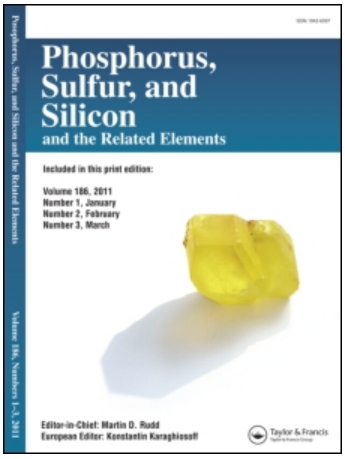

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SOME CHLOROHYDROXYBENZENESULFONYL DERIVATIVES

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SOME CHLOROHYDROXYBENZENESULFONYL DERIVATIVES

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2,4-; 2,6-; 2,3-; 3,4-; 2,5-; and 3,5-dichlorophenols by reaction with chlorosulfonic acid were converted to the following substituted benzenesulfonyl chlorides: 3,5-dichloro-2-hydroxy-; 3,5-dichloro-4-hydroxy-; 2,3-dichloro-4-hydroxy-; 4,5-dichloro-2-hydroxy-; 2,5-dichloro-4-hydroxy-; and 2,6-dichloro-4-hydroxy-respectively. In addition *o*-chlorophenol gave 5-chloro-4-hydroxybenzene-1,3-*bis*-sulfonyl chloride. The various sulfonyl chlorides have been condensed with nucleophilic reagents, e.g. ammonia, amines, hydrazine, phenylhydrazine, N,N-dimethylhydrazine, and sodium azide. 3,5-Dichloro-2-hydroxybenzenesulfonyl azide has been reacted with norbornene, triphenylphosphine, dimethylsulfoxide, and cyclohexene. 3,5-Dichloro-2-hydroxybenzenesulfonyl chloride with phenylisocyanate gave the 2-(N-phenylcarbamoyloxy) derivative which on heating gave a heterocyclic compound. The chlorohydroxybenzenesulfonyl derivatives are of interest as potential herbicides and their ir and nmr spectral characteristics are briefly discussed.

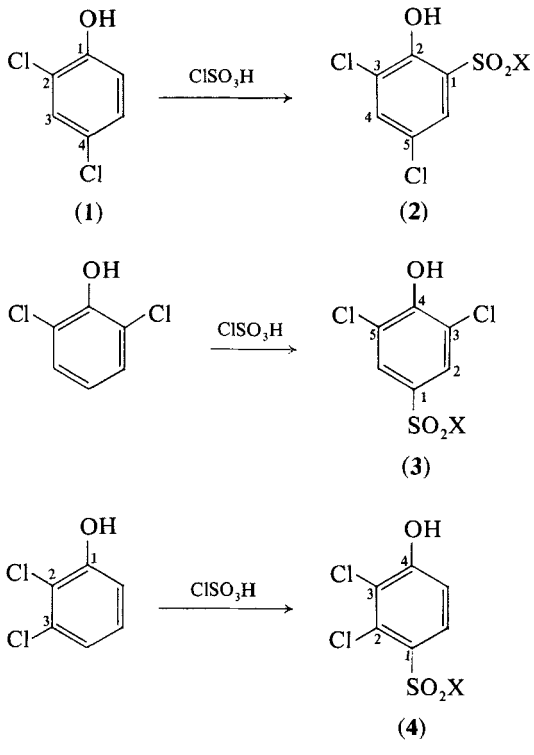
INTRODUCTION

Chlorophenols are well-established biocides, and they have found extensive application as bactericides, fungicides, and herbicides.[1] In addition previous studies have demonstrated fungicidal activity in sulfonamides[2] and sulfonohydrazides;[3–5] also certain sulfonyl azides are nematicidal.[6]

It therefore appeared valuable to prepare a range of chlorophenol sulfonyl derivatives as potential pesticides especially since 3,5-dihalogeno-2-hydroxybenzenesulfonamides are effective acaricides.[7,8] Hydroxybenzenesulfonyl fluorides have been evaluated as rapid plant desiccants[9] and as soil fungicides.[10]

DISCUSSION

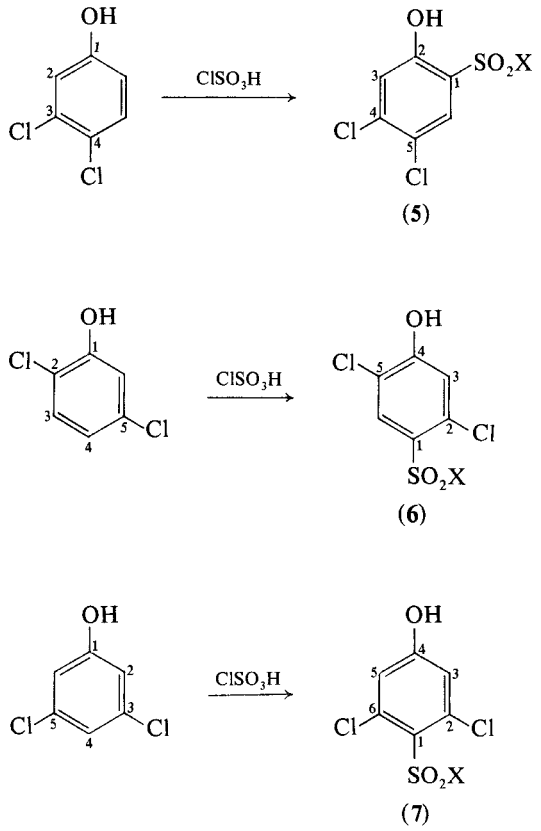
Treatment of 2,4-(**1**); 2,6-; 2,3-; 3,4-; 2,5-; and 3,5-dichlorophenols with chlorosulfonic acid afforded the following substituted benzenesulfonyl chlorides: 3,5-dichloro-2-hydroxy-(**2**; X = Cl); 3,5-dichloro-4-hydroxy-(**3**; X = Cl); 2,3-dichloro-4-hydroxy-(**4**); 4,5-dichloro-2-hydroxy-(**5**; X = Cl); 2,5-dichloro-4-hydroxy-(**6**; X = Cl); and 2,6-dichloro-4-hydroxy-(**7**; X = Cl) respectively (Scheme 1):



