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CHLORINATION OF AROMATIC HALIDES WITH CHLOROSULFONIC ACID

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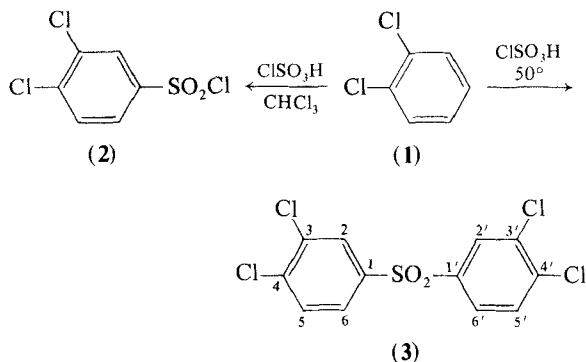
Chlorosulfonic acid–iodine mixture has been shown to chlorinate a number of aromatic halides under mild conditions. In reaction with *p*-dichlorobenzene, the maximum yield (82%) of hexachlorobenzene required 5 mol of chlorosulfonic acid and 2.5 mol of iodine. The yield of product increased with the amount of iodine present. A mechanism of chlorination is proposed involving iodine-catalysed homolytic decomposition of the intermediate sulfonyl chlorides followed by heterolytic chlorination by the evolved iodine monochloride.

The reaction of *o*-, *m*-, and *p*-dichlorobenzenes with chlorosulfonic acid has been investigated. *o*-Dichlorobenzene at 100° gave a good yield (85%) of 3,4,3',4'-tetrachlorodiphenylsulfone although *m*- and *p*-dichlorobenzenes gave only the expected sulfonyl chlorides. This difference arises from the lack of steric hindrance in the *p*-position of *o*-dichlorobenzene leading to facile sulfone formation.

This was confirmed by the observation that 3,4-dichlorobenzenesulfonyl chloride undergoes the Friedel–Crafts reaction with *o*-dichlorobenzene to give 3,4,3',4'-tetrachlorodiphenylsulfone (60%), but *m*- and *p*-dichlorobenzenes did not give any appreciable amounts of the corresponding sulfones under identical conditions.

INTRODUCTION

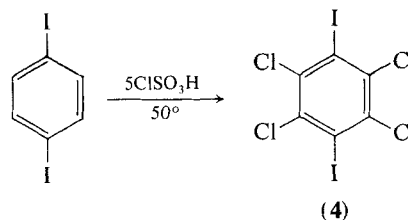
In 1940 Huntress and Carten¹ reported that *o*-dichlorobenzene (1) by reaction with an excess of chlorosulfonic acid in chloroform at room temperature (Procedure 1) gave the expected sulfonyl chloride (2). On the other hand, when the reaction was carried out at 50° in the absence of chloroform (Procedure 2) the major product was 3,4,3',4'-tetrachlorodiphenylsulfone (3):



But with *m*- and *p*-dichlorobenzenes reaction with chlorosulfonic acid by both procedures went normally to give the corresponding sulfonyl chlorides.

Huntress and Carten also observed¹ that the chlorosulfonation of *p*-diiodobenzene at 50° did not

yield the sulfonyl chloride but instead chlorination occurred to give the tetrachlorodiiodobenzene (4):



The reaction of *p*-chloriodobenzene with chlorosulfonic acid was also reported¹ as “unsatisfactory” because the sulfonyl chloride was not obtained, presumably again due to extensive chlorination.

Chlorosulfonic acid is, of course, known² to function as a chlorinating agent for aromatic substrates at comparatively high temperatures: *p*-dichlorobenzene with chlorosulfonic acid is reported³ at 140° to give 1,2,4,5-tetrachlorobenzene, and at 210–220° hexachlorobenzene. There are several references^{1,4–7} to the conversion of 1,2,4,5-tetrachlorobenzene to hexachlorobenzene by prolonged boiling (165°) with chlorosulfonic acid.

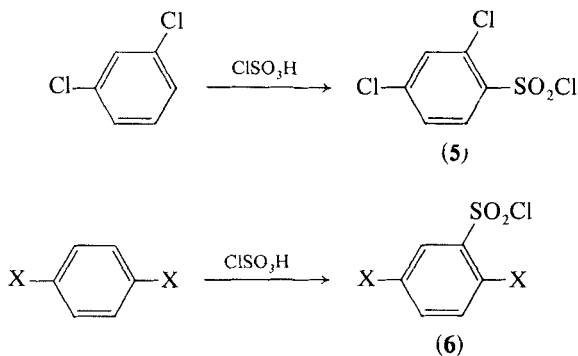
However, the interesting feature of the anomalous reaction of *p*-diiodobenzene with chlorosulfonic acid is that chlorination is achieved under surprisingly mild conditions. These anomalous reactions of chlorosulfonic acid therefore appeared to

merit further study, since they might provide a convenient route to the synthesis of polychlorobenzenesulfonyl derivatives.

