888. *The Action of Sulphur Monochloride on Aromatic Hydrocarbons.*

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The uncatalysed action of sulphur monochloride on aromatic hydrocarbons has been studied. Many of the more reactive hydrocarbons give di-, tri-, or tetra-sulphides. The chlorodithio-derivative ($R{\cdot}S_2Cl$) * obtained from anthracene is readily converted into a tetrasulphide; while naphthacene gives a di(chlorodithio-derivative). Possible mechanisms of the reactions are discussed.

A VARIETY of products has been reported by different workers as formed by the action of sulphur monochloride, S_2Cl_2, on aromatic hydrocarbons in presence of catalysts such as aluminium, aluminium chloride, and iodine. For example, linear sulphides, thianthrene, and thianthrene polymers have been made from benzene,[1] polymeric sulphides from naphthalene [2,3] and anthracene,[2] and ClS_2-derivatives from naphthalene,[4] anthracene,[5] 1,2-benzanthracene, 3,4-benzopyrene, and 10-methyl-1,2-benzanthracene.[6] Some of the results are so unusual as to merit further investigation, and as a whole the work has not been logically developed. This paper describes the reaction of sulphur monochloride on aromatic hydrocarbons, usually at room temperature, with an inert solvent, and without a catalyst. The annexed Table lists the compounds and their products.

Hydrocarbon	Product	Hydrocarbon	Product
$C_6H_3Me_3$, 1,2,4-	R_2S_2	Naphthalene	$(RS)_x$
1,3,5-	R_2S_2, R_2S_4	Anthracene	RS_2Cl, R_2S_4
$C_6H_2Me_4$, 1,2,3,5-	R_2S_3, R_2S_4	Naphthacene	$X(S_2Cl)_2$
1,2,4,5-	R_2S_4		
C_6HMe_5	R_2S_3		

There was no reaction, with benzene, toluene or the xylenes, or with t-butylbenzene, di- and tri-phenylmethane, triphenylbenzene, fluorene, phenanthrene, pyrene, or chrysene under our conditions. Activation of the benzene nucleus by three or more methyl groups is sufficient.

The products listed were readily isolated from the reaction mixture but it is not claimed that they were the sole products; indeed simultaneous formation of mono- and polysulphides in such reactions has often been observed.[7]

The di-(2,4,5-trimethylphenyl) disulphide obtained from 1,2,4-trimethylbenzene and the related thiol are inadequately identified in the literature. Cohen and Skirrow [8] obtained a thiol, m. p. 87—90°, which they believed to be identical with a compound, m. p. 86—87°, isolated by Beilstein and Kögler.[9] Radloff [10] gave m. p. 85° for this compound, and by its oxidation prepared a disulphide, m. p. 115°; analytical data for these compounds are missing or incomplete. The thiol, m. p. 92°, and disulphide, m. p. 89°, have now been synthesized from 1,2,4-trimethylbenzene by the routes illustrated. The

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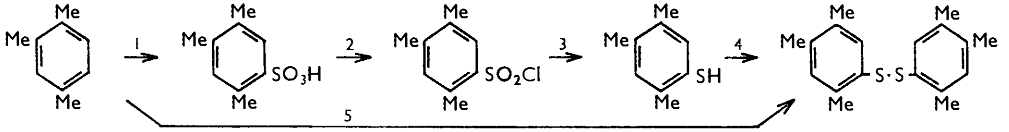
* Formerly known as dithiochlorides.

[1] Schmidt, *Ber.*, 1878, **11**, 1168; Damanski and Kostic, *Bull. Soc. chim. Beograd*, 1948, **13**, 209.
[2] Damanski and Kostic, *Bull. Soc. chim. Beograd*, 1947, **12**, 243.
[3] Damanski and Binenfeld, *Compt. rend.*, 1959, **249**, 1678; *Bull. Soc. chim. France*, 1961, 679.
[4] Airan and Shah, *J. Indian Chem. Soc.*, 1945, **22**, 359.
[5] Lippmann and Pollak, *Ber.*, 1901, **34**, 2767.
[6] Wood and Fieser, *J. Amer. Chem. Soc.*, 1940, **62**, 2674.
[7] Wieland, Weiberg, Fischer, and Hörlein, *Annalen*, 1954, **587**, 146; Roberts, Wiles, and Kent, *J.*, 1932, 1792; Ariyan and Wiles, unpublished work.
[8] Cohen and Skirrow, *J.*, 1899, **75**, 887.
[9] Beilstein and Kögler, *Annalen*, 1866, **137**, 317.
[10] Radloff, *Ber.*, 1878, **11**, 32.