SCHEME 1

(*continued over*)

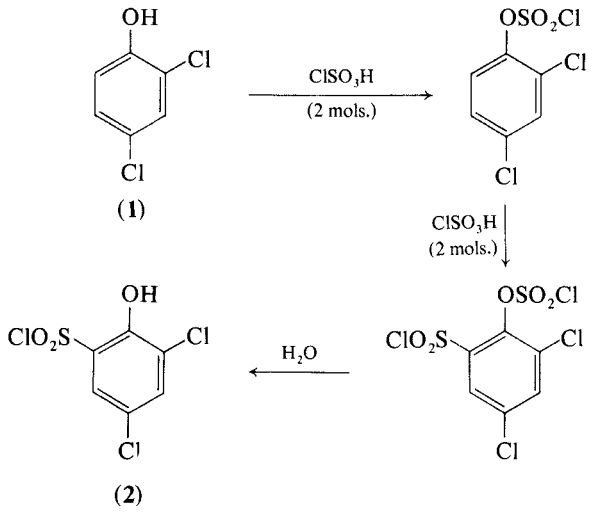
(*continued*)



SCHEME 1

The orientation of chlorosulfonation is controlled by the electron-releasing hydroxyl group, so that where possible sulfonation occurs *para* to this group (e.g. Compounds **3**, **4**, **6**, **7**), however when this position is blocked by a substituent sulfonation takes place *ortho* to the hydroxyl group (e.g. Compounds **2**, **5**).

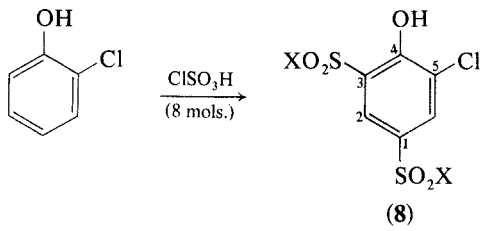
Experiments showed that the maximum yields of the sulfonyl chlorides (**2–7**) from the appropriate dichlorophenols required the use of a large excess (≏5 mol. equivs.) of chlorosulfonic acid. This situation resembled that already encountered[11] during the chlorosulfonation of aromatic carboxylic acids and arises from the condensation of chlorosulfonic acid with the phenolic hydroxyl group. So at least 4 mol. equivs. of chlorosulfonic acid are needed for chlorosulfonation. For instance with 2,4-dichlorophenol (**1**), the course of chlorosulfonation is shown in Scheme 2:



SCHEME 2

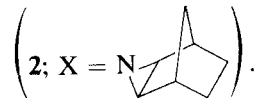
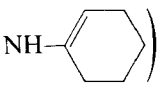
In the final step, treatment with ice-water decomposes the unstable phenoxysulfonyl chloride intermediate liberating 3,5-dichloro-2-hydroxybenzenesulfonyl chloride (**2**).

o-Chlorophenol, by reaction with a large excess of chlorosulfonic acid (≏8 mol. equivs) gave 5-chloro-4-hydroxybenzene-1,3-*bis*-sulfonyl chloride (**8**; X = Cl) since this phenol contains vacant *ortho* and *para* positions relative to the OH group which are available for sulfonation:

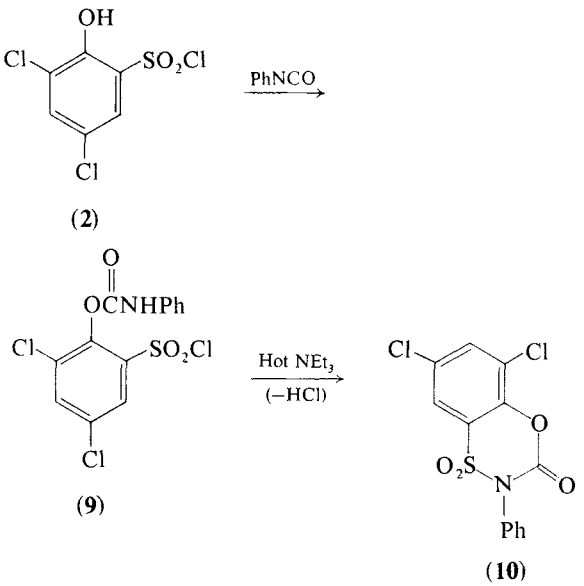


To obtain a range of novel chlorohydroxybenzenesulfonyl derivatives for examination as potential pesticides, the various sulfonyl chlorides (**2–8**; X = Cl) were reacted with nucleophilic reagents, e.g. ammonia, amines, hydrazines, and sodium azide to give the corresponding sulphonamides (X = NH_2, or RNH), sulfonohydrazides (X = NH–NH_2 or NHNHR), or sulfonyl azides (X = N_3).

The sulfonyl azides show some interesting reactions;[6] for instance 3,5-dichloro-2-hydroxybenzenesulfonyl azide (**2**; X = N_3) undergoes a 1,3-

dipolar addition reaction with norbornene to give an unstable triazoline which decomposes with formation of the aziridine (**2**; X = ). On the other hand in an analogous reaction with cyclohexene containing a less sterically stained double bond, the product was the enamine (**2**; X = ). These results were similar to those reported[12] in analogous reactions with tetrachlorobenzenesulfonyl azides. The sulfonyl azide (**2**; X = N_3) also reacted similarly with triphenylphosphine to give the imino-phosphorane (**2**; X = N = PPh_3), and with dimethylsulfoxide to give the S,S-dimethylsulfoximine (**2**; X = $S(:O)(CH_3)_2$) (cf. Ref. 12).