DISCUSSION

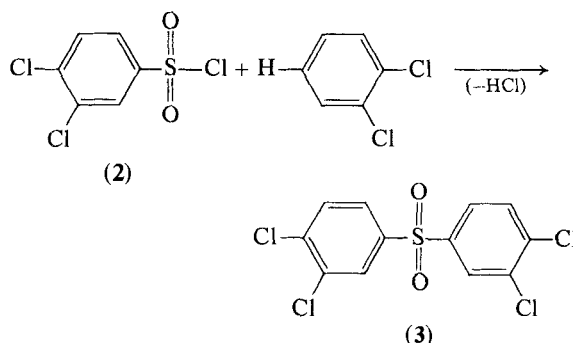
o-, *m*-, and *p*-Dichlorobenzenes were reacted with chlorosulfonic acid in the presence of chloroform at room temperature (Procedure 1) and in the absence of solvent at 65°† (Procedure 2). With *o*-dichlorobenzene (1) procedure 1 afforded a low yield (15%) of the sulfonyl chloride (2) while procedure 2 gave larger amounts (25%) of the sulfone (3). In both cases most of the dichlorobenzene was recovered unchanged; so that while the products are the same as previously reported¹ we discovered that in order to obtain good yields, higher reaction temperatures were needed (see Table II in the Experimental Section). Thus when *o*-dichlorobenzene (1) was treated with chlorosulfonic acid in boiling chloroform (65°) the yield of the sulfonyl chloride (2) was 81%; while reaction with chlorosulfonic acid alone at 100° afforded 85% of the sulfone (3).

In contrast, when *m*- and *p*-dichlorobenzenes and *p*-dibromobenzene were reacted with chlorosulfonic acid only the sulfonyl chlorides were isolated. However, neither *p*-dichloro- nor *p*-dibromo-benzene reacted with chlorosulfonic acid at room temperature, although on heating at 65° or 100° both procedures 1 and 2 afforded good yields (60–99%) of the sulfonyl chlorides (5, 6; X = Cl or Br):

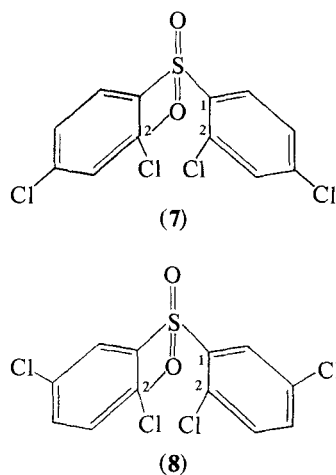


Examination of models of *o*-, *m*-, and *p*-dichlorobenzenes and the corresponding sulfonyl chlorides revealed why sulfone formation only occurred in the reaction of *o*-dichlorobenzene with chlorosulfonic

acid. In this isomer lack of steric hindrance about the chlorosulfonyl group favours the condensation reaction between the sulfonyl chloride (2) and *o*-dichlorobenzene leading to the formation of the 3,4,3',4'-tetrachlorosulfone (3) especially at higher temperatures; at 65° the yield of sulfone was 4% but at 100° was 85% (Table II):



In contrast, with both *m*- and *p*-dichlorobenzenes the condensation reaction leading to the sulfones (7 and 8) will be inhibited by steric hindrance between the 2,2'-chlorine atoms in the sulfones (7 and 8) and consequently only the sulfonyl chlorides (5 and 6) are formed.



To confirm this hypothesis, the Friedel–Crafts reaction between the various dichlorobenzene-sulfonyl chlorides and the corresponding dichlorobenzenes in the presence of aluminium chloride catalyst was examined. 3,4-Dichlorobenzene-sulfonyl chloride (2) condensed with *o*-dichlorobenzene at 100° to give the sulfone (3) (60%), but *m*- and *p*-dichlorobenzenes by reaction with 2,4-dichlorobenzene-sulfonyl chloride or 2,5-dichlorobenzene-sulfonyl chloride did not give appreciable amounts of the sulfones (7 and 8).

† Repetition of Huntress and Carten's original experiment¹ at 50° in the absence of solvent gave a complex mixture of products.

TABLE I

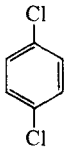
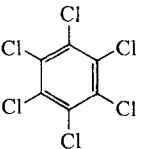
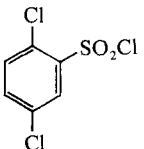
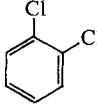
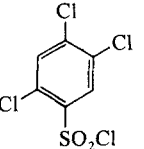
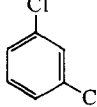
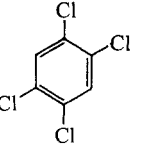
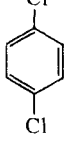
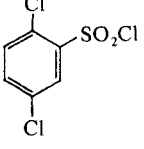
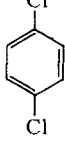
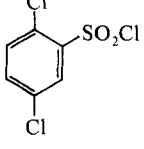
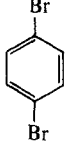
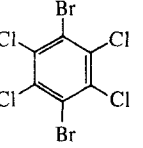
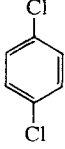
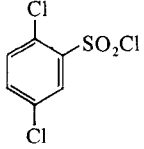

