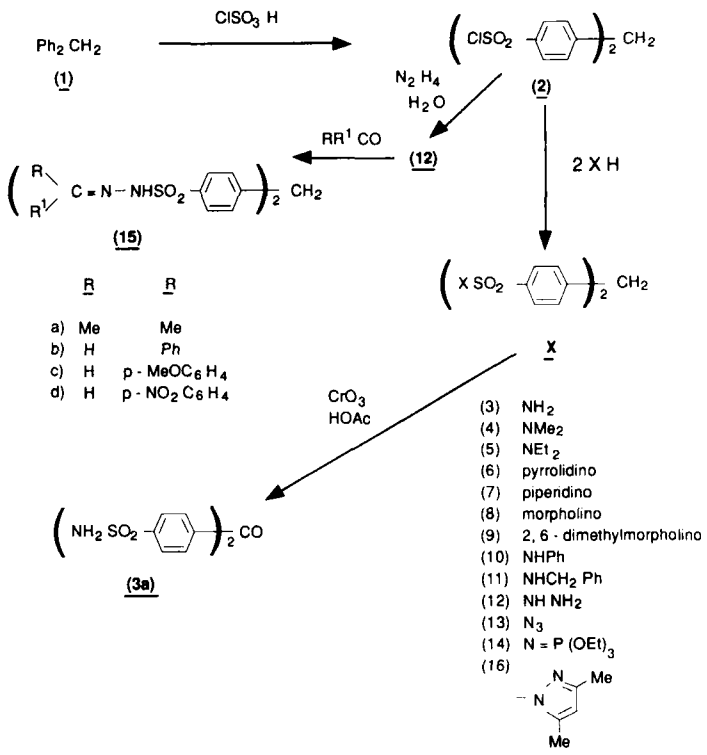


CHART 1

TABLE I

Physical data for diphenylmethanesulfonyl derivatives

Compd. no.	Yield (%)	m.p. (°C)	Molecular formula	Microanalysis found (Calc.) % C	H	N	MS (M^+)
3	37	180 (lit[4] 182–3)	$C_{13}H_{14}N_2O_4S_2$	47.6 (47.9)	4.2 (4.3)	8.3 (8.6)	326
4	64	168–170	$C_{17}H_{22}N_2O_4S_2$	53.5 (53.4)	5.8 (5.8)	7.1 (7.3)	382
5	65	148–150	$C_{21}H_{30}N_2O_4S_2$	57.7 (57.5)	7.0 (6.8)	6.3 (6.4)	438
6	15	165	$C_{21}H_{26}N_2O_4S_2$	58.3 (58.1)	6.1 (6.0)	6.2 (6.4)	434
7	50	163–165	$C_{23}H_{30}N_2O_4S_2$	60.0 (59.7)	6.5 (6.5)	5.8 (6.1)	462
8	60	193–195	$C_{21}H_{26}N_2O_6S_2$	53.8 (54.1)	5.4 (5.6)	5.9 (6.0)	466
9	55	174–175	$C_{25}H_{34}N_2O_6S_2$	57.8 (57.5)	6.5 (6.5)	5.2 (5.4)	522
10	22	181	$C_{26}H_{22}N_2O_4S_2$	63.5 (63.7)	4.7 (4.5)	5.9 (5.7)	490
11	36	160	$C_{27}H_{26}N_2O_4S_2$	63.7 (64.0)	4.8 (5.1)	5.6 (5.5)	506
12	50	160–162 (lit.[23] 164)	$C_{13}H_{16}N_4O_4S_2$	43.4 (43.8)	4.8 (4.5)	15.4 (15.7)	
13	48	128–129	$C_{13}H_{10}N_6O_4S_2$	41.9 (41.7)	2.6 (2.6)	22.6 (22.5)	378
14	10	72–73	$C_{25}H_{40}N_2O_{10}P_2S_2$	45.6 (45.9)	5.9 (6.1)	4.1 (4.3)	654
15a	40	176–178	$C_{19}H_{24}N_4O_4S_2$	52.0 (52.3)	5.5 (5.5)	12.5 (12.8)	—
15b	43	148–149	$C_{27}H_{24}N_4O_4S_2 \cdot \frac{1}{2}H_2O$	60.5 (60.9)	4.6 (4.5)	10.3 (10.5)	—
15c	86	112	$C_{29}H_{28}N_4O_6S_2$	58.6 (58.8)	4.9 (4.7)	9.3 (9.5)	—
15d	59	193–194	$C_{27}H_{22}N_6O_8S_2$	52.4 (52.1)	3.6 (3.5)	13.4 (13.5)	—
16	18	178–180	$C_{23}H_{24}N_4O_4S_2$	57.3 (57.0)	4.8 (5.0)	11.4 (11.6)	484

forcing conditions (6 hours, reflux), degradation of the sulfonamide appeared to occur, possibly due to fission of the weaker C—N bond in preference to the C—H bond.

The action of chlorosulfonic acid on dibenzyl (**17**) has been reported[6] to give the disulfonyl chloride. For the purposes of comparison of reactivity, we used the modified procedure described for diphenylmethane. Dibenzyl (**17**) reacted more easily with the reagent (4.5 equivalents) at room temperature (24 hours) to give the 4,4′-disulfonyl chloride (**18**) (80%), which was characterized as the derivatives (**19–28**) (Chart 2 and Table II). The hydrazide (**28**) was reacted with carbonyl compounds to give the hydrazones (**30**, **a–e**). The 3,5-dimethylpyrazole (**31**) was obtained by reaction with pentane-2,4-dione and the azide (**29**) by use of sodium azide.