3,5-Dichloro-2-hydroxybenzenesulfonyl chloride (**2**) by reaction with phenylisocyanate gave the N-phenylcarbamoyloxy derivative (**9**) which on heating with triethylamine cyclised to the heterocyclic compound (**10**):



(**2**)

(**9**)

(**10**)

The i.r. spectra of the various chlorohydroxybenzenesulfonyl derivatives showed a broad OH stretching band in the 3580–3190 cm^{-1} region; intermolecular hydrogen bonded OH groups are reported[13a] to show a strong broad band at 3450–3200 cm^{-1}. The SO_2 group showed two characteristic S–O stretching absorptions at 1380–1315 and 1195–1130 cm^{-1}; these vibrations are reported at 1350–1300 and 1160–1140 cm^{-1} [13b] (cf. Ref. 14). The N–H stretching vibrations appeared within the overall range 3460–3150 cm^{-1}, and the asymmetric stretching mode of the NH_2 group generally appeared at slightly higher frequencies (3460–3330 cm^{-1}) than those of other N–H groups; this is in agreement with previous observations.[14] The sulfonyl azides are characterized by a strong sharp absorption at 2175–2120 cm^{-1} associated with the asymmetric stretch of the N = N = N group. This band generally appears[13c] at 2175–2120 cm^{-1}; the 1,3-*bis*-sulfonyl azide (**8**; X = N_3) shows two bands at 2175 and 2120 cm^{-1}. The C–Cl stretching band appears in the region 730–660 cm^{-1} in reasonable agreement with the quoted[13d] range of 750–700 cm^{-1}.

In the nmr spectra the proton of the phenolic hydroxyl group showed as a singlet at δ10.62–9.54; these protons have been reported[15] to resonate at δ10.5–4.0. The SO_2NH protons appear at δ8.86–6.80 similar to the general range (δ9.4–6.0) quoted[15] for amidic protons. The position of both OH and NH proton resonancies are known[15] to vary widely according to the degree of intermolecular hydrogen bonding, consequently the chemical shifts associated with these protons are sensitive to such factors as molecular structure, and the temperature, concentration, and nature of the solvent. The aromatic protons showed as multiplets (δ7.48–6.70), although the protons adjacent to the electron-withdrawing sulfonyl group were deshielded and consequently resonated at slightly lower field (δ8.20–7.70), in reasonable agreement with the reported range in substituted benzenes (δ8.00–6.50).[16a] The methyl protons of the $N(CH_3)_2$, $SO(CH_3)_2$, and N = $C(CH_3)_2$ groups resonated at δ2.82–2.30, 3.50–2.82, and 1.83 respectively; the latter signal is a doublet (*J*, 2Hz) due to geometric isomerism about the rigid carbon-nitrogen double bond. In support the position of the CH_3 resonance is known[16b] to vary widely (δ3.8–0.9) depending on the nature of the attached groups.

EXPERIMENTAL

Ir spectra were determined as Nujol mulls using a Perkin Elmer 237 spectrometer. Nmr spectra were measured with a Varian HA 100 spectrometer using tetramethylsilane as internal standard and deuterated dimethylsulfoxide unless otherwise stated. Mass spectra were determined with an AEI MS9 spectrometer at 70 eV. Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Tlc was carried out on silica gel G plates developed with iodine vapour. Microanalyses were carried out by Butterworth Microanalytical Consultancy Limited, Teddington, England.

3,5-Dichloro-2-Hydroxybenzenesulfonyl Chloride (**2**; X = Cl)

2,4-Dichlorophenol (**1**) (4.8 g) was gradually added to chlorosulfonic acid (10 ml; 5 mol. equivs.) at 0°. After 1 h at room temperature, the solution was poured onto crushed ice, and the precipitate was filtered off, and washed with ice-water. Recrystallization (CCl_4) gave the sulfonyl chloride (6.1 g, 79%), mp 75–76° (lit.[17] 81°, lit.[9] 82.5–83.5°). ν_{max} 3450 br (OH), 1320, 1180 (SO_2), 720 (C—Cl) cm^{-1}.

The following benzenesulfonyl chlorides were similarly prepared:

(i) *From 2,6-dichlorophenol, 3,5-dichloro-4-hydroxy* (**3**; X = Cl) (98%), mp 118–119° (lit.[17] 122°, lit.[18] 126°). ν_{max} 3410 br (OH), 1575 (arom C=C), 1360, 1180 (SO_2), 730 (C—Cl) cm^{-1}.

(ii) *From 2,3,-dichlorophenol, 2,3-dichloro-4-hydroxy* (**4**; X = Cl) (63%), mp 82–83°. ν_{max} 3400 br (OH), 1360, 1180 (SO_2), 690 (C—Cl) cm^{-1}.

(iii) *From 3,4,-dichlorophenol, 4,5-dichloro-2-hydroxy* (**5**; X = Cl) (69%), mp 68–69°. ν_{max} 3420 br (OH), 1380, 1170 (SO_2), 670 (C—Cl) cm^{-1}.

(iv) *From 2,5-dichlorophenol, 2,5-dichloro-4-hydroxy* (**6**; X = Cl) Reaction at room temperature gave a water soluble material but at 80° for 1 h, the above *sulfonyl chloride* (**6**; X = Cl) was obtained (63%), mp 30–31°. ν_{max} 3500 br (OH), 1315, 1180 (SO_2), 680 (C—Cl) cm^{-1}.

(v) *From 3,5-dichlorophenol, 2,6-dichloro-4-hydroxy* (**7**; X = Cl) The optimum yield was obtained by reaction of 3,5-dichlorophenol with chlorosulfonic acid (8 mol. equivs.) at 80° for 2 h to give the *sulfonyl chloride* (**7**; X = Cl) (36%), mp 98–99°. ν_{max} 3270 br (OH), 1380, 1180 (SO_2), 670 (C—Cl) cm^{-1}.