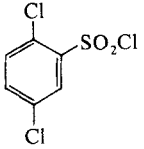
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	X	Y	(A)	(B)
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2		5ClSO ₃ H 0.1 I ₂	C ₆ Cl ₆ (36%) +	 (17%)
3		5ClSO ₃ H 0.1 I ₂	C ₆ Cl ₆ (34%) +	 (16%)
4		5ClSO ₃ H in the dark	C ₆ Cl ₆ (10%) +	 (30%)
5		5ClSO ₃ H uv light	C ₆ Cl ₆ (31%) +	 (13%)
6		5ClSO ₃ H 0.2 I ₂	 (73%)	
7		5ClSO ₃ H 0.05 I ₂		 (72%)
8		5ClSO ₃ H 0.5 I ₂	C ₆ Cl ₆ (65%) +	 (13%)

TABLE I—continued

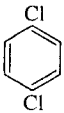
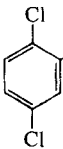

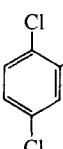
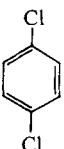
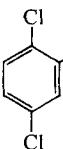
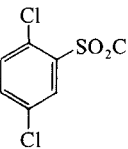
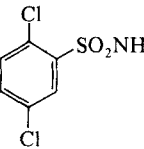
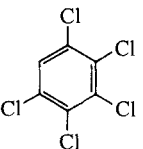
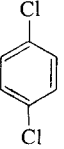
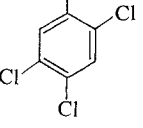
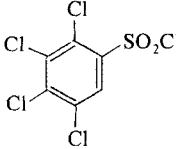
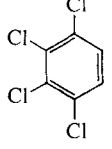
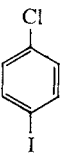
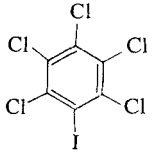
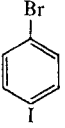
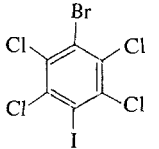
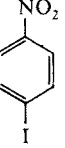
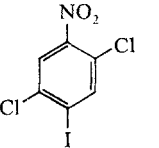
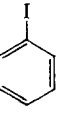
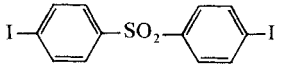
Expt. No.	Reactants		Products	
	X	Y	(A)	(B)
9		5ClSO ₃ H 1.0 I ₂	C ₆ Cl ₆ (76%) +	 (5%)
10		5ClSO ₃ H 2.5 I ₂	C ₆ Cl ₆ (82%) +	 (4%)
11		5ClSO ₃ H 0.1 (PhCO) ₂ O	A similar result also at 100°	 (60%)
12		5ClSO ₃ H 1.0 I ₂	C ₆ Cl ₆ (62%) With 0.1 mol I ₂ there was no reaction	
13		5ClSO ₃ H 1.0 I ₂	 (48%)	
14		5ICl	 (52%)	
15		5ICl	C ₆ Cl ₆ (58%)	
16		5ICl	C ₆ Cl ₆ (69%)	

TABLE I—continued

Expt. No.	Reactants		Products	
	X	Y	(A)	(B)
17		5ClSO ₃ H		(51%)
18		5ClSO ₃ H		(84%)
19		5ClSO ₃ H		(75%)
20		5ClSO ₃ H		(53%)

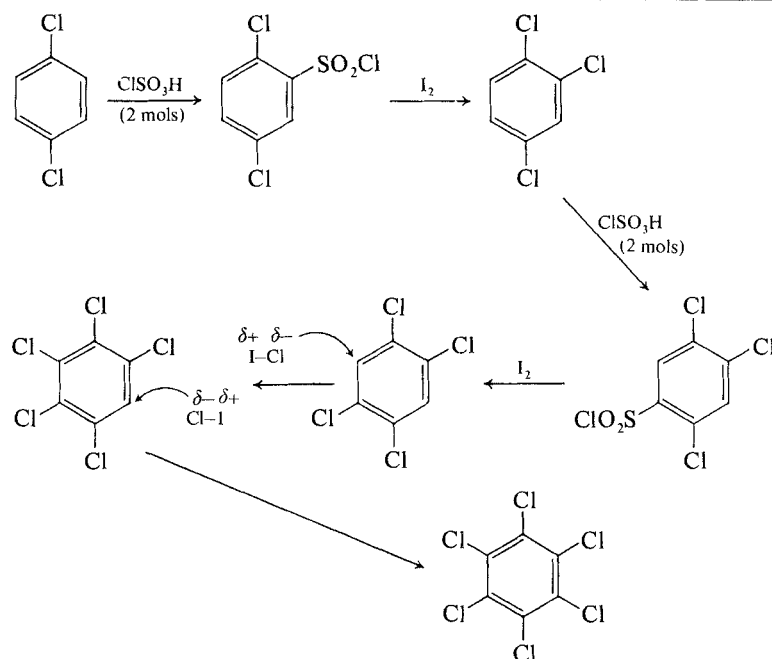
We considered that the facile chlorination of *p*-diiodobenzene by chlorosulfonic acid previously reported¹ may be due to the presence of free iodine in the reaction which promotes chlorination. To test the validity of this hypothesis, various halogeno-aromatic substrates (X) were reacted with chlorosulfonic acid-iodine or iodine monochloride (Y) at 60–80° for 3 h. The results of the experiments (1–20) are summarized in Table I; in each case the % products represent those isolated after crystallization, and the numbers in front of the reactants (Y) are molar equivalents.

