329. *Chlorodithio-compounds and their Properties: the Reaction of Anthracene, Naphthacene, and Dehydroviolanthrene with Sulphur Monochloride.*

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A study of the reaction of anthracene and sulphur monochloride has resolved a discrepancy in the literature. The reactions of 9-chlorodithioanthracene to give polysulphides, Ar•S_n•R where $n = 2$, 3, or 4, and of 5,11-di(chlorodithio)naphthacene giving a cyclic disulphide, have been investigated. The products from the reaction of the polynuclear hydrocarbon, dehydroviolanthrene, and sulphur monochloride are also discussed.

The reactivity of a hydrocarbon with sulphur monochloride can generally be predicted from the maximum free valency of the hydrocarbon.

AROMATIC sulphenyl chlorides, Ar•SCl, have been thoroughly studied, particularly by Kharasch and his co-workers,[1] but the related chlorodithio-compounds, Ar•S_2Cl, are relatively unknown since few of them are sufficiently stable for investigation. The following compounds are reported to react with sulphur monochloride forming monochlorodithio-derivatives: naphthalene;[2] anthracene;[3,4] 1,2-benzanthracene; 3,4-benzopyrene; and 10-methyl-1,2-benzanthracene.[5] Di(chlorodithio)-compounds are recorded for anthracene [2] and naphthacene.[6] We have previously commented [6] on the doubtful existence of 1-chlorodithionaphthalene and 9,10-di(chlorodithio)anthracene [2] and on the unreliable data given for 9-chlorodithioanthracene.[4] Only one compound, *o*-chlorodithionitrobenzene (obtained [7] from the reaction of *o*-nitrothiophenol and sulphur dichloride) has been thoroughly studied, but a few reactions of 9-chlorodithioanthracene [4] are known.

In this paper we report a re-examination of the reaction of anthracene and sulphur monochloride, and some further properties of 9-chlorodithioanthracene and of 5,11-di-(chlorodithio)naphthacene. The action of dehydroviolanthrene (formerly known as isoviolanthrene) and sulphur monochloride has also been studied.

Lippmann and Pollak [3] obtained from anthracene and sulphur monochloride a compound, m. p. 212°, which they believed to be 9-chlorodithioanthracene. Their work was challenged by Friedländer and Simon [4] who isolated, under milder conditions, a compound of m. p. 117—118° which from its reactions was undoubtedly 9-chlorodithioanthracene. More recently Lippmann and Pollak's results again received some support.[8] We repeated their experiment, and isolated a crude product, m. p. *ca.* 212°, which was stable to hydroxylic solvents and was not decomposed by boiling dilute sodium hydroxide solution. This clearly was not a chlorodithio-compound. It was further purified (m. p. 223—224°) and from its reactions, and an alternative preparation (I—IV), shown to be di-(10-chloro-9-anthryl) tetrasulphide (IV). Reduction gave 10-chloroanthracene-9-thiol (V) which was oxidised to the disulphide (VI). We agree with Friedländer and Simon that, in the cold, anthracene and sulphur monochloride give 9-chlorodithioanthracene (VII). We also examined the reaction at higher temperatures and obtained 9,10-dichloroanthracene (IX). We have previously reported [6] the ready conversion of 9-chlorodithioanthracene into the tetrasulphide (VIII). The annexed scheme illustrates these relations.

Table 1 lists derivatives Ar•S_n•R of 9-chlorodithioanthracene not previously reported

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[1] See Kharasch, Potempa, and Wehrmeister, *Chem. Rev.*, 1946, **39**, 269—331; Kharasch, *J. Chem. Educ.*, 1956, **33**, 585.

[2] Airan and Shah, *J. Indian Chem. Soc.*, 1945, **22**, 359.

[3] Lippmann and Pollak, *Ber.*, 1901, **34**, 2767.

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

[5] Wood and Fieser, *J. Amer. Chem. Soc.*, 1940, **62**, 2674.

[6] Ariyan and Wiles, *J.*, 1961, 4510.

[7] (*a*) Lecher and Simon, *Ber.*, 1922, **55**, 2423; (*b*) Harris, Ph.D. Thesis, Univ. of Pennsylvania, 1953.

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

(Ar = 9-anthryl). These are condensation products from which the reactive chlorine atom has been eliminated. For example, the chlorodithio-group reacts with thiophenols to give trisulphides, and *N*-dimethylaniline condenses in the *para*-position forming a disulphide. Primary aromatic amines and potassium cyanide also give disulphides, while reduction forms anthracene-9-thiol. Other aromatic sulphenyl chlorides react in a comparable way.[1]