3,5-Dichloro-2-Hydroxybenzenesulfonamide (**2**; X = Cl)

3,5-Dichloro-2-hydroxybenzenesulfonyl chloride (1 g) was reacted with excess of ammonium hydroxide (15 ml of 0.88) in ethanol (15 ml) at room temperature. After 30 min the solution was acidified (concentrated hydrochloric acid), and the precipitate filtered off. Recrystallisation (aq. EtOH) afforded the sulfonamide (0.6 g, 70%), mp 229° (decomp. (lit.[17] 225°). ν_{max} 3400 br (OH), 3380, 3360 (NH_2), 1320 1180 (SO_2), 720 (C—Cl) cm^{-1}.

The following benzenesulfonamides were similarly prepared:

(i) *2,5-Dichloro-4-hydroxy* (**6**; X = NH_2) (93%), mp 216–218° (Found: C, 30.1; H, 2.4; N, 6.0. $C_6H_5Cl_2NO_3S$ requires C, 29.8; H, 2.1; N, 5.8%). ν_{max} 3400 br (OH), 3370, 3270 (NH_2), 1590, 1560 (arom C=C), 1340, 1170 (SO_2), 680 (C—Cl) cm^{-1}.

(ii) *2,6-Dichloro-4-hydroxy* (**7**; X = NH_2) (81%), mp 198–200° (decomp.) (Found: C, 29.5; H, 1.9; N, 5.2. $C_6H_5Cl_2NO_3S$ requires C, 29.8; H, 2.1; N, 5.8%). ν_{max} 3400 br (OH), 3380, 3280 (NH_2), 1580, 1550 (arom C=C), 1380, 1160 (SO_2), 660 (C—Cl) cm^{-1}.

(iii) *3,5-Dichloro-4-hydroxy* (**3**; X = NH_2) (76%), mp 203–204° (lit.[17] 205°). ν_{max} 3400 br (OH), 3380, 3270 (NH_2), 1570 (arom) C=C), 1330, 1170 (SO_2), 670 (C—Cl) cm^{-1}.

3,5-Dichloro-2-Hydroxybenzene N-Dimethylsulfonamide (**2**; X = $N(CH_3)_2$)

3,5-Dichloro-2-hydroxybenzenesulfonyl chloride (**2**; X = Cl) (2 g) was refluxed with dimethylamine (1.2 g of 33% ethanolic solution; 2 mol. equivs.) in acetonitrile (10 ml) for 4 h. The solvents were evaporated and the solid residue extracted with benzene (20 ml); the solution was washed with 10% hydrochloric acid (2 × 15 ml) and water. Evaporation under reduced pressure gave the *N-dimethylsulfonamide* (1 g, 50%), mp 87–88°. (Found: C, 35.8; H, 3.4; N, 5.0. $C_8H_9Cl_2NO_3S$ requires C, 35.6; H, 3.3; N, 5.2%). ν_{max} 3340 br (OH), 1380, 1165 (SO_2), 710 (C—Cl) cm^{-1}. Nmr δ10.62 br (1H O*H*), 7.70 d (2Ar*H*, J2Hz), 2.82 s (6H, $N(CH_3)_2$). The signal at δ10.62 was removed after D_2O treatment. Ms. showed the molecular ion (M^+, 270).

The following N-dimethylbenzenesulfonamides were similarly prepared:

(i) *3,5-Dichloro-4-hydroxy* (**3**; X = $N(CH_3)_2$) (55%), mp 137–138°. (Found: C, 35.9; H, 3.0; N, 5.3. $C_8H_9Cl_2NO_3S$ requires C, 35.6; H, 3.3; N, 5.2%). ν_{max} 3360 br (OH), 1380, 1150 (SO_2), 670 (C—Cl) cm^{-1}. Nmr δ9.98 s (1H, OH), 7.70 s (2ArH), 2.70 s (6H, $N(CH_3)_2$). The signal at δ9.98 was removed after D_2O treatment.

(ii) *2,3-Dichloro-4-hydroxy* (**4**; X = $N(CH_3)_2$) (40%), m.p. 165–166°. (Found: C, 35.4; H, 3.5; N, 5.2. $C_8H_9Cl_2NO_3S$ requires C, 35.6; H, 3.3; N, 5.2%). ν_{max} 3350 br (OH), 1340, 1180 (SO_2) cm^{-1}.

(iii) *2,5-Dichloro-4-hydroxy* (**6**; X = $N(CH_3)_2$) (76%), mp 99–100° (decomp.). (Found: C, 35.4; H, 3.2; N, 5.0. $C_8H_9Cl_2NO_3S$ requires C, 35.6; H, 3.3; N, 5.2%). ν_{max} 3390 br (OH), 1590, 1550 (arom C=C), 1350, 1195 (SO_2), 680 (C—Cl) cm^{-1}.

2,3-Dichloro-4-Hydroxy-N-Morpholinobenzenesulfonamide (**4**; X = morpholino)

2,3-Dichloro-4-hydroxybenzenesulfonyl chloride was reacted with morpholine (3 mol. equivs.) in acetonitrile for 2 h to give the *morpholinosulfonamide* (33%, from petroleum ether 40–60°), mp 153–155° (decomp.) (Found: C, 38.8; H, 3.5; N, 4.2. $C_{10}H_{11}Cl_2NO_4S$ requires C, 38.5; H, 3.5; N, 4.5%). ν_{max} 3300 br (OH), 1590, 1560 (arom C=C), 1350, 1170 (SO_2) cm^{-1}.