In the majority of experiments with chlorosulfonic acid/iodine (1–6, 8–10, 12–13 and 17–19) some chlorination of the aromatic substrate occurred. We found that alteration of the substitution pattern of dichlorobenzenes did not appreciably alter the degree of chlorination (experiments 1–3) although replacement of chlorine by bromine increased the yield of chlorinated product (cf. experiments 1 and 8 with 6). The side products are of interest since these are the likely intermediates in the formation of hexachlorobenzene. This suggestion is

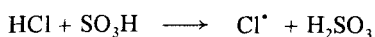
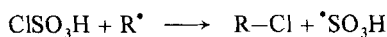
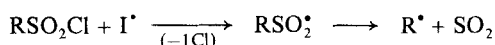
supported by the observation that by products decrease with increasing yield of hexachlorobenzene. Thus in experiments (7–10) the yield of 2,5-dichlorobenzenesulfonyl chloride decreases from 72 to 4% while simultaneously the yield of hexachlorobenzene rises from 0 to 82%. The experiments (7–10) also clearly demonstrate the influence of the quantity of iodine on the degree of chlorination. The maximum yield (82%) of hexachlorobenzene was obtained in the presence of 2.5 moles of iodine which implies that iodine is, at least partially, involved in a heterolytic process. This is probably heterolytic chlorination of the aromatic substrate by iodine monochloride (Scheme 1). Iodine also appears to catalyze the homolytic decomposition of the intermediate sulfonyl chlorides *via* the formation of iodine radicals by homolysis of the relatively weak iodine-iodine bond. Subsequent steps may involve reaction of the aryl free radical with chlorosulfonic acid and with a chlorine radical (Scheme 2). Overall the reaction mechanism depicted in Schemes 1 and 2 requires 5 moles of chlorosulfonic acid and 2 moles of iodine monochloride;

the latter partly arising from interaction of the sulfonyl chlorides with iodine:

13): The sulfonyl chloride gave hexachlorobenzene whereas the corresponding sulfonamide only affor-



SCHEME 1



(R = aromatic substrate)

SCHEME 2

Evidence for free radical chlorination is provided by the influence of light in increasing the degree of chlorination. When *p*-dichlorobenzene was reacted with chlorosulfonic acid-iodine in the absence of light the yield of hexachlorobenzene was only 10% (experiment 4), but in the presence of light the yield increased to 31% (experiments 1 and 5). On the other hand, attempts to replace iodine by dibenzoyl peroxide, a well known radical initiator^{8a}, failed to effect any chlorination (experiment 11). Further evidence for the intermediacy of 2,5-dichlorobenzenesulfonyl chloride in the chlorination of *p*-dichlorobenzene is afforded by experiments (12 and

ded pentachlorobenzene. In both cases the sulfonyl moiety is displaced so the reaction cannot be applied to the synthesis of polychlorobenzenesulfonyl derivatives.

The influence of iodine in promoting low temperature chlorination by chlorosulfonic acid is probably partly due to the formation of iodine monochloride during reaction. Experiments (14-16) show that iodine monochloride will chlorinate chlorobenzenes. Iodine monochloride is a well-known iodinating agent^{8b} for benzene derivatives containing electron-donor groups such as OH and NH₂. On the other hand, heterolytic chlorination by iodine monochloride is unusual, but should be facilitated by the presence of the electron-withdrawing chlorine atoms and probably accounts for the conversion of tetra- to hexa-chlorobenzene (Scheme 1).

In the original experiments, Huntress and Carten¹ observed the chlorination of *p*-di-iodobenzene on treatment with chlorosulfonic acid. We decided to investigate the reaction of some iodobenzene derivatives with chlorosulfonic acid under similar

conditions (Table I, experiments 17–19). In each case chlorination occurred, although with *p*-iodonitrobenzene only two chlorine atoms were introduced into the aromatic nucleus. In this instance, perhaps the bulky nature of the nitro group inhibits further chlorination. In contrast, with iodobenzene no chlorination took place and the product was 4,4'-diiododiphenylsulfone (experiment 20). This surprising result may be due to the lack of steric hindrance in the *p*-position of iodobenzene which facilitates rapid condensation of *p*-iodobenzenesulfonyl chloride with unreacted iodobenzene to give the sulfone.