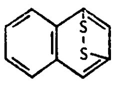
disulphides obtained by the two methods were identical. The thiol was readily distinguished by its solubility in alkali and its infrared spectrum (SH stretching band at 2550 cm.$^{-1}$).



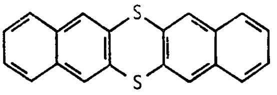
Reagents: 1, H_2SO_4. 2, PCl_5 + Na salt. 3, Zn–H_2SO_4. 4, $FeCl_3$. 5, S_2Cl_2.

The ready formation of a trisulphide from pentamethylbenzene shows the absence of steric effects. It has been considered [11] that steric hindrance in forming polysulphides is only encountered when the groups concerned are larger than isopropyl or phenyl. This statement must, however, be modified when the approach of a sulphur monochloride molecule to a hydrogen atom is involved in forming sulphides from hydrocarbons. Thus 1,3,5-triphenylbenzene in which there is steric repulsion between hydrogen atoms [12] did not react with sulphur monochloride in our uncatalysed reaction; di- and tri-phenylmethane, both non-planar, were also unreactive, though the former with an aluminium–mercury catalyst gives dibenzylthianthrene.[13]

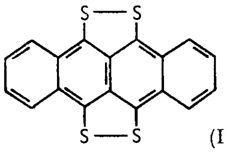
Naphthalene reacts with sulphur monochloride under many different conditions. Heating with zinc chloride gave a resin considered to be a mixture of naphthyl sulphides and polysulphides.[14] With a trace of bismuth chloride a ClS_2-derivative has been reported,[4] and in acetic acid at 100° without a catalyst a disulphide (I) [15] (no molecular weight was published for this compound) was obtained.



(I)



(II)



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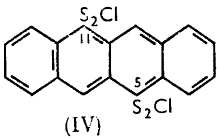

(IV)

The dibenzothianthrene (II) is said to have been obtained from naphthalene with aluminium as catalyst but again no molecular weight was given.[2] Later work [3] yielded two isomeric polymeric disulphides.

We failed to obtain the ClS_2-derivative isolated by Airan and Shah [4] under their conditions and also with modifications. The products were always polymeric sulphides of molecular weight *ca.* 550, probably formed from an intermediate ClS_2-derivative. Our experience is that such derivatives are readily hydrolysed, and it is difficult to understand how recrystallisation of this compound from hydroxylic solvents could have been effected by the Indian workers.

Friedländer and Simon [16] obtained 9-chlorodithioanthracene from anthracene and sulphur monochloride. This compound, stirred in ethereal solution in the dark, has now given the 9-anthryl tetrasulphide, m. p. 190° (*M* 460), a type of reaction not hitherto observed.

Shingte, Rege, Pishavikar, and Shah [15] treated anthracene and sulphur monochloride in glacial acetic acid. They reported a disulphide, m. p. 180° (no molecular weight given), which they considered to be 9,10-epidithioanthracene, but other attempts [17] to prepare this disulphide failed and the product of m. p. 180° was probably our tetrasulphide.

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[11] Pearson, Caine, and Field, *J. Org. Chem.*, 1960, **25**, 867.

[12] Pauling, "The Nature of the Chemical Bond," Oxford Univ. Press, 3rd edn., 1960, p. 293.

[13] Rây, *J.*, 1921, **119**, 1959.

[14] Signaigo, U.S.P. 2,402,685/1946.

[15] Shingte, Rege, Pishavikar, and Shah, *J. Univ., Bombay*, 1952, **21**, 28.

[16] Friedländer and Simon, *Ber.*, 1922, **55**, 3969.

[17] Hiyama, Ito, and Noguchi, *J. Chem. Soc. Japan*, 1949, **52**, 252.