Other N-substituted benzenesulfonamides were similarly prepared:

(i) *2,6-Dichloro-4-hydroxy N-morpholine* (**7**; X = morpholino) boiled for 2 h, (50%), mp 130–131°. (Found: C, 38.7; H. 3.4; N, 4.6. $C_{10}H_{11}Cl_2NO_4S$ requires C, 38.5; H, 3.5; N, 4.5%). ν_{max} 3190 br (OH), 1590, 1560 (arom C=C), 1340, 1175 (SO_2), 710 (C—Cl) cm^{-1}.

(ii) *4,5-Dichloro-2-hydroxy N-(p-chlorophenyl)* (**5**; X = *p*-ClC_6H_4NH), refluxed 3 h, (54%), mp 148–149°. (Found: C, 41.1; H, 2.4; N, 3.8. $C_{12}H_8Cl_3NO_3S$ requires C, 40.9; H, 2.3; N, 4.0%). ν_{max} 3360 br (OH), 3250 (NH), 1595 (arom C=C), 1330, 1160 (SO_2), 690 (C—Cl) cm^{-1}.

(iii) *2,6-Dichloro-4-hydroxy N-(p-Chlorophenyl)* (**7**; X = *p*-ClC_6H_4NH), refluxed 2 h, (67%), mp 127–128°. (Found: C, 40.8; H, 2.5; N, 4.0. $C_{12}H_8Cl_3NO_3S$ requires C, 40.9; H, 2.3; N, 4.0%). ν_{max} 3270 br (OH), 3150 (NH), 1590, 1560 (arom C=C), 1380, 1180 (SO_2), 680 (C—Cl) cm^{-1}.

(iv) *4,5-Dichloro-2-hydroxy N-cyclohexyl* (**5**; X = $C_6H_{11}NH$) 20 h at room temperature, (54%), mp 160–161° (decomp.). (Found: C, 44.4; H, 4.3; N, 4.0. $C_{12}H_{14}Cl_2NO_3S$ requires C, 44.6; H, 4.3; N, 4.3%). ν_{max} 3310 br (OH), 3150 (NH), 1380, 1195 (SO_2), 710 (C—Cl) cm^{-1}.

(v) *2,3-Dichloro-4-hydroxy N-(2,4-dichlorophenyl)* (**4**; X = $2,4Cl_2C_6H_3NH$). 2,4-dichloroaniline (2 mol. equivs.) refluxed 6 h with the sulfonyl chloride, (26% from toluene), mp 159–160°. (Found: C, 37.4; H, 1.9; N, 3.8. $C_{12}H_7Cl_4NO_3S$ requires C, 37.2; H, 1.8; N, 3.6%). ν_{max} 3430 br (OH), 3330 (NH), 1580 (arom C=C), 1380, 1180 (SO_2), 695 (C—Cl) cm^{-1}.

3,5-Dichloro-2-Hydroxybenzenesulfonyl Azide (**2**; X = N_3)

3,5-Dichloro-2-hydroxybenzenesulfonyl chloride (**2**; X = Cl) (5.2 g) dissolved in acetone (20 ml) was treated with a solution of sodium azide (2.6 g; 2 mol. equivs.) in water (8 ml). After 3 h at room temperature, dilution with ice-water (80 ml) and acidification (concentrated hydrochloric acid, 5 ml) gave a solid product. Recrystallization (CCl_4) afforded the *sulfonyl azide* (4.6 g, 87%), mp 89–90°. (Found: C, 27.2; H, 1.2; N, 15.5. $C_6H_3Cl_2N_3O_3S$ requires C, 26.9; H, 1.1; N, 15.7%). ν_{max} 3400 br (OH), 2160 (N_3), 1370, 1180 (SO_2) cm^{-1}. Ms. showed the molecular ion (M^+, 268).

The following benzenesulfonyl azides were similarly prepared:

(i) *3,5-Dichloro-4-hydroxy* (**3**; X = N_3) (87%), mp 85–86° (Found: C, 27.3; H, 1.0; N, 15.3. $C_6H_3Cl_2N_3O_3S$ requires C, 26.9; H, 1.1; N, 15.7%). ν_{max} 3400 br (OH), 2150 (N_3), 1580 (arom C=C), 1380, 1190 (SO_2), 670 (C—Cl) cm^{-1}.

(ii) *2,3-Dichloro-4-hydroxy* (**4**; X = N_3) (56%), mp 62–63°. (Found: C, 26.8; H, 1.2; N, 15.6. $C_6H_3Cl_2N_3O_3S$ requires C, 26.9; H, 1.1; N, 15.7%). ν_{max} 3500 br (OH), 2130 (N_3), 1365, 1180 (SO_2), 690 (C—Cl) cm^{-1}

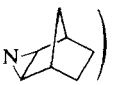
(iii) *4,5-Dichloro-2-hydroxy* (**5**; X = N_3) (85%), mp 78–79°. (Found: C, 26.6; H, 1.3; N, 15.8. $C_6H_3Cl_2N_3O_3S$ requires C, 26.9; H, 1.1; N, 15.7%). ν_{max} 3510 br (OH), 2160 (N_3), 1350, 1160 (SO_2), 680 (C—Cl) cm^{-1}.

(iv) *2,5-Dichloro-4-hydroxy* (**6**; X = N_3) (89%), oil n_D^{20} 1.546. ν_{max} 3450 br (OH), 2140 (N_3), 1590, 1560 (arom C=C), 1350, 1170 (SO_2), 690 (C—Cl) cm^{-1}.

(v) *2,6-Dichloro-4-hydroxy* (**7**; X = N_3) (53%), mp 80–81°. (Found: C, 26.7; H, 1.0; N, 15.5. $C_6H_3Cl_2N_3O_3S$ requires C, 26.9; H, 1.1; N, 15.7%). ν_{max} 3300 br (OH), 2140 (N_3), 1600, 1570 (arom C=C), 1380, 1150 (SO_2), 670 (C—Cl) cm^{-1}.