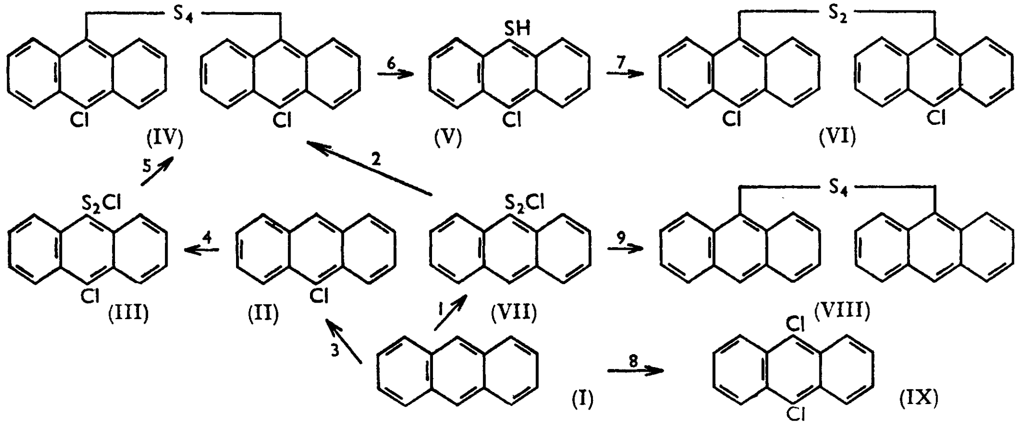
TABLE 1.

Products Ar·S$_n$·R from 9-chlorodithioanthracene.

R	n	Yield (%)	M. p.	Found (%) C	Found (%) H	Found (%) N	Found (%) S	Formula	Required (%) C	Required (%) H	Required (%) N	Required (%) S
Ph	3	68[b]	97°[e]	68·3	3·9	—	27·6	$C_{20}H_{14}S_3$	68·5	4·0	—	27·45
Bz	3	56[b]	137[f]	66·7	3·9	—	25·25	$C_{21}H_{14}OS_3$	66·6	3·7	—	25·4
p-MeO·C_6H_4	3	73[b]	107[g]	66·5	4·1	—	25·6	$C_{21}H_{16}OS_3$	66·3	4·2	—	25·3
p-NMe$_2$·C_6H_4	2	45[b]	142[g]	73·2	5·1	3·9	17·7	$C_{22}H_{19}NS_2$	73·1	5·3	3·9	17·7
Ph·CH$_2$·NH...	2	50[b]	140[h]	72·3	4·8	4·1	18·3	$C_{21}H_{17}NS_2$	72·6	4·9	4·0	18·5
C_9H_6[a]	2	75[c]	159[h]	77·5	4·2	—	18·05	$C_{23}H_{16}S_2$	77·5	4·5	—	18·0
CN	2	55[b]	135—136[i]	67·2	3·2	5·0	24·3	$C_{15}H_9NS_2$	67·4	3·4	5·2	24·0
H	1	60[d]	91[j]	—	—	—	—	—	—	—	—	—

[a] 1-Indenyl. [b] Reaction in the cold. [c] Reaction under reflux. [d] Reaction with Zn–HCl. Solvents for recrystn.: [e] EtOH–light petroleum (b. p. 40—60°); [f] AcOH; [g] C_6H_6–light petroleum (b. p. 40—60°); [h] C_6H_6; [i] light petroleum (b. p. 60—80°); (*j*) as (*i*), see ref. 4.

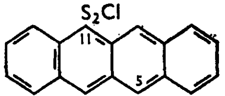
9-Chlorodithioanthracene and *o*-chlorodithionitrobenzene generally react in the same manner, except with 2-naphthol. *o*-Chlorodithionitrobenzene appears to react at the α-position, giving 2-hydroxy-1-naphthyl *o*-nitrophenyl disulphide,[7b] while 9-chlorodithioanthracene causes union at the reactive α-positions, to give 2,2′-dihydroxy-1,1′-binaphthyl.



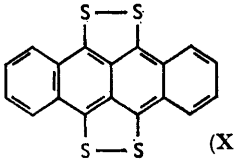
Reagents: 1, S_2Cl_2 (cold). 2, S_2Cl_2–C_6H_6. 3, $CuCl_2$. 4, S_2Cl_2–C_6H_6. 5, As 4 but refluxed. 6, Zn–HCl. 7, $FeCl_3$. 8, S_2Cl_2 (hot). 9, In the dark.

Chlorodithio-compounds were also obtained from 9,10-dihydro-, 9-chloro-, and 9-bromo-anthracene. The 9-chloro-product readily decomposed, to give a tetrasulphide (IV), but the 9-bromo-product gave a trisulphide. The tetrasulphide is formed by the reaction $2Ar{\cdot}S_2Cl \longrightarrow Ar{\cdot}S_4{\cdot}Ar + Cl_2$; the trisulphide may arise from the reaction of the chlorodithio-compound and a sulphenyl chloride: $Ar{\cdot}S_2Cl + ClS{\cdot}Ar \longrightarrow Ar{\cdot}S_3{\cdot}Ar + Cl_2$. The formation of this trisulphide supports our view[6] that sulphenyl chlorides and chlorodithio-compounds may both be intermediates in reactions of sulphur monochloride which give polysulphides.