The electron impact mass spectra of the majority of the derivatives from the chlorosulfonation of diphenylmethane (**1**) and dibenzyl (**17**) (Tables I and II)

CHART 2

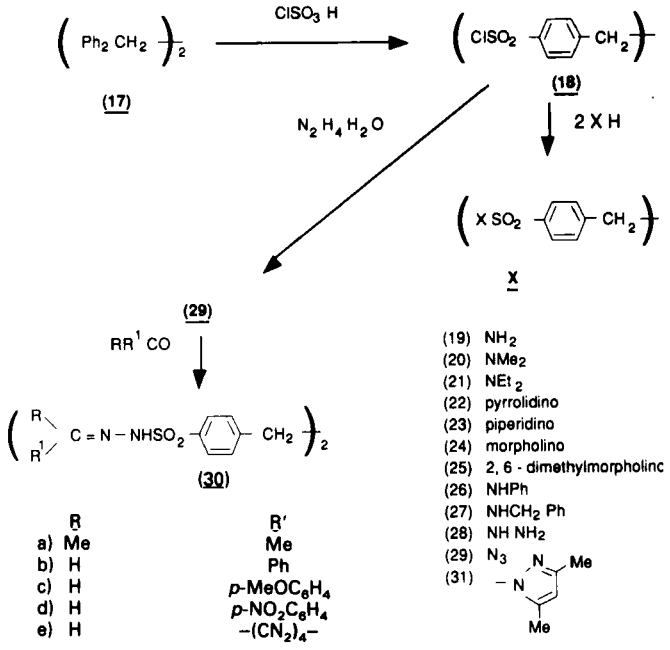


CHART 2

showed the molecular ions (M^+), apart from, rather unexpectedly, compound **20**, together with the hydrazide and hydrazones which suffered extensive fragmentation, in agreement with previous observations.[7,8] The orientation of chlorosulfonation in diphenylmethane (**1**) and dibenzyl (**17**) was determined from the ^{1}H NMR spectra of the derivatives, e.g. the diethylamides (**5**, **21**), which showed the respective aromatic regions (δ 7.9–7.2) as well-defined AA'BB' patterns. Substitution thus takes place in the *para*-positions (4,4'-) in each case, as would be expected on stereoelectronic grounds.

The influence of acyclic unsaturation was investigated by treating stilbene and 1,4-diphenylbutadiene with chlorosulfonic acid under a variety of conditions. Stilbene afforded a mixture of 3 products (TLC) which could not be converted into a pure dimethylamide derivative,[9] while 1,4-diphenylbutadiene only afforded water-soluble products. These results are probably not surprising, as both substrates may undergo acid-catalysed polymerization.

It was of further interest to study the influence of α-substituents in diphenylmethane upon the course of the reaction with chlorosulfonic acid.

The action of the reagent on diphenylmethanol (**32**) and diphenylmethyl chloride (**33**) gave ill-defined products before and after the reaction with dimethylamine. Initially the mass spectra showed differences, but after 5 minutes each gave an ion, M^+ 382, corresponding to the bis-dimethyl-sulfonamide of (**33**), but higher mass ions were also present.

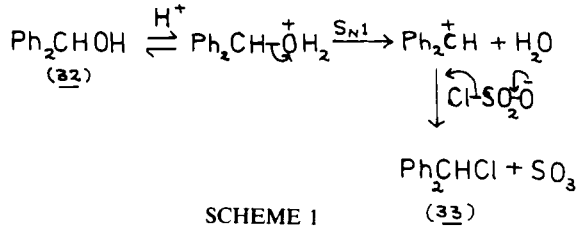
The reaction of diphenylmethanol (**32**) with concentrated sulfonic acid is known[10,11] to give a mixture of products. The similarity in the behaviour of the

TABLE II

Physical data for dibenzylsulfonyl derivatives

Compd. no.	Yield (%)	m.p. (°C)	Molecular formula	Microanalysis found (Calc.) % C	H	N	MS (M^+)
19	20	263–265	$C_{14}H_{16}N_2O_4S_2 \cdot \frac{1}{2}H_2O$	48.0 (48.1)	4.5 (4.8)	7.1 (7.4)	340
20	70	188–190	$C_{18}H_{24}N_2O_4S_2$	54.7 (54.5)	6.0 (6.1)	7.2 (7.1)	
21	69	114	$C_{22}H_{32}N_2O_4S_2$	58.4 (58.4)	7.2 (7.1)	6.1 (6.2)	452
22	73	214–216	$C_{22}H_{28}N_2O_4S_2$	59.0 (58.9)	6.3 (6.3)	5.9 (6.3)	448
23	80	224–225	$C_{24}H_{32}N_2O_4S_2$	60.3 (60.5)	6.8 (6.7)	5.6 (5.9)	476
24	45	230	$C_{22}H_{28}N_2O_6S_2$	54.7 (55.0)	5.9 (5.8)	5.6 (5.8)	480
25	40	187–189	$C_{26}H_{36}N_2O_6S_2$	58.0 (58.2)	6.9 (6.7)	5.0 (5.2)	536
26	15	192–194	$C_{26}H_{24}N_2O_4S_2$	63.4 (63.4)	4.9 (4.9)	5.5 (5.7)	492
27	76	192–193	$C_{28}H_{28}N_2O_4S_2$	63.8 (64.0)	5.2 (5.4)	5.5 (5.4)	520
28	34	185–187	$C_{14}H_{18}N_4O_4S_2$	45.1 (45.4)	5.2 (4.9)	14.8 (15.1)	—
29	35	126–127	$C_{14}H_{12}N_6O_4S_2$	43.1 (42.9)	3.3 (3.1)	21.1 (21.4)	392
30a	67	204–205	$C_{20}H_{24}N_4O_4S_2$	57.5 (57.7)	6.1 (5.8)	13.1 (13.5)	—
30b	39	203–205	$C_{28}H_{26}N_4O_4S_2$	60.3 (60.5)	6.9 (6.7)	6.2 (5.9)	—
30c	73	209	$C_{30}H_{30}N_4O_6S_2$	59.6 (59.4)	5.2 (4.9)	9.5 (9.2)	—
30d	73	225–226	$C_{28}H_{24}N_6O_8S_2$	52.4 (52.8)	3.8 (3.8)	13.2 (13.2)	—
30e	40	195	$C_{24}H_{30}N_4O_4S_2$	57.0 (57.3)	6.3 (6.0)	10.9 (11.2)	—
31	53	179–181	$C_{24}H_{26}N_4O_4S_2$	57.7 (57.8)	5.3 (5.2)	11.1 (11.2)	498

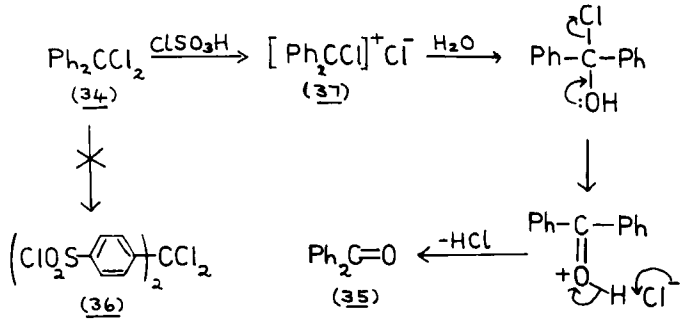
substrates (**32**, **33**) with chlorosulfonic acid may arise from the conversion of **32** into **33** in this medium, as shown (Scheme 1):



SCHEME 1

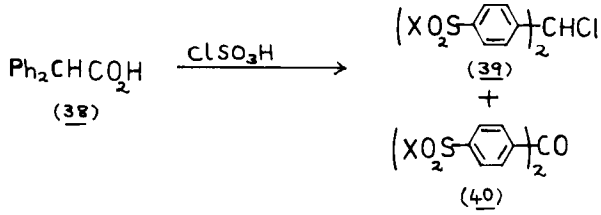
Diphenylmethylene dichloride (**34**) reacted with chlorosulfonic acid (12 equivalents) with effervescence and formation of a deep orange solution. The product was benzophenone (**35**) (85%) and not the expected disulphonyl chloride (**36**).