Marschalk and his co-workers[18] treated naphthacene with sulphur monochloride in 1,2,4-trichlorobenzene at 125°. 5,11-Dichloronaphthacene was first formed and this was then converted into the tetrasulphide (III). We found that this reaction, at ordinary temperature, without a solvent, gave a red, granular material which was rapidly hydrolysed in moist air. This was a di(chlorodithio)-derivative, probably (IV), a type not previously authenticated. We assign the substituents to the 5,11-positions by analogy with the dichloride just mentioned.

Reaction Mechanisms.—For the formation of linear sulphides, thianthrenes, and chlorodithio-compounds by the action of sulphur monochloride on aromatic hydrocarbons there are three possible explanations.

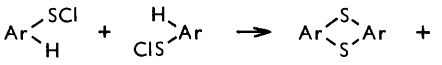
(i) The conversion of sulphur monochloride into other sulphur halides, and subsequent reaction of these with the aromatic compound. Many different equilibria involving sulphur monochloride have been postulated, *e.g.*:

$$S_2Cl_2 \rightleftharpoons SCl_2 + S$$
$$S_2Cl_2 + S \rightleftharpoons S_3Cl_2$$
$$S_2Cl_2 + SCl_2 \rightleftharpoons S_3Cl_4$$

Patrick and Hackerman[19] found that the molecular weight of dilute solutions of sulphur monochloride changed with time, temperature, nature of the solvent, and concentration. Spong[20] showed the density to be altered if the compound is heated at 100° or irradiated by ultraviolet light. Many sulphur chlorides (chlorosulphanes) have now been characterised by Fehér and his co-workers,[21] but the reactions with hydrocarbons have not been studied. The existence of these compounds as intermediates could explain the production of mono- and poly-sulphides. Monosulphides did not react further with sulphur monochloride under our conditions.

(ii) The formation of a chlorodithio-derivative ($R{\cdot}S_2Cl$) and hydrogen chloride, the former then condensing with the aromatic hydrocarbon to give a disulphide or eliminating chlorine to give a tetrasulphide. An example of the former reaction is the condensation of *o*-(chlorodithio)nitrobenzene with anthracene to give 9-anthryl *o*-nitrophenyl disulphide.[22] We have discovered one of the latter in conversion of 9-chlorodithioanthracene into di-9-anthryl tetrasulphide in ethereal suspension in the dark.

(iii) The formation of a sulphenyl chloride (RSCl) by homolytic or heterolytic fission of sulphur monochloride. The sulphenyl chloride could then condense with an aromatic hydrocarbon to give a monosulphide or eliminate chlorine to give a disulphide. The former of these reactions is exemplified by the Friedel–Crafts condensations of 2,4-dinitrobenzenesulphenyl chloride with a series of hydrocarbons,[23] the latter by the rapid conversion of naphthalene-2-sulphenyl chloride into the disulphide in dry air.[24] Equally thianthrenes could result from sulphenyl chlorides (see i), suggested by Fries[25] though he could not obtain them in this way. During the present work we have had indications that thianthrene and thianthrene polymers can be obtained from benzenesulphenyl chloride but no sulphenyl chloride was obtained by the direct use of sulphur monochloride.



$$Ar\genfrac{}{}{0pt}{}{SCl}{H} + \genfrac{}{}{0pt}{}{H}{ClS}Ar \longrightarrow Ar\genfrac{}{}{0pt}{}{S}{S}Ar + 2HCl \quad \cdots\cdots\cdots \quad (i)$$

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[18] Marschalk and Stumm, *Bull. Soc. chim. France*, 1948, 418; Clar and Marschalk, *ibid.*, 1950, 433.
[19] Patrick and Hackerman, *J. Phys. Chem.*, 1936, **40**, 679.
[20] Spong, *J.*, 1934, 485.
[21] Fehér, *Chem. Soc. Special Publ.*, No. 12, 1958, 305.
[22] Harris, Ph.D. Thesis, Univ. of Pennsylvania, 1953.
[23] Buess and Kharasch, *J. Amer. Chem. Soc.*, 1950, **72**, 3529.
[24] Zincke and Eismayer, *Ber.*, 1918, **51**, 751.
[25] Fries, *Ber.*, 1912, **45**, 2965.

If a chlorodithio-derivative and a sulphenyl chloride were formed simultaneously their interactions would explain the variety of products which arise.