Scheme 1 involves both 2,5-dichlorobenzenesulfonyl chloride and 1,2,4,5-tetrachlorobenzene which have both been isolated as by products in the chlorination experiments (1 and 3).

Scheme 2 leads to the formation of sulfurous acid, which is in agreement with the reported⁴ isolation of bis(pentachlorophenyl) sulfide as a by product in the high temperature chlorination of 1,2,4,5-tetrachlorobenzene by chlorosulfonic acid; since the sulfide probably arises from reduction of pentachlorobenzenesulfonyl chloride by sulfurous acid.⁴

The chlorination of *p*-dichlorobenzene cannot be due to the presence of chlorine, because when *p*-dichlorobenzene was treated with chlorine gas in hot concentrated sulfuric acid no chlorination was observed.

EXPERIMENTAL

Ir spectra was determined as liquid films or Nujol mulls using a Perkin–Elmer 127 spectrometer. Nmr spectra were measured with a Varian HA 100 spectrometer with tetramethylsilane as internal standard. 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 performed by Butterworth Microanalytical Consultants Ltd., Teddington, England.

General Procedure for Reaction of Dichlorobenzenes with Chlorosulfonic Acid

The dihalogenobenzene was dissolved in dry chloroform and the ice-cold solution treated dropwise with chlorosulfonic acid (5 mol equivs.). After the initial evolution of hydrogen chloride, the solution was left at the temperature under investigation for 2 h, and was poured onto crushed ice. The chloroform layer was separated and washed with H₂O (× 2), and filtered to remove the solid sulfone. The filtrate was distilled *in vacuo* to give the sulfonyl chloride, this was boiled under reflux with ammonia (10 mol equivs. of 0.88) for 15 min. The solid was recrystallized (aq. EtOH) and further purified by dissolution in 2N-aqueous sodium hydroxide solution (to remove traces of the sulfone). The filtrate, on acidification (conc. HCl), afforded the dihalogenobenzenesulfonamide.

The results of the experiments are summarized in Table II, where A = sulfonyl chloride; B = sulfonamide; C = sulfone; D = starting material.

3,4,3',4'-Tetrachlorodiphenylsulfone (3)

o-Dichlorobenzene (2.4 g) was stirred at 0° with 3,4-dichlorobenzenesulfonyl chloride (5 g; 1 mol equiv.) and anhydrous aluminium chloride (1 g) added portionwise. The mixture was heated at 100° for 2 h, poured onto ice-water (80 ml) and extracted with ether (100 ml). The extract was washed with H₂O (2 × 50 ml), dried (MgSO₄), and concentrated to small volume. Cooling gave 3,4,3',4'-tetrachlorodiphenylsulfone (4.5 g, 60%) (from EtOH), mp 178–179° (lit.¹ 175–176°). Nmr (CD₃)₂SO, CDCl₃) δ: 8.40 d (2H, ArH₂H₂, *J*_{2,6}2Hz), 8.16 d (2H, ArH₆H₆, *J*_{5,6}8Hz), 8.07 d (2H, ArH₃H₃, *J*_{5,6}8Hz).

Attempted Preparation of 2,4,2',4'-Tetrachlorodiphenylsulfone by Friedel–Crafts Reaction

m-Dichlorobenzene (1.7 g) was reacted with 2,4-dichlorobenzenesulfonyl chloride (2.8 g; 1 mol equiv.) and aluminium chloride (1 g) under similar conditions. Only unchanged sulfonyl chloride (2 g), mp 48° (lit.¹ 52–53°) was obtained. Tlc (HOAc:BuOH:Et₂O:H₂O 6:9:3:1) showed one spot, *R*_F 0.80. The sulfonyl chloride was characterized by conversion to the sulfonamide (75%), mp 173–174° (lit.¹ 179°).

A similar attempt to prepare 2,5,2',5'-tetrachlorodiphenylsulfone by Friedel–Crafts reaction of 2,5-dichlorobenzenesulfonyl chloride and *p*-dichlorobenzene was also unsuccessful.

Reaction of Dichlorobenzenes with Chlorosulfonic Acid in the Presence of Iodine (Table I)

Chlorosulfonic acid (12 ml; 5 mol equivs.) was added gradually to the dichlorobenzene (5 g) and iodine (0.4 g, 0.1 mol equiv.) and heated at 60–80° for 3 h by which time most of the colour of the iodine had disappeared. The mixture was poured onto ice-water (200 ml), subsequent filtration gave solid crystals (A), and a brown oil (B). The solid (A) was washed with warm H₂O and triturated with pentane. The oil (B), after standing in water, solidified and was recrystallized from petroleum ether (bp 40–60°) and the sulfonyl chloride was characterized as the sulfonamide derivative after recrystallization from aqueous ethanol.