The orange colour is probably consistent with the formation of the stabilized carbocation (**37**), which would be resistant to sulfonation but would be susceptible to nucleophilic attack by water leading to **35** (Scheme 2):



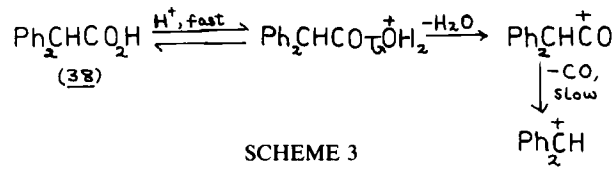
SCHEME 2

Diphenylacetic acid (**38**) by warming (60°C) with excess chlorosulfonic acid (12 equivalents) afforded a mixture of the sulfonyl chlorides (**39**, **40**; X = Cl):



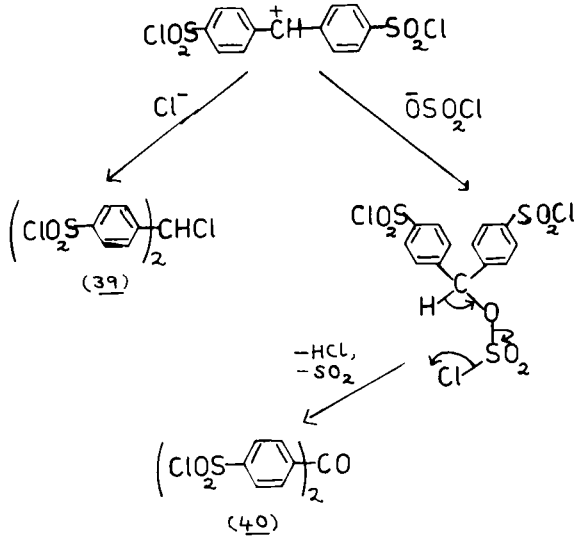
Treatment with dimethylamine gave the dimethylamides (**39**, **40**; X = NMe_2). The identities were confirmed by microanalytical and spectroscopic data. Thus, the mass spectra showed the molecular ion cluster for **39** (M^+, 416, 418) and the molecular ion for **40** (M^+, 396). The halogen atom was confirmed by the sodium fusion test and the carbonyl group by the IR spectrum (1660 cm^{-1}). The H^1 NMR spectrum showed the expected AA'BB' pattern for the aromatic protons of **39**, but the aromatic protons in **40** appeared as a singlet. The accidental chemical shift equivalence of these latter pairs of protons can be attributed to the combined electron-withdrawing and anisotropic effects of the SO_2 and CO groups. Integration indicated an approximate 2:1 ratio for **39**:**40** and this is supported by microanalytical data (found: C, 50.5; requires for 2:1 ratio C, 49.8%).

Benzophenone is known[5] to require much more forcing conditions for chlorosulfonation in the 3,3'-positions and it is therefore concluded that sulfonation must occur early in the reaction sequence. As shown, diphenylmethyl chloride (**33**) does not form the 4,4'-disulfonyl chloride and it cannot therefore be an intermediate in this reaction. Kinetic studies[12] of the decomposition of diphenylacetic acid (**38**) in 100% sulfuric acid, indicated the sequential formation of the diphenylmethane carbocation as shown (Scheme 3):



SCHEME 3

When **38** was treated with chlorosulfonic acid, by analogy with the reaction with sulfuric acid depicted above, rapid sulfonation of the phenyl rings should occur *before* loss of carbon monoxide. On the other hand, in the case of diphenylmethanol (**32**) the carbocation is probably formed before sulfonation, which may account for the different behaviour of **32** and **38** with the reagent. The formation of the two sulfonyl chlorides (**39**, **40**; X = Cl) may be ascribed to competitive attack by the Cl and $ClSO_2O$ anions (Scheme 4)

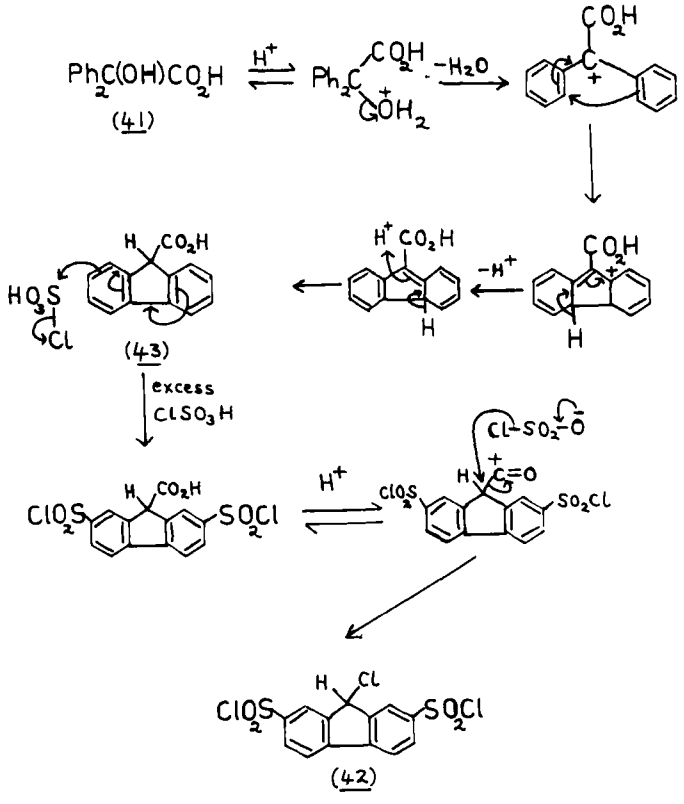


SCHEME 4

Benzilic acid (**41**) was claimed[13] to react with chlorosulfonic acid (12 equivalents) in boiling chloroform to yield the 4,4′-disulfonyl chloride of benzophenone (29%). However, repetition of this reaction afforded 9-chlorofluorene-2,7-disulfonyl chloride (**42**) (38%). The ^{1}H NMR spectrum showed the resonance for the 9-proton as a singlet (δ 5.9) and a clearly defined ABC pattern (δ 8.4–7.9) for the aromatic protons. The latter pattern is indicative of symmetrical disubstitution. The positions of substitution were confirmed by a nuclear Overhauser experiment which showed that irradiation of the 9-proton resonance increased the intensity of the narrow doublet in the aromatic region assigned to H1 and H8.