Reactions of 3,5-Dichloro-2-Hydroxybenzenesulfonyl Azide (**2**; X = N_3)

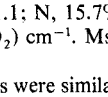
(i) *With norbornene.* A solution of the azide (1.34 g) in ether (10 ml) was added dropwise to norbornene (0.47 g; 1 mol. equiv.) in ether (5 ml) and the mixture refluxed for 3 h. After 24 h at room temperature evaporation of the ether, and recrystallization (EtOH) gave *3-(3',5'-dichloro-2-hydroxybenzenesulfonyl 3-azatricyclo* [3,2,1,$0^{2,4}$] *octane*

(**2**; X = ) (0.7 g; 42%), m.p. 151–152°. (Found: C, 46.5; H, 3.7; N, 4.0. $C_{13}H_{13}Cl_2NO_3S$ requires C, 46.7; H, 3.9; N, 4.2%). ν_{max} 3380 br (OH), 1380, 1150 (SO_2), 680 (C—Cl) cm^{-1}. Ms showed the molecular ion (M^+, 334).

(ii) *With triphenylphosphine.* A solution of the azide (1.34 g) in ether (20 ml) was added dropwise to triphenylphosphine (1.31 g; 1 mol. equiv.) in ether (20 ml) and the solution was refluxed for 5 h. After 12 h at room temperature, the ether was removed and the solid recrystallized (EtOH) to give *triphenyl (3,5-dichloro-2-hydroxybenzenesulfonylimino)-phosphorane* (**2**; X = N = PPh_3) (0.5 g, 56%), mp 146–147° (decomp.) (Found: C, 57.1; H, 3.5; N, 2.6. $C_{24}H_{18}Cl_2NO_3PS$ requires C, 57.4; H, 3.6; N, 2.8%). ν_{max} 3350 br (OH), 1360, 1160 (SO_2), 670 (C—Cl) cm^{-1}.

(iii) *With dimethylsulfoxide.* The azide (1 g) was refluxed with dimethylsulfoxide (20 ml) at 160° for 6 h. The solution was cooled, diluted with benzene (20 ml) and evaporated under reduced pressure to give a solid. Recrystallization (benzene) gave *S, S-dimethyl-N-(3,5-dichloro-2-hydroxybenzenesulfonyl) sulfoximine* (2; X = N = S (:O) $(CH_3)_2$) (0.8 g; 62%), mp 174–175°. (Found: C, 30.8; H, 2.9; N, 4.8. $C_8H_9Cl_2N_3O_4S_2$ requires C, 30.8; H, 2.9; N, 5.1%). ν_{max} 3340 br (OH), 1340, 1180 (SO_2), 680 (C—Cl) cm^{-1}. Nmr δ10.62 br (1H, OH), 7.72 d (2ArH), 2.82 s (6H, $S(CH_3)_2$). The signal at δ10.62 was removed after D_2O treatment.

(iv) *With cyclohexene.* The azide (1.8 g) was refluxed with cyclohexene (20 ml) for 8 h. Evaporation gave a solid residue (1.2 g) which was crystallized from ethanol to give *3,5-dichloro-2-hydroxy-N-(cyclohex-1-enyl)benzenesulfonamide*

(**2**; X = NH— ) (0.3 g, 15%, mp 170–171°. (Found: C, 44.5; H, 3.7; N, 4.2; S, 10.3. $C_{12}H_{13}Cl_2NO_3S$ requires C, 44.7; H, 4.0; N, 4.3; S, 9.9%). ν_{max} 3320 br (OH), 3220 (NH), 1330, 1160 (SO_2) cm^{-1}. Tlc (Pr^iOH-toluene-EtOAc-H_2O 5:1:2.5:1.25) showed a single spot, R_F 0.84.

Reaction of 3,5-Dichloro-4-Hydroxybenzenesulfonyl Azide with Norbornene

The azide (**3**; X = N_3) by refluxing with norbornene (1 mol. equiv.) in ether for 4 h gave the *aziridine* (36% from EtOH), mp 175–176°. (Found: C, 46.5; H, 3.9; N, 4.4. $C_{13}H_{13}Cl_2NO_3S$ requires C, 46.7; H, 3.9; N, 4.2%). ν_{max} 3350 br (OH), 1380, 1170 (SO_2), 680 (C—Cl) cm^{-1}.

3,5-Dichloro-2-Hydroxybenzene N-Phenylsulfonohydrazide (**2**; X = NHNHPh)

3,5-Dichloro-2-hydroxybenzenesulfonyl chloride (**2**; X = Cl) (2.6 g) was condensed with phenylhydrazine (2.2 g; 2 mol. equivs.) in acetonitrile (10 ml) at room temperature. After 12 h, the mixture was diluted with ether (60 ml) washed with water, dried ($MgSO_4$), and evaporated to yield the *N-phenylsulfonohydrazide* (1.3 g, 40%), mp 122–123°. (Found: C, 43.3; H, 3.1; N, 8.4. $C_{12}H_{10}Cl_2N_2O_3S$ requires C, 43.2; H, 3.0; N, 8.4%). ν_{max} 3400 br (OH), 3310, 3230 (NH), 1610 (arom C=C), 1335, 1160 (SO_2), 680 (C—Cl) cm^{-1}. Nmr δ9.64 s (1H, OH), 7.77 (1H, SO_2NH), 7.70 d (2H, $C_6H_2Cl_2$, J 2 Hz), 7.40 s (1H, NHPh), 7.26–7.78 m (5H, C_6H_5). The signals at δ9.64, 7.77 and 7.40 were removed by D_2O treatment.