p-Dichlorobenzene (Table I, experiment 1) gave hexachlorobenzene (A) (3 g, 31%), mp 198–200° (lit.¹ 218–219°). The ir spectrum showed absence of C–H bonds and was identical to that of authentic hexachlorobenzene. Product (B) was 2,5-dichlorobenzenesulfonyl chloride (2.7 g, 33%), mp 38° (lit.¹ 38°). *v*_{max} 1370, 1180 (SO₂), 690 (C–Cl) cm⁻¹; the ir spectrum was identical to that of the authentic sulfonyl chloride. 2,5-Dichlorobenzenesulfonamide was prepared (94%), mp 179° (lit.¹ 179°). *v*_{max} 3380, 3270 (NH₂), 3090 (C–H), 1550 (arom C=C), 1350, 1170 (SO₂), 680 (C–Cl) cm⁻¹.

o-Dichlorobenzene (Table I, experiment 2) gave hexachlorobenzene (A) (3.5 g, 36%), mp 198–200° (mmp with an authentic sample of hexachlorobenzene 215–218°). Product (B) was 2,4,5-trichlorobenzenesulfonyl chloride (1.6 g, 17%), mp 30–31° (lit.¹ 31°). Reaction with ammonia gave 2,4,5-trichlorobenzenesulfonamide (90%), mp 219–220° (lit.¹ > 200°) (mmp with authentic 2,4,5-trichlorobenzenesulfonamide was 217–220°). *v*_{max} 3360, 3250 (NH₂), 3080 (Ar–H), 1330, 1170 (SO₂), 680 (C–Cl) cm⁻¹. (Found: C, 27.6; H, 1.6; N, 5.3. Calc. for C₆H₄Cl₃NO₂S: C, 27.6; H, 1.5; N, 5.4%.)

TABLE II

Dihalogenobenzene	Experimental conditions Temp. (°C); Time (h); ClSO ₃ H (mol); solvent	Product(s); % Yield; mp (°C)	Lit. mp (°C)
<i>o</i> -Dichloro	23; 2; 3; CHCl ₃	A; 15; Oil B; 15; 134 C; 8; 170 D; 75	135 ¹ , 140 ^{10c} 175 ¹
<i>o</i> -Dichloro-	65; 2; 3; CHCl ₃	A; 81; Oil B; 81; 134 C; 4 D; 15	135 ¹ , 140 ^{10c}
<i>o</i> -Dichloro-	100; 2; 3; ClSO ₃ H	A; 10 B; 10; 134 C; 75; 170 D; 15	135 ¹ , 140 ^{10c} 175 ¹
<i>o</i> -Dichloro-	65; 2; 5; CHCl ₃	A; 86 B; 82; 134 ^a C; 4; 170 D; 10	135 ¹ , 140 ^{10c} 175 ¹
<i>o</i> -Dichloro-	100; 2; 5; ClSO ₃ H	C; 85; 171 ^b	175 ¹
<i>m</i> -Dichloro-	23; 2; 5; CHCl ₃	A; 21; 50	52 ¹ , 55 ^{10c}
<i>m</i> -Dichloro-	65; 2; 5; CHCl ₃	A; 65; 50 B; 60; 178	52 ¹ , 55 ^{10c} 179 ¹ , 182 ^{10c}
<i>m</i> -Dichloro-	100; 2; 5; ClSO ₃ H	A; 88; 50 B; 80; 178	52 ¹ 179 ¹ , 182 ^{10c}
<i>p</i> -Dichloro-	23; 2; 5; ClSO ₃ H	No reaction	
<i>p</i> -Dichloro-	23; 2; 5; CHCl ₃	No reaction	
<i>p</i> -Dichloro-	65; 2; 5; CHCl ₃	A; 93; 35 B; 85; 177	38 ¹ , 39 ⁹ , 37 ^{10c} 179 ¹ , 181 ⁹ , 185–186 ^{10c}
<i>p</i> -Dichloro-	100; 2; 5; CHCl ₃	A; 94; 35 B; 85; 177	38 ¹ , 39 ⁹ , 37 ^{10c} 179 ¹ , 181 ⁹ , 185–186 ^{10c}
<i>p</i> -Dibromo-	23; 2; 5; CHCl ₃	No reaction	
<i>p</i> -Dibromo-	23; 2; 5; ClSO ₃ H	No reaction	
<i>p</i> -Dibromo-	65; 2; 5; CHCl ₃	A; 93; 68 ^c	71 ¹ , 10d
<i>p</i> -Dibromo-	100; 2; 5; ClSO ₃ H	A; 99; 68	71 ¹ , 10d

^a Found: C, 31.9; H, 2.2; N, 5.9%. Calc. for C₆H₅Cl₂NO₂S: C, 31.9; H, 2.2; N, 6.1%. Nmr (CD₃)₂SO, CDCl₃) δ : 8.34–7.50 m (3ArH), 7.60 s (2H, NH₂). The signal at δ 7.60 was removed by D₂O treatment.