Benzilic acid (**41**) cyclises with aluminium chloride or with concentrated sulfuric acid to give fluorene-9-carboxylic acid[14–16] or a mixture of fluorene derivatives[17] respectively. In the present investigation, cyclisation almost certainly involves the initial formation of a carbocation, which can be formed by *either* (i) protonation of the carboxylic acid group and subsequent elimination of water and carbon monoxide, *or* (ii) protonation of the alcoholic hydroxyl group followed by loss of water. Route (i) appears unlikely, since by analogy with diphenylacetic acid the loss of carbon monoxide is a slow process—consequently sulfonation should occur in the 4,4′-positions before formation of the carbocation. This route should therefore lead to 3,6- rather than to 2,7-substitution in the benzo rings. Route (ii) involves carbocation formation *before* cyclisation giving fluorene-9-carboxylic acid

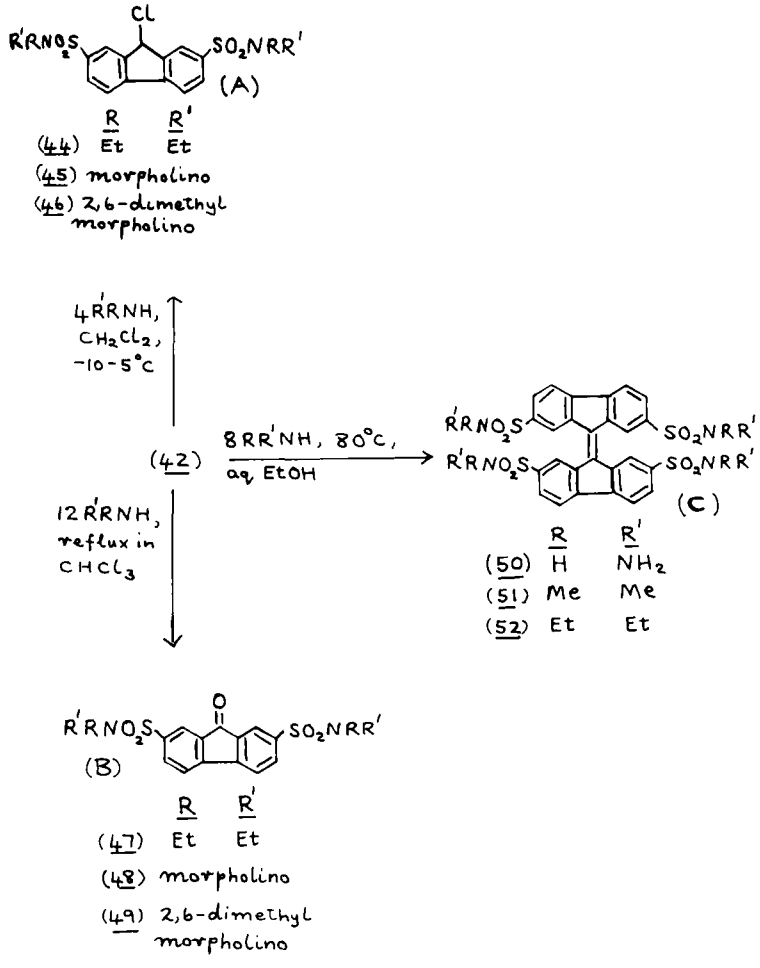
(**43**). Subsequent sulfonation should occur in the 2,7-positions. The mechanism is given in Scheme 5.



SCHEME 5

The mechanism is supported by the work of Cohen *et al.*[18,19] who demonstrated that when the carboxylic acid group in **43** is replaced by the strongly electron-withdrawing trifluoromethyl group, cyclisation in 100% sulfuric acid gave 9-(trifluoromethyl)fluorene. The failure of diphenylmethanol to cyclise in chlorosulfonic acid, suggests that the presence of an electron-withdrawing group on the 9-carbon atom is a prerequisite for cyclisation. In an effort to substantiate the mechanism, the proposed intermediate, fluorene-9-carboxylic acid (**43**) was reacted with chlorosulfonic acid under identical conditions. TLC and LCMS showed that 3 products were formed, the major one being the 2,7-disulfonyl chloride (**42**). This was confirmed by mass spectrometry by accurate mass measurement of the fragment ion obtained after loss of SO_2Cl. The other products were shown by their mass spectra to be an isomer of (**42**) and a dichlorosulfonyl derivative of 9-fluorenone (see accurate mass data in Experimental).

The reaction of the 2,7-disulfonyl chloride (**42**) with amines (5 equivalents) in aqueous methanol afforded mixtures of the three products A, B and C. However, under carefully controlled conditions, pure samples of each product could be isolated, (Scheme 6).



SCHEME 6

Compounds A (**44–46**) (*Table III*) were obtained by rapid reaction of **42** with the *anhydrous* amine (4 equivalents) in dilute dichloromethane solution at −10° to 5°C.

Compounds B (**47–49**). (**42**) was treated with the anhydrous amine (12 equivalents) in boiling chloroform (4 hours), this reaction probably involves autoxidation of the 9-hydrogen atom (cf. Reference 20).