Of the three mechanisms, only the formation of a chlorodithio-derivative by reaction of an aromatic hydrocarbon (*e.g.*, anthracene) and sulphur monochloride is definitely established. Although the formation of a sulphenyl chloride in this type of reaction has never been observed, there is no reason why sulphur monochloride should not be polarised as $\mathrm{Cl{-}\overset{\delta+}{S}{-}\overset{\delta-}{S}{-}Cl}$ and then undergo heterolysis. Bateman, Moore, and Porter[26] have concluded that homolysis of disulphide bonds is restricted to reactions involving photo-initiation, high temperature, or attack by other radicals. In favour of heterolytic fission are the catalysed reactions of aromatic hydrocarbons and sulphur monochloride, and it is noteworthy that the hydrocarbons which we find to react most readily with this reagent are (with the exception of durene) those which couple with reactive diazonium salts.

EXPERIMENTAL

General Procedure.—Commercial sulphur monochloride (500 g.) was purified by distillation from sulphur (20 g.) and charcoal (5 g.). The fraction of b. p. 135—137° was stored in a dark bottle in a refrigerator. To the redistilled hydrocarbon in sodium-dried " AnalaR " ether was added the calculated quantity of sulphur monochloride in ether. The mixture was left in daylight (usually for some days) until a sample did not deposit sulphur when treated with water. It was then shaken with sodium carbonate solution, the ethereal layer was dried, the ether removed, and the oily product steam-distilled. The residue was then again extracted with ether, dried, and recovered. The compound usually crystallised. In some cases the oil was chromatographed on an alumina column.

Di-(2,4,5-*trimethylphenyl*) *Disulphide.*—1,2,4-Trimethylbenzene (22 g., 0·2 mole) and sulphur monochloride (13·5 g., 0·1 mole) were left in ether (200 ml.) for 5 days. Repeated recrystallisation from light petroleum (b. p. 40—60°) gave a pale yellow solid, m. p. 88—89° (64%) (Found: C, 71·3; H, 7·7; S, 21·2. $C_{18}H_{22}S_2$ requires C, 71·5; H, 7·3; S, 21·2%).

2,4,5-*Trimethylbenzenethiol.*—2,4,5-Trimethylbenzenesulphonyl chloride[27] (10·2 g., 0·05 mole) was added in small portions with stirring during ½ hr. to ice (72 g.) and 98% sulphuric acid (13 ml.), and the mixture kept at between −5° and 0° during addition of zinc dust (12 g.), then was refluxed for 4—6 hr. The *thiol* was removed in steam and recrystallised from alcohol as plates, m. p. 92° (62%) (Found: C, 70·6; H, 7·8; S, 21·4. $C_9H_{12}S$ requires C, 71·0; H, 7·9; S, 21·1%).

40% Aqueous ferric chloride (10 ml.) was added to the thiol (1·5 g., 0·01 mole) in acetic acid (5 ml.), and the mixture was boiled. A yellow compound, insoluble in alkali, separated after a short time. Recrystallised from alcohol it had m. p. 89° alone or mixed with the compound obtained by reaction of 1,2,4-trimethylbenzene and sulphur monochloride as above.

Di-(2,4,6-*trimethylphenyl*) *Tetra- and Di-sulphide.*—A mixture of 1,3,5-trimethylbenzene (22 g., 0·2 mole) and sulphur monochloride (13·5 g., 0·1 mole) in ether (200 ml.) was left for 4 days. Treatment according to the general procedure and recrystallisation from light petroleum (b. p. 40—60°) gave a yellow *tetrasulphide*, m. p. 100° (42%) [Found: C, 59·6; H, 6·1; S, 34·4%; *M* (cryoscopic in C_6H_6), 360. $C_{18}H_{22}S_4$ requires C, 59·0; H, 6·1; S, 34·9%; *M*, 367]. The petroleum filtrate, on evaporation, gave the disulphide as an orange oil which crystallised. Repeated recrystallisation from light petroleum gave yellow needles, m. p. 125° (19%) in agreement with Holtmeyer[28] (Found: C, 72·0; H, 7·7; S, 20·9. Calc. for $C_{18}H_{22}S_2$: C, 71·5; H, 7·3; S, 21·2%).