The following N-phenylsulfonohydrazides were similarly obtained:

3,5-Dichloro-4-hydroxy (**3**; X = NHNHPh) (40%), mp 123–124°. (Found: C, 43.4; H, 3.2; N, 8.1. $C_{12}H_{10}Cl_2N_2O_3S$ requires C, 43.2; H, 3.0; N, 8.4%). ν_{max} 3410 br (OH), 3350 (NH), 1615 (arom C=C), 1345, 1170 (SO_2), 690 (C—Cl) cm^{-1}. Nmr δ9.54 (1H, OH), 8.0 s (1H, SO_2NH), 7.78 s (2H, $C_6H_2Cl_2$), 7.28–6.75 m (5H, C_6H_5), 6.80 (1H, PhNH). The signals at δ9.54 8.0 and 6.80 were removed by D_2O treatment.

2,3-Dichloro-4-hydroxy (**4**; X = NHNHPh) (90%), mp 98–99°. (Found: C, 43.0; H, 3.1; N, 8.2. $C_{12}H_{10}Cl_2N_2O_3S$ requires C, 43.2; H, 3.0; N, 8.4%). ν_{max} 3550 br (OH), 3400, 3250 (NH), 1380, 1175 (SO_2), 1610 (arom C=C), 700 (C—Cl) cm^{-1}.

2,5-Dichloro-4-hydroxy (**6**; X = NHNHPh) (97%), mp 122–123°. (Found: C, 42.9; H, 2.9; N, 8.1. $C_{12}H_{10}Cl_2N_2O_3S$ requires C, 43.2; H, 3.0; N, 8.4%). ν_{max} 3580 br (OH), 3360, 3310 (NH), 1610, 1590 (arom C=C), 1350, 1170 (SO_2), 680 (C—Cl) cm^{-1}.

4,5-Dichloro-2-hydroxy (**5**; X = NHNHPh) (76%), mp 131–132°. (Found: C, 43.3; H, 3.0; N, 8.3. $C_{12}H_{10}Cl_2N_2O_3S$ requires C, 43.2; H, 3.0; N, 8.4%). ν_{max} 3300 br (OH), 3315, 3215 (NH), 1380, 1180 (SO_2), 680 (C—Cl) cm^{-1}.

3,5-Dichloro-4-Hydroxybenzene-N,N-Dimethylsulfonohydrazide (**3**; X = $NHN(CH_3)_2$)

3,5-Dichloro-4-hydroxybenzenesulfonyl chloride (**3**; X = Cl) (2.0 g) was reacted with N,N-dimethylhydrazine (1.0 g; 2 mol. equivs.) in ethanol (10 ml) for 12 h at 4°. Addition of ice-water (80 ml) and acidification (concentrated hydrochloric acid) gave a solid. This was collected and recrystallized (aq. EtOH) to give the *N,N-dimethylsulfonohydrazide* (1.8 g, 82%), mp 106–107° (decomp.) (Found: C, 33.5; H, 3.3; N, 9.8. $C_8H_{10}Cl_2N_2O_3S$ requires C, 33.7; H, 3.5; N, 9.8%). ν_{max} 3360 br (OH), 3210 (NH), 1570 (arom C=C), 1380, 1160 (SO_2), 710 (C–Cl) cm^{-1}. Nmr δ10.0 s (1H, OH), 8.0 s (1H, NH), 7.75 s (2 ArH), 2.28 s (6H, $N(CH_3)_2$). The signals at δ10.0 and 8.0 were removed after D_2O treatment.

2,3-Dichloro-4-hydroxy (**4**: X = $NHN(CH_3)_2$), was similarly obtained (45%), mp 118–119°. (Found: C, 33.6; H, 3.5; N, 9.5. $C_8H_{10}Cl_2N_2O_3S$ requires C, 33.7; H, 3.5; N, 9.8%). ν_{max} 3300 br (OH), 3200 (NH), 1350, 1170 (SO_2), 670 (C–Cl) cm^{-1}.

3,5-Dichloro-4-Hydroxybenzenesulfonohydrazide (**3**; X = $NHNH_2$)

3,5-Dichloro-4-hydroxybenzenesulfonyl chloride (**3**; X = Cl) (2 g) was stirred with hydrazine hydrate (1.8 ml of 98%; 4 mol. equivs.) in carbon tetrachloride (20 ml) at 0°. After 3 h, the solvent was evaporated under reduced pressure, and the residual solid treated with concentrated hydrochloric acid, and washed with water. Trituration (CH_3OH) gave the *hydrazide* (1.3 g, 63%), mp 160–161° (decomp.). (Found: C, 27.7; H, 2.5; N, 11.1. $C_6H_6Cl_2N_2O_3S$ requires C, 28.0; H, 2.3; N, 10.9%). ν_{max} 3410 br (OH), 3330, 3260, 3200 (NH), 1625, 1580 (arom C=C), 1360, 1180 (SO_2), 670 (C–Cl) cm^{-1}.

The hydrazide was converted into the following hydrazones:

(a) *Acetone* (**3**; X = NHN = $C(CH_3)_2$) (80% from aq MeOH), mp 198–199°. (Found: C, 36.4; H, 3.3; N, 9.5. $C_9H_{10}Cl_2N_2O_3S$ requires C, 36.4; H, 3.4; N, 9.4%). ν_{max} 3400 br (OH), 3230 (NH), 1570 (arom C=C), 1330, 1180 (SO_2), 710 (C–Cl) cm^{-1}. Nmr δ9.94 s (1H, OH), 8.0 s (1H, NH), 7.80 s (2ArH), 1.83 d (6H, $C(CH_3)_2$, J2Hz).

(b) *p-Nitrobenzaldehyde* yellow needles (53% from EtOH), mp 275–276°. (Found: C, 40.2; H, 2.5; N, 10.5 $C_{13}H_9Cl_2N_3O_5S$ requires C, 40.0; H, 2.3; N, 10.8%). ν_{max} 3340, 3300 (NH), 1600 (arom C=C), 1350, 1160 (SO_2), 1520, 1330 (NO_2), 690 (C–Cl) cm^{-1}.