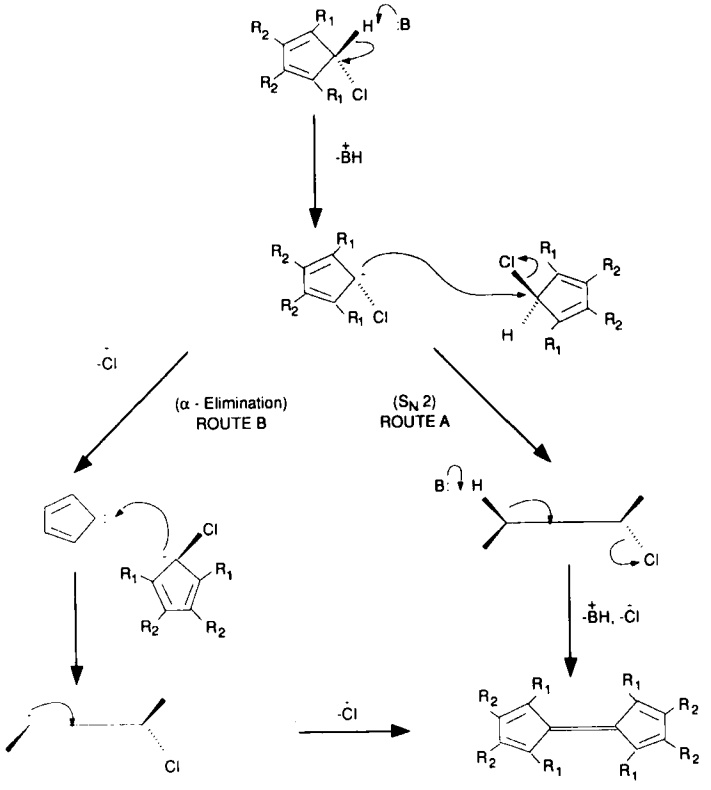
Compounds C (**50–52**) here the disulfonyl chloride (**42**) was added to a warm aqueous solution of the amine (8 equivalents) and the mixture left 12 hours. The products were orange-red crystalline solids due to extended conjugation through both fluorene nuclei. The formation of the compounds (**50–52**) probably involves dehydrochlorination *via* the carbanion; the latter is stabilized by the electron-withdrawing sulfonyl groups (Scheme 7) (Route A). However, the products may also arise by route B involving carbene formation; this may be more favourable because steric factors may inhibit the S_N2 reaction step in route A.

TABLE III

Physical data for derivatives from reaction of fluorene-2,7-disulfonyl chlorides with amines under various conditions.

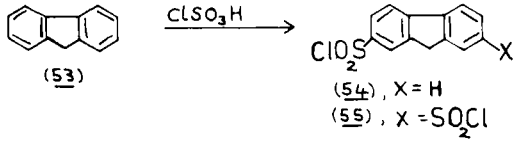
Compd. No.	Yield %	m.p. °C	Molecular formula	Microanalysis found (calc.) % C	H	N	MS (M^+)
44	45	183–185	$C_{21}H_{27}ClN_2O_4S_2$	53.8 (53.6)	5.6 (5.7)	5.8 (6.0)	* 472
45	40	168–170	$C_{21}H_{23}ClN_2O_6S_2$	50.9 (50.6)	4.4 5.8 (4.6)(5.6)	Cl, 6.9 (Cl, 7.1)	* 500
46	38	184–188	$C_{25}H_{31}ClN_2O_6S_2$	54.6 (54.1)	5.6 (6.0)	4.7 (5.0)	* 522
47	40	189–190	$C_{21}H_{26}N_2O_5S_2$	56.1 (56.0)	5.8 (5.8)	6.2 (6.2)	450
48	25	213–214	$C_{21}H_{22}N_2O_7S_2$	53.0 (52.7)	4.4 (4.6)	5.7 (5.9)	478
49	40	198–199	$C_{25}H_{30}N_2O_7S_2$	56.4 (56.2)	5.5 (5.6)	5.0 (5.2)	534
50	70	260	$C_{26}H_{20}N_4O_8S_2$ $1H_2O$	47.3 (47.1)	3.4 (3.3)	8.5 (8.5)	—
51	65	250–253	$C_{34}H_{36}N_4O_8S_2$	53.9 (53.9)	5.0 (4.8)	7.1 (7.4)	757†
52	75	250–254	$C_{42}H_{52}N_4O_8S_2$	58.0 (58.1)	5.8 (6.0)	6.4 (6.5)	

* The highest molecular mass of the cluster ions.
† $M^+ + 1$ ion obtained by FAB MS.



SCHEME 7 (For ease of representation R_1, and R_2 represent the 2-/7-substituted benzo rings.)

Fluorene (**53**) has been reported[21] to react with concentrated sulfuric acid to give the 2,7-disulfonic acid. We examined the reaction of (**53**) with chlorosulfonic acid (6 or 12 equivalents, or 3 equivalents in thionyl chloride). The product in each case was treated with an excess of dimethylamine and a mixture was obtained (TLC two spots, R_F 0.6, 0.4). On the basis of the sulfonation of fluorene, it seems probable that the product of chlorosulfonation was a mixture of the 2-sulfonyl chloride (**54**) and the 2,7-disulfonyl chloride (**55**) as a result of the +M directing influence of the conjugated π system. The ^{1}H NMR spectrum of the aromatic region was too complex to confirm the substitution patterns. However, the mono- and bis-products are supported by the presence of mass spectral ions 272 and 380, while microanalysis suggested a 1:1 mixture.



EXPERIMENTAL

Melting points were determined using an electrical Gallenkamp apparatus and are uncorrected. IR spectra were recorded as Nujol mulls on a Unicam SP1000 spectrophotometer. ^{1}H NMR spectra were recorded using a Bruker WP80 spectrometer using TMS as internal standard in deuterochloroform unless otherwise stated, an asterisk indicates a resonance removed by D_2O treatment. Mass spectra were recorded with a Micromass F16 spectrometer operating at 70 eV. TLC was carried out using Camlab silica gel plates sensitized to UV256 nm and ethyl acetate-cyclohexane (1:1) as eluant unless otherwise indicated.

Diphenylmethane-4,4'-disulfonyl chloride (**2**) Diphenylmethane (**1**) (20 g, 0.12 mol) was added to chlorosulfonic acid (63 g, 0.54 mol) without cooling. The solution was left for 48 hours, the precipitate was collected using a sintered glass filter. The gummy solid was slurried with ice-ethanol mixture (50 ml) filtered and air-dried to give **2** (30.4 g, 70%), m.p. 124–125°C (lit.[4] 122–123°C).