^b Found: C, 40.5; H, 1.8; S, 9.2. Calc. for C₁₂H₆Cl₄O₂S: C, 40.5; H, 1.7; S, 9.0%. Nmr (CD₃)₂SO, CDCl₃) δ : 8.40 d (2H, ArH₂H₂, $J_{2,6}$ 2Hz), 8.16 d (2H, ArH₆H₆, $J_{5,6}$ 8Hz), 8.07 d (2H, ArH₅H₅, $J_{5,6}$ 8Hz) (see formula 3, p. 2).

^c Nmr (CD₃)₂SO, CDCl₃) δ : 8.45 d (1H, ArH₆, $J_{4,6}$ 2Hz), 7.90 s (2ArH).

m-Dichlorobenzene (Table I, experiment 3) gave hexachlorobenzene (A) (3.3 g, 34%), mp 209–210°. Product (B) was 1,2,4,5-tetrachlorobenzene (1.2 g, 16%), mp 134–135° (lit.^{10a} 139.5–140.5°). The ir spectrum was identical to that of 1,2,4,5-tetrachlorobenzene and the mmp with an authentic sample was 133–137°. (Found: C, 33.5; H, 1.1. Calc. for C₆H₂Cl₄: C, 33.3; H, 0.90.) Sodium fusion test showed absence of sulfur.

(b) In Ultra-violet light (Table I, experiment 5) the analogous reaction gave hexachlorobenzene (A) (3.1 g, 31%), and 2,5-dichlorobenzenesulfonyl chloride (B) (1.1 g, 13%), mp 38–39° (lit.¹ 38°), characterized as the sulfonamide (94%), mp 178–179° (lit.¹ 179°). ν_{\max} 3375, 3270 (NH₂), 3090 (ArC–H), 1340, 1170, (SO₂), 685 (C–Cl) cm⁻¹.

Reaction of *p*-Dibromobenzene with Chlorosulfonic Acid and Iodine (Table I, experiment 6)

Chlorosulfonic acid (12.3 g; 5 mol equivs.) was gradually added to a mixture of *p*-dibromobenzene (5 g) and iodine (0.6 g; 0.2 mol equiv.) at 0° and then warmed at 70° for 3 h. The mixture was poured onto ice to give 1,4-dibromo-2,3,5,6-tetrachlorobenzene (A) (5.8 g, 73%), mp 224–225° (decomp.) (lit.¹¹ 246–247° decomp.) (Found: C, 18.9; Cl, 37.7. Calc. for C₆Br₂Cl₄: C, 19.3; Cl, 38.0%).

With *p*-Dichlorobenzene (a) in the Dark (Table I, experiment 4)

Product (A) was hexachlorobenzene (1 g, 10%) mp 219–220° and product (B) was 2,5-dichlorobenzenesulfonyl chloride (2.5 g, 30%), mp 38–39° (lit.¹ 38°) which was converted to the corresponding sulfonamide (93%), mp 178–179° (lit.¹ 179°).

Reaction of p-Dichlorobenzene and Chlorosulfonic Acid in Presence of Different Amounts of Iodine

Chlorosulfonic acid (12 ml; 5 mol equivs.) was added to *p*-dichlorobenzene (5 g) with iodine (0.05–2.5 mol equivs.) (experiments 7–10). After 15 min in sunlight and heating at 60–80° for 2½ h, the mixture was poured onto ice-water and the precipitated solid weighed and shaken with 10% aqueous NaOH and water (to remove the sulphonamide as the sodium salt). Filtration gave hexachlorobenzene (A) and the filtrate by acidification (concentrated HCl) afforded the sulfonyl chloride (B), characterized as the sulfonamide. With large amounts of iodine, the crude solid needed to be well washed with warm H₂O and treated with sodium thiosulfate (50 ml of 30% solution) to remove the excess iodine. The results of these experiments are shown in Table I (experiments 7–10).

Reaction in Presence of Dibenzoyl Peroxide (Table I, experiment 11)

Chlorosulfonic acid (12 ml; 5 mol equivs.) was gradually added to *p*-dichlorobenzene (5 g) and dibenzoyl peroxide (0.8 g, 0.1 mol equiv.). The mixture was heated at 60–80° for 3 h to give 2,5-dichlorobenzenesulfonyl chloride (B) (5 g, 60%), mp 36–37° (lit.¹ 38°) and characterized as the sulfonamide (78%), mp 175–176° (lit.¹ 179°).

A similar result was obtained when the reaction was carried out at 100° for 3 h.

Reaction of 2,5-Dichlorobenzenesulfonyl Chloride with Chlorosulfonic Acid–Iodine (Table I, experiment 12)

Chlorosulfonic acid (7 ml; 5 mol equivs.) was gradually added to a mixture of 2,5-dichlorobenzenesulfonyl chloride (5 g) and iodine (1.3 g; 1 mol equiv.). After heating at 60° for 3 h the reaction gave hexachlorobenzene (A) (3.5 g, 62%) from EtOH, mp 209–210°. In a similar experiment using less iodine (0.1 mol equiv.) the only isolated product was 2,5-dichlorobenzenesulfonyl chloride (B).