3,5-Dichloro-2-(N-Phenylcarbamoyloxy)benzenesulfonyl Chloride (**9**)

3,5-Dichloro-2-hydroxybenzenesulfonyl chloride (**2**; X = Cl) (2.6 g) was reacted with phenylisocyanate (1.4 g; 1 mol. equiv.) in refluxing benzene (20 ml). After 12 h, the benzene was evaporated and the product washed with water. Crystallization (EtOH) gave the *N-phenylcarbamoyloxysulfonyl chloride* (**9**) (2 g, 53%), mp 155–156°. (Found: C, 41.2; H, 2.1; N, 3.5. $C_{13}H_8Cl_3NO_4S$ requires C, 41.0; H, 2.1; N, 3.7%). ν_{max} 3270 (NH), 1740, 1650 (CO), 1600 (arom C=C), 1380, 1130 (SO_2), 670 (C–Cl) cm^{-1}. Nmr δ8.86 br (1H, N*H*Ph), 7.65 d (2ArH, J2 Hz), 7.48–6.88 m (5H, C_6H_5). The signal at δ8.86 was removed after D_2O treatment.

Cyclization of 3,5-Dichloro-(N-Phenylcarbamoyloxy)benzenesulfonyl Chloride (**9**)

The N-phenylcarbamoyloxybenzenesulfonyl chloride (0.6 g) was refluxed with triethylamine (0.2 ml) in benzene (10 ml) for 3 h. The solution was diluted with benzene (20 ml) and washed with water (5 × 20 ml), dried ($MgSO_4$), and evaporated. The residue by recrystallization (aq. EtOH), gave the *heterocyclic product* (**10**) (0.5 g, 93%), mp 212–213°. (Found: C, 45.4; H, 2.3; N, 3.9. $C_{13}H_7Cl_2NO_4S$ requires C, 45.4; H, 2.0; N, 4.0%). Nmr δ7.70 d (2 ArH, J 2Hz), 7.60–7.10 m (5H, C_6H_5). Ms. showed the molecular ion (M^+, 344). Tlc (EtOAc-petroleum ether 1 : 1) showed one spot, R_F 0.58.

5-Chloro-4-Hydroxybenzene-1,3-bis-Sulfonyl Chloride

o-Chlorophenol (10 g) was gradually added to chlorosulfonic acid (40.4 ml; 8 mol. equivs.) at 0°. The solution was left at 0° for 1 h, then heated at 100° for 1 h, and poured onto ice. The precipitate was filtered off, washed with water, and dried *in vacuo* (P_2O_5) to give the *bis-sulfonyl* chloride (**8**; X = Cl) (12.5 g, 59%), mp 105–106°. (Found: C, 23.1; H, 1.0; S, 20.9. $C_6H_3Cl_3O_4S_2$ requires C, 23.3; H, 1.0; S, 20.7%). ν_{max} 3350 br (OH, 1580 (arom C=C), 1330, 1180 (SO_2) cm^{-1}.

The *bis*-sulfonyl chloride was converted into the following derivatives:

(a) *1,3-bis-Sulfonamide* (**8**; X = NH_2) (57%), mp 214–215°. (lit.[19] 217°). ν_{max} 3520 (OH), 3380, 3240, 3150 (NH), 1580 (arom C=C), 1330, 1175 (SO_2) cm^{-1}.

(b) *1,3-bis N,N¹-Tetramethylsulfonamide* (**8**; X = $N(CH_3)_2$) (50%), mp 165–166. (Found: C, 35.4; H, 4.4; N, 8.0. $C_{10}H_{15}ClN_2O_5S_2$ requires C, 35.1; H, 4.4; N, 8.2%). ν_{max} 3340 br (OH), 1590 (arom C=C), 1350, 1180 (SO_2), 710 (C–Cl) cm^{-1}. Nmr ($CDCl_3$) δ6.80 br (1H, OH), 6.20 (2ArH), 2.32 s (12H, 2xN(CH_3)$_2$. The signal at δ6.80 was removed after D_2O treatment.

(c) *1,3-bis-sulfonyl azide* (**8**; X = N_3) (90% from CCl_4), mp 129–130°. (Found: C, 21.5; H, 1.2; N, 25.0. $C_6H_3ClN_6O_5S_2$ requires C, 21.3; H, 1.0; N, 24.8%). ν_{max} 3330 (OH), 2175, 2120 (N_3), 1325, 1180 (SO_2) cm^{-1}.

5-Chloro-4-Hydroxybenzene-1,3-bis N-Phenylsulfonohydrazide (**8**; X = NHNHPh)

The 1,3-*bis*-sulfonyl chloride (1 g) was treated with phenylhydrazine (1.4 g; 4 mol. equivs.) in acetonitrile (10 ml) overnight at 4°. The mixture was diluted with ether (50 ml) and washed with water (5 × 50 ml), dried ($MgSO_4$), and evaporated to give the *bis N-phenylsulfonohydrazide* (0.8 g, 57%), mp 115–116° (decomp.) (Found: C, 46.4; H, 3.7; N, 11.6. $C_{18}H_{17}ClN_4O_5S_2$ requires C, 46.1; H, 3.6; N, 11.9%). ν_{max} 3515 br (OH), 3340 (NH), 1610 (arom C=C), 1330, 1175 (SO_2), 700 (C–Cl) cm^{-1}. Nmr δ9.56 s (1H, OH), 8.20 d (1H, H(2), *J* 2Hz), 8.06 d (1H, H(6), *J* 2Hz), 7.44 br (2H, $2SO_2NH$), 7.20–6.74 m (10H, 2 × C_6H_5), 6.86 s (2H, 2PhN*H*). The signals at δ9.56, 7.44, and 6.86 were removed by D_2O treatment.

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