Dibenzyl-4,4'-disulfonyl chloride (**18**) Dibenzyl (**17**) (10 g, 0.055 mol) was rapidly added to chlorosulfonic acid (29 g, 0.25 mol) without cooling. A precipitate appeared almost immediately, the suspension was left for 24 hours and the solid filtered off under suction. The product was triturated with ice-ethanol (50 ml) and filtered off to give **18** (16.5 g, 80%), m.p. 161–163°C. TLC showed 1 spot R_F 0.70. (Found: C, 44.1; H, 3.1. $C_{14}H_{12}Cl_2O_4S_2$ requires C, 44.3; H, 3.2%). IR ν_{max} 1600 (ArC = C), 1385, 1170 (SO_2) cm^{-1}. ^{1}H NMR: δ 7.9–7.2 (m, AA'BB', 8H, ArH), 3.0 (s, 4H, CH_2). MS: 382, 380, 378 (M^+), 345, 343 ($M^+ - Cl$), 180 ($M^+ - 2SO_2Cl$), 189, 90 (C_7H_6).

General procedure for the reaction of the sulfonyl chlorides with amines The sulfonyl chloride (0.01 mol) was added, to a stirred solution of the appropriate amine (0.05 mol) in methanol (30 ml). The mixture was left for 3 hours and added to crushed ice (100 g). The precipitate was filtered off, washed with water (3 × 50 ml), and recrystallized from methanol to yield the amides (**3–9**, **19–25** Tables I and II). In the preparation of the derivatives (**10**, **11**, **26**, **27**) from aromatic amines, the condensation was performed in acetonitrile for 24 hours.

Compound (**4**) TLC showed 1 spot R_F 0.76. IR ν_{max} 1590 (ArC = C), 1350, 1170 (SO_2) cm^{-1}. ^{1}H NMR: δ 7.8–7.2 (m, 8H, AA'BB', ArH), 4.2 (s, 2H, CH_2), 2.6 (s, 12H, CH_3). MS: 382 (M^+), 274 (M^+—SO_2NMe_2), 165 (M—$2SO_2NMe_2$).

Compound (**20**) TLC showed 1 spot R_F 0.60. IR ν_{max} 1600 (ArC = C), 1340, 1140 (SO_2) cm^{-1}. ^{1}H NMR: δ 7.9–7.2 (m, 8H, AA'BB', ArH), 3.0 (s, 4H, CH_2), 2.7 (s, 12H, CH_3), MS: 352 (M^+—NMe_2), 288 (M^+—SO_2NMe_2), 180 (M^+—$2SO_2NMe_2$).

The preparation of the hydrazides (**12, 28**) *and hydrazones* (**15a–d, 30a–e**) The sulphonyl chloride (**2** or **18**, 0.01 mol) was reacted with 98% hydrazine hydrate (0.06 mol) in methanol (30 ml). The reaction was initially kept at 0°C and left at room temperature for 3 hours. The mixture was poured onto crushed ice (100 g), the precipitate was collected, washed with water (3 × 50 ml) and dried to give the hydrazides (**12, 28**) (Tables I and II). The acetone hydrazones (**15a, 30a**) were obtained by dissolving the hydrazide (0.005 mol) in acetone (20 ml). The solution was left for 2 hours, added to ice-water (20 ml) and the crystals collected. For the aromatic hydrazones (**15b–d, 30b–d**), the hydrazide (0.005 mol) was reacted with the aromatic aldehyde (0.01 mol) in acetonitrile (20 ml) containing concentrated sulfuric acid (1 drop). The mixture was refluxed (15 minutes); the products were filtered off and recrystallized from ethanol.

Compound (**12**) TLC showed 1 spot R_F 0.15. IR ν_{max} 3360, 3260, 3200 ($NHNH_2$), 1595 (ArC = C), 1310, 1165 (SO_2) cm^{-1}.

^1H NMR (δDMSO-d_6): δ 10.8* (s, 2H, NH), 7.8–7.4 (m, AA'BB', 8H, ArH), 4.2 (s, 2H, CH_2), 4.05* (s, 4H, NH_2). Characterized as the *acetone hydrazone* (**15a**): TLC 1 spot, R_F 0.4. IR ν_{max} 3210 (NH), 1600 (ArC = C), 1340, 1170 (SO_2). ^1H NMR (DMSO-d_6): δ 9.2* (s, 2H, NH), 8.0–7.2 (m, AA'BB', 8H, ArH), 4.1 (s, 2H, CH_2), 1.7 (2s, 12H, CH_3).

Compound (**28**) TLC showed 1 spot R_F 0.10. IR ν_{max} 3420, 3380, ($NHNH_2$), 1610 (ArC = C), 1330, 1140 (SO_2) cm^{-1}. ^1H NMR δ: 12.1* (s, 2H, NH), 7.9–7.2 (m, AA'BB', 8H, ArH), 5.2* (s, 4H, NH_2), 3.0 (s, 4H, CH_2).

Acetone hydrazone (**30a**): TLC 1 spot, R_F 0.30. IR ν_{max} 3125 (NH), 1590 (ArC = C), 1380, 1170 (SO_2) cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.9* (s, 2H, NH), 7.9–7.3 (m, AA'BB', 8H, Ar H), 3.0 (s, 4H, CH_2), 1.8 (s, 12H, CH_3).

The 3,5-Dimethylsulfonyl pyrazoles (**16, 31**) The hydrazides (**12, 28**) (0.005 mol) were refluxed with acetylacetone (0.01 mol) in ethanol (30 ml) for 3 hours to give the pyrazoles (**16, 31**)

Compound (**16**) TLC showed 1 spot R_F 0.47, IR ν_{max} 1595 (ArC = C), 1380, 1180 (SO_2) cm^{-1}. ^1H NMR (DMSO-d_6) δ: 8.0–7.3 (m, AA'BB', 8H, ArH), 6.2 (s, 2H, pyrazole-4H), 4.1 (s, 2H, CH_2), 2.6 (s, 3H, pyrazole 3-CH_3), 2.1 (s, 6H, pyrazole 5-CH_3). MS: 484 (M^+), 357 (M^+—$C_5H_7N_2O_2$), 193 (M^+—$SO_2C_5H_7N_2O_2$), 165, 95.

Compound (**31**) TLC showed 1 spot R_F 0.80. IR ν_{max} 1590 (ArC = C), 1370, 1180 (SO_2) cm^{-1}. ^1H NMR (DMSO-d_6) δ: 8.2–7.4 (m, AA'BB', 8H, Ar H), 6.1 (s, 2H, pyrazole-4H), 3.6 (s, 2H, CH_2) 2.5 (s, 6H, pyrazole 3-CH_3), 2.1 (s, 6H, pyrazole 5-CH_3). MS: 498 (M^+), 404 (M^+—$C_5H_7N_2$), 340 (M^+—$SO_2C_5H_7N_2$), 276, 185, 95.