Di-(2,3,4,6-*tetramethylphenyl*) *Tri- and Tetra-sulphide.*—1,2,3,5-Tetramethylbenzene (1·3 g., 0·01 mole) and sulphur monochloride (1·3 g., 0·01 mole) were left in ether (20 ml.) for 1 week. The usual treatment gave the *tetrasulphide* as a yellow oil (43%) which boiled with decomposition under reduced pressure (Found: C, 60·0; H, 6·5; S, 33·2. $C_{20}H_{26}S_4$ requires C, 60·9; H, 6·6; S, 32·5%).

This reaction, but at 100° for 2 hr., gave the *trisulphide* as a light yellow oil (62%) which

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[26] Bateman, Moore, and Porter, *J.*, 1958, 2866.

[27] Schreinemakers, *Rec. Trav. chim.*, 1897, **16**, 411.

[28] Holtmeyer, *Z. Chem.*, 1867, 688.

boiled with decomposition under reduced pressure (Found: C, 65·8; H, 6·9; S, 27·2. $C_{20}H_{26}S_3$ requires C, 66·3; H, 7·2; S, 26·5%).

Di-(2,3,5,6-*tetramethylphenyl*) *Tetrasulphide*.—1,2,4,5-Tetramethylbenzene (13·4 g., 0·1 mole) and sulphur monochloride (13·5 g., 0·1 mole) were left in ether (200 ml.) for 5 days. The usual procedure gave, after repeated recrystallisation from light petroleum–acetone, the pale-yellow *tetrasulphide*, m. p. 165° (55%) (Found: C, 61·3; H, 6·7; S, 32·0. $C_{20}H_{26}S_4$ requires C, 60·9; H, 6·6; S, 32·5%).

Di(*pentamethylphenyl*) *Trisulphide*.—Pentamethylbenzene (7·4 g., 0·05 mole) and sulphur monochloride (6·25 g., 0·05 mole) were left in ether for 1 week. The precipitated *trisulphide*, when recrystallised several times from benzene, was pale yellow and had m. p. 189° (43%) (Found: C, 67·9; H, 7·6; S, 24·3. $C_{22}H_{30}S_3$ requires C, 67·6; H, 7·7; S, 24·6%).

Naphthyl Polysulphide.—Naphthalene (12·8 g., 0·1 mole) and sulphur monochloride (13·5 g., 0·1 mole) were left in ether for 10 days. A yellow, amorphous solid containing C, H, and S was isolated [*M* (Rast), *ca*. 550].

9-*Chlorodithioanthracene*.—Sulphur monochloride (13·5 g., 0·1 mole) was poured on anthracene (8·9 g., 0·05 mole). After a short time vigorous evolution of hydrogen chloride occurred. When this was complete red needles separated. This derivative, when washed with ether and then light petroleum, had m. p. 117—118° (90%) (Found: C, 60·3; H, 3·0; Cl, 12·4; S, 22·7. Calc. for $C_{14}H_9ClS_2$: C, 60·7; H, 3·3; Cl, 12·8; S, 23·2%).

Di-9-*anthryl Tetrasulphide*.—The foregoing derivative (13·8 g., 0·05 mole) was suspended in ether (200 ml.) and stirred in the dark for one day. Removal of the ether and recrystallisation from benzene gave the tetrasulphide as orange plates, m. p. 190° (64%) in agreement with Cooke, Heilbron, and Walker [29] [Found: C, 68·8; H, 3·5; S, 26·4%; *M* (cryoscopic in C_6H_6), 460. Calc. for $C_{28}H_{18}S_4$: C, 69·7; H, 3·8; S, 26·6%; *M*, 483].

5,11-*Di*(*chlorodithio*)*naphthacene*.—Sulphur monochloride (4·1 g., 0·03 mole) was poured on naphthacene (2·2 g., 0·01 mole). Vigorous evolution of hydrogen chloride occurred and the reaction was controlled by adding a few ml. of hexane. A red oily *derivative* separated and, triturated with light petroleum, gave a granular red solid (70%) which was hydrolysed rapidly in moist air and melted with decomposition (Found: C, 51·3; H, 2·9; Cl, 16·5; S, 28·9. $C_{18}H_{10}Cl_2S_4$ requires C, 50·8; H, 2·4; Cl, 16·7; S, 30·1%).

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[29] Cooke, Heilbron, and Walker, *J.*, 1925, **127**, 2250.