Reaction of 2,5-Dichlorobenzenesulfonamide with Chlorosulfonic Acid–Iodine (Table I, experiment 13)

2,5-Dichlorobenzenesulfonamide (3 g) was similarly reacted with chlorosulfonic acid (5 ml; 5 mol equivs.) and iodine (1.3 g; 1 mol equiv.) to give pentachlorobenzene (A) (1.6 g; 48%) (from EtOH), mp 86–87° (lit.^{10b} 86%). Mmp with an authentic sample was 84–86°.

Reaction of Halogenobenzenes with Iodine Monochloride (Table I, experiments 14–16)

(a) *p*-Dichlorobenzene (5 g) was added to a mixture of iodine monochloride (27.1 g; 5 mol equivs.) and concentrated sulfuric acid (10 ml) at 0°. The solution was heated at 60–80° for 3 h and poured onto ice water to give 1,2,4,5-tetrachlorobenzene (A) (3.6 g, 50%), mp 137–139° (CH₃CN) (lit.^{10a} 139.5–140.5°) (mmp with the authentic material was 137–139°). The ir spectrum also corresponded with that of 1,2,4,5-tetrachlorobenzene. (Found: C, 33.1; H, 0.8; Cl, 66.0; I, 0. Calc. for C₆H₂Cl₄: C, 32.8; H, 0.6; Cl, 66.3%.)

A similar experiment in the absence of sulfuric acid gave 1,2,4,5-tetrachlorobenzene (A) (52%), mp 136–138°.

(b) 2,3,4,5-Tetrachlorobenzenesulfonyl chloride similarly gave hexachlorobenzene (58%), mp 210–211°.

(c) 1,2,3,4-Tetrachlorobenzene similarly afforded hexachlorobenzene (69%) mp 209–210°.

Reactions of Iodobenzenes with Chlorosulfonic Acid (Table I, experiments 17–20)

(a) With *p*-Chloriodobenzene. *p*-Chloriodobenzene (5 g) was heated with chlorosulfonic acid (12.5 g; 5 mol equivs.) at 60° for ½ h. Vigorous evolution of sulfur dioxide was observed and the mixture was poured onto ice-water to give pentachloriodobenzene (A) (3.6 g, 51%), mp 209° (lit.¹² 210–211°). (Found: C, 18.9; Cl, 47.0; I, 33.9. Calc. for C₆Cl₅I: C, 19.2; Cl, 47.1; I, 33.7%.)

(b) *p*-Bromiodobenzene. Chlorosulfonic acid (5 mol equivs.) at 60–80° for 3 h gave 4-bromo-2,3,5,6-tetrachloriodobenzene (A) (84%), mp 209–210°. (Found: C, 17.4; H, 0.0; Br, 18.9; Cl, 34.0. C₆BrCl₄I requires: C, 17.1; H, 0.0; Br, 19.0; Cl, 33.7%.) The ir spectrum indicated absence of C–H bonds and the SO₂ group. Tlc (Pr¹OH:toluene:EtOAc:H₂O 5:1:2:5) showed a single spot *R_f* 0.79.

(c) *p*-Iodonitrobenzene. Reaction under similar conditions to (b) gave 2,5-dichloro-4-iodonitrobenzene (A) (75%), mp 98–99° (from EtOH). (Found: C, 25.6; H, 1.1; Cl, 12.8. C₆H₂Cl₂INO₂ requires C, 25.4; H, 1.1; Cl, 12.5%.) *v*_{max} 3080 (ArC–H), 1520, 1340 (NO₂), 680 (C–Cl) cm⁻¹. Tlc (Pr¹OH:toluene:EtOAc:H₂O 5:1:2.5:1.25) showed a single spot, *R_f* 0.80.)

(d) Iodobenzene under similar conditions to (b) and (c) gave 4,4'-di-iododiphenylsulfone (53%) (from CH₃CN), mp 203–204° (lit.¹ 201–202°). *v*_{max} 3080 (ArC–H), 1370, 1170 (SO₂) cm⁻¹. Sodium fusion was positive for S, but negative for Cl.

Attempted Reaction of p-Dichlorobenzene with Chlorine

p-Dichlorobenzene (10 g) was dissolved in concentrated sulfuric acid (20 ml) and chlorine gas bubbled through the hot solution (80°) for 3 h. The mixture was poured onto ice to give unchanged *p*-dichlorobenzene (8.8 g), mp 48–50° (from petroleum ether bp 40–60°) (lit.^{10c} 54–56°) (mmp with authentic *p*-dichlorobenzene was 48–50°). The ir spectrum was identical to that of *p*-dichlorobenzene. Tlc (EtOAc:petroleum ether 1:1) showed a single spot, *R_f* 0.74. An authentic sample of *p*-dichlorobenzene had a similar *R_f* value.

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