Azides (**13, 29**) The sulfonyl chlorides (**2, 18**, 0.01 mol) were stirred with a solution of sodium azide (0.02 mol) in aqueous acetone (30 ml) for 3 hours. The suspension was added to crushed ice (200 g); the solid was collected and recrystallized from aqueous acetone to give the producs.

Compound (**13**) TLC showed 1 spot R_F 0.77. IR ν_{max} 2150 (N_3), 1590 (ArC = C), 1380, 1160 cm (SO_2)$^{-1}$. MS: 378 (M^+), 336 (M^+—N_3), 272 (M^+—SO_2N_3), 230, 165.

The azide (0.003 mol) was heated with triethyl phosphite (0.003 mol) in toluene (30 ml) at 80°C for 2 hours to give the triethoxy phosphinimine (**14**). TLC showed one spot R_F 0.20. IR ν_{max} 1595 (ArC = C), 1350, 1150 (SO_2) cm^{-1}. ^1H NMR (DMSO-d_6) δ: 7.8–7.3 (m, 8H, ArH), 4.2–4.0 (q, 12H, OCH_2CH_3), 3.3 (s, 2H, CH_2), 1.3–1.0 (t, 18H, OCH_2CH_3). MS: 654 (M^+), 639 (M^+—CH_3), 609 (M^+—OC_2H_5), 165.

Oxidation of diphenylmethane-4'-sulfonamide (**3**) The amide (**3**) (1 g) was suspended in glacial acetic acid (20 ml) and slowly added to a stirred solution of chromic anhydride (1 g) in glacial acetic acid (10 ml). The brown solution was refluxed for $3\frac{1}{2}$ hours. The mixture was poured onto water (300 ml) and left at 5°C for 12 hours. The solid was filtered off, washed with water (2 × 20 ml), and recrystallized from aqueous ethanol to give 4,4'-disulfonamide of benzophenone (**3a**) as a pale yellow solid (0.23 g, 22%), m.p. 247–248°C (lit.[4] 247–248°C.) TLC showed one spot R_F 0.86. (Found: C, 45.8; H, 3.4; N, 8.0. $C_{13}H_{12}N_2O_5S_2$ requires C, 45.9; H, 3.5; N, 8.2%). IR ν_{max} 3400, 3240 (NH_2), 1650 (C = 0), 1595 (ArC = C), 1330, 1160 (SO_2) cm^{-1}. ^1H NMR (DMSO-d_6) δ: 8.0 (d, 8H, ArH), 7.5* (s, 4H, NH_2). MS: 340 (M^+), 260 (M^+—SO_2NH_2).

Reaction of diphenylmethylene dichloride (**34**) *with chlorosulfonic acid* Diphenylmethylene dichloride (**34**) (10 g, 0.042 mol) was added dropwise to chlorosulfonic acid (59 g, 0.5 mol), there was rapid effervescence and the solution became deep red. After 2 days, the solution was added to crushed ice and the white precipitate filtered off. Recrystallization (petroleum ether b.p. 60–80°C) afforded benzophenone (6.5 g, 85%), m.p. 48–49°C (lit.[22] 48.5–49°C), no depression on m.m.p. with an authentic sample.

Reaction of diphenylacetic acid (**38**) *with chlorosulfonic acid* Diphenylacetic acid (5 g, 0.024 mol) was gradually added to chlorosulfonic acid (33 g, 0.28 mol) with stirring and cooling. Effervescence was observed and when this ceased, the mixture was heated (60°C) for 1 hour. The orange solution was poured onto ice; the gummy solid was collected, washed with water and sodium hydrogen carbonate solution. The product was reacted with excess dimethylamine (30% aqueous solution) for 2 hours, and recrystallized from ethanol to give a mixture of the 4,4′-disulfonyl chloride of benzophenone (**40**; X = NMe_2) and α-chlorodiphenyl methane-4,4′-disulfonyl chloride (**39**; X = NMe_2) (3 g), m.p. 194–196°C. TLC showed 2 spots R_F 0.80, 0.60. The Beilstein test for chlorine was positive. (Found: C, 50.5; H, 5.0; N, 6.9. (**40**; X = NMe_2), $C_{17}H_{20}N_2O_5S_2$ requires C, 51.5: H, 5.1; N, 7.1 and (**39**, X = NMe_2), $C_{17}H_{21}ClN_2O_4S_2$ requires C, 49.0; H, 5.0; N, 6.7%). IR ν_{max} 1660 (C = O), 1600 (ArC = C), 1340, 1165 (SO_2) cm^{-1}. ^1H NMR: δ 7.95 (s, 8H, *p*-$SO_2C_6H_4CO$), 7.9–7.5 (m, AA′BB′, 16H, *p*-$SO_2C_6H_4CHCl$), 6.3 (s, 2H, $CHCl$), 2.75 (s, CH_3, $COC_6H_4SO_2NMe_2$), 2.70 (s, CH_3, $CH(Cl)C_6H_4SO_2NMe_2$). MS 396 (M^+ for **40**), 418, 416 (M^+ for **39**).

Reaction of benzilic acid (**41**) *with chlorosulfonic acid* Chlorosulfonic acid (307 g, 2.63 mol) was gradually added to a stirred solution of benzilic acid (**41**) (50 g, 0.22 mol) in dry chloroform (500 ml). Effervescence occurred and the solution became deep red; the mixture was refluxed for 2 hours and left overnight. The solution was added to ice, the chloroform layer separated, dried ($MgSO_4$) and the solvent evaporated *in vacuo*. The residual oil solidified on trituration with cold ethanol (50 ml) and the precipitate was collected to give 9-chlorofluorene-2,7-disulfonyl chloride (**42**) as an off-white solid (33 g, 38%), m.p. 226–228°C. TLC showed 1 spot R_F 0.51 (Found:C, 39.0; H, 1.8; Cl, 28.3. $C_{13}H_7Cl_3O_4S_2$ requires C, 39.2; H, 1.8; Cl 26.8%). IR ν_{max} 1600, 1580 (ArC = C), 1360, 1160 (SO_2) cm^{-1}. ^1H NMR: δ 8.4–7.9 (m, ABC, 6H, ArH), 5.9 (s, H, 9CH). MS: 400, 398, 396 (M^+), 363 (M^+—Cl), 299 (M^+—SO_2Cl), 262 (M^+—SO_2Cl, −Cl), 198 (M^+—$2SO_2Cl$), 163.

General procedure for the preparation of the sulfonamides (*A*) (**44–46**) (*Table III*) 9-Chlorofluorene-2,7-disulfonyl chloride (**42**) (2 g, 0.005 mol) was dissolved in dichloromethane (200 ml) and cooled to −10 to −5°C. A solution of the anhydrous amine (0.021 mol) in dichloromethane (50 ml) was gradually added to **42** with vigorous stirring. After 5 minutes, the solvent was evaporated *in vacuo* and the crude sulfonamide purified by recrystallization from ethanol.

Compound (**44**) TLC showed one spot R_F 0.60. IR: ν_{max} 1600, 1580 (ArC = C), 1360, 1155 (SO_2) cm^{-1}. ^1H NMR: δ 8.3–7.9 (m, ABC, 6H, ArH), 5.9 (s, 1H, 9CH), 3.1–2.8 (q, 8H, $\underline{CH_2}CH_3$), 1.2–1.0 (t, 12H, $CH_2\underline{CH_3}$), MS: 472, 470 (M^+), 443, 441 (M^+—C_2H_5), 362, 360 (M^+—$SO_2\overline{NEt_2}$), 163.

General procedure for preparation of the 9-oxofluonamides (*B*) (**47–49**) (*Table III*) The anhydrous amine (0.06 mol) was gradually added to a stirred solution of **42** (0.005 mol) in chloroform (100 ml). The mixture was refluxed for 4 hours and allowed to cool. The chloroform layer was washed with water (3 × 300 ml), dried ($MgSO_4$) and evaporated *in vacuo*. The residual solid was recrystallized from petroleum ether (60–80°C) and ethanol to give the sulfonamides **47–49** (Table III).

Compound (**48**) TLC showed one spot R_F 0.50. IR ν_{max} 1730 (C = O), 1600 (ArC = C), 1110 (C—O—C), 1340, 1150 (SO_2) cm^{-1}. ^1H NMR δ: 8.3–7.9 (m, ABC, 6H, Ar, H), 3.6–3.3 (m, 8H, $\underline{CH_2}O\underline{CH_2}$), 3.0–2.8 (m, 8H, $\underline{CH_2}N\underline{CH_2}$). MS: 478 ($M^+$), 434 ($M^+$—$C_2H_4O$), 284 (M—$SO_2C_4H_8\overline{NO}$), 178 ($M^+$—$2SO_2C_4N_8\overline{NO}$), 86 ($C_4H_8NO$).

The preparation of the 9,9′-di(fluorenylidene)tetrasulfonamides (**50–52**) (*Table III*) **42** (0.005 mol) was added to a solution of the amine (0.04 mol) in 50% aqueous ethanol (100 ml) and heated at 80°C for 4 hours. The mixture was cooled (0°C); the precipitate was filtered off, washed with water (2 × 50 ml), ethanol (2 × 50 ml) and ether (1 × 50 ml) to give the sulfonamides (**50–52**) as red or orange solids.

Compound (**51**) TLC (methanol) showed 1 spot R_F 0.60. IR ν_{max} 1600 (ArC = C), 1370, 1165 (SO_2) cm^{-1}. ^1H NMR δ: 8.4–7.9 (m, ABC, 12H, ArH), 3.0 (s, 24H, CH_3). MS (FAB) 757 ($M^+ + 1$).

Reaction of fluorene-9-carboxylic acid (**43**) *with chlorosulfonic acid* Chlorosulfonic acid (33.3 g, 0.29 mol) was added to a solution of **43** (5 g, 0.024 mol) in dry chloroform (50 ml). After the initial effervescence had subsided, the solution was refluxed for 2 hours and left overnight. The mixture was poured onto crushed ice and the chloroform layer separated, washed with water (2 × 50 ml), dried ($MgSO_4$) and evaporated *in vacuo*. The residual yellow oil solidified on trituration with cold ethanol (25 ml) to give a pale yellow solid (4.2 g), m.p. 226–228°. TLC showed 2 spots R_F 0.62, 0.40. (Found: C, 39.2; H, 1.7; Cl 28.3; S, 15.9. $C_{13}H_7Cl_3O_4S_2$ requires C, 39.2; H, 1.8; Cl 26.8; S, 16.1%). IR ν_{max} 1650 (C = 0, weak), 1600, 1580 (ArC = C), 1370, 1150 (SO_2) cm^{-1}. LCMS showed 3 peaks for which the highest molecular ions were M_1^+ 396 (major product), M_2^+ 396 (minor) and M_3^+ 276 (minor). The fragment ions corresponding to M^+—SO_2Cl were measured for each product due to the greater intensity of these ions as cf. the molecular ions (M^+). The observed mass of M_1^+—SO_2Cl was 296.9542 (theory for $C_{13}H_7Cl_2O_2S$: 296.9545) and for M_3^+—SO_2Cl 276.9726 (theory of $C_{13}H_6ClO_3S$: 276.9727).

Reaction of fluorene (**53**) *with chlorosulfonic acid* Chlorosulfonic acid (21 g, 0.18 mol) was added to a solution of fluorene (**53**) (10 g, 0.06 mol); the mixture was refluxed for 2 hours and left overnight. The solution was added to ice-ethanol mixture (200 ml) and the gummy solid immediately reacted with excess aqueous dimethylamine. The product was recrystallized from ethanol to give a mixture of the sulfonamides (**54**, **55**) (8 g), m.p. 230–233°C. TLC showed 2 spots R_F 0.50, 0.40. (Found: C 58.8; H, 5.3; N, 6.0. Compound (**54**), $C_{15}H_{15}NO_2S$ requires C, 65.9, H, 5.5; N, 5.1%. Compound (**55**), $C_{17}H_{20}N_2O_4S_2$ requires C, 53.7; H, 5.3; N, 7.4%. IR ν_{max} 1600, 1590 (ArC = C), 1370, 1160 (SO_2) cm^{-1}. ^1H NMR δ: 8.4–7.7 (m, 6H, ArH), 4.2 (s, 2H, $\underline{CH_2}$), 2.7 (2 × s, 10H, $N\underline{CH_3}$). MS: 380 (M^+), 336 (M^+—NMe_2), 272 (M^+—SO_2NMe_2), 228, 164 (M^+—$2SO_2NMe_2$).

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