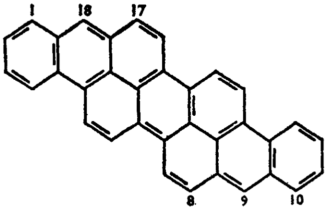
We have reported[6] that sulphur monochloride and naphthacene afford 5,11-di(chlorodithio)naphthacene (X). This compound, when refluxed in 1,2,4-trichlorobenzene in a stream of nitrogen, gave the 5,6:11,12-bisdisulphide (XI), which was prepared by Marschalk and his co-workers [9] from naphthacene and sulphur monochloride.



(X)



(XI)



(XII)

Aromatic hydrocarbons vary greatly in their reactivity to sulphur monochloride.[6] Benzene and naphthalene react only when catalysed. With increasing numbers of nuclei, reaction occurs readily and chlorodithio-compounds can sometimes be isolated. Table 2 shows that there is generally a close agreement between the reactivity of a hydrocarbon towards sulphur monochloride and the free-valency value of its most reactive carbon atoms.

TABLE 2.

The maximum free valency of hydrocarbons and their reactions with sulphur monochloride.

Hydrocarbon	Reactive positions	Max. free valency [a]	Products	
			Uncatalysed	Catalysed
Benzene	—	0·398	No reaction	Sulphides
Phenanthrene	9, 10-	0·451	,,	—
Naphthalene	1-	0·452	,,	Sulphides
Chrysene	6,12-	0·457	,,	—
Pyrene	1,3,6,8-	0·469	,,	—
1,2 : 5,6-Dibenzanthracene	9,10-	0·498	,,	—
1,2-Benzanthracene	10-	0·514	10-ClS$_2$	—
Anthracene	9,10-	0·520	9-ClS$_2$; (VIII)	—
3,4-Benzopyrene	5-	0·529	5-ClS$_2$	—
Naphthacene	5,6,11,12-	0·530	(X); (XI)	—
Dehydroviolanthrene	9,18-	0·540	Unidentified	—

[a] Free valency calculated by molecular-orbital methods.[10]

Hydrocarbons which have no carbon atom with a free valency $> \sim 0{\cdot}5$ react with sulphur monochloride only when catalysed. No catalyst is required when one or more carbon atoms have a free valency $>0{\cdot}5$. Anthracene (0·520) forms a monochlorodithio-compound. Naphthacene (0·530) gives a di(chlorodithio)-derivative (X), and having four such reactive positions forms the cyclic disulphide (XI) from this intermediate. Of the peripheral carbon atoms of dehydroviolanthrene (XII) which carry hydrogen those at positions 9 and 18 have free valencies of 0·540. The remaining positions have free valencies considerably less than 0·5.[10b] It is therefore not surprising that dehydroviolanthrene reacts slowly with sulphur monochloride. Evolution of hydrogen chloride in the cold was very slow. The reaction was readier at 100° and a brownish-purple powder was isolated. This contained chlorine and sulphur but in variable amounts. Dehydroviolanthrene and these derivatives are insoluble and high-melting and it was not possible to isolate a pure compound. Treatment of these powders with an excess of sulphur monochloride gave an intensely blue dye which is mentioned in the patent literature [11] but with no analytical figures. We find its empirical formula to be $C_{34}H_6Cl_4S_8$, for which

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[9] Marschalk and Stumm, *Bull. Soc. chim. France*, 1948, 418; Clar and Marschalk, *ibid.*, 1950, 433.

[10] (*a*) B. Pullman and A. Pullman, in " Progress in Organic Chemistry," ed. Cook, Butterworths Scient. Publns., London, 1958, Vol. IV, p. 211; (*b*) B. Pullman, Proc. Third Conference on Carbon, Pergamon, London, 1959, p. 3.

[11] Braun, G.P. 761,599/1953.

hypothetical structures having four chlorine substituents and four disulphide bridges (as in XI) can be written.

The hydrocarbons studied by Wood and Fieser[5] all have carbon atoms with free-valency values >0·5, which support the existence of the chlorodithio-compounds which they mention. They placed the order of reactivity to sulphur monochloride as 1,2-benzanthracene < anthracene < 3,4-benzopyrene, which is the order of their maximum free valencies. They also noted that 1,2,5,6-dibenzanthracene (0·498) did not react with sulphur monochloride at 65°. The relatively low free valency of naphthalene (0·452) supports our contention[6] that this compound does not give a stable chlorodithio-compound. The maximum free valencies for mesitylene and higher benzene homologues have not been determined, but on the basis of their ready reaction with sulphur monochloride[6] values >0·5 are to be expected.

EXPERIMENTAL

General Methods for the Preparation of Mixed 9-*Anthryl Polysulphides.*—Sulphur monochloride was purified as described previously.[6]

(*a*) To a stirred solution of 9-chlorodithioanthracene (5·5 g., 0·02 mole) in chloroform (50 ml.), the appropriate thiophenol (0·03 mole) was added in small quantities during 15 min. The trisulphide usually separated when the mixture was kept, or on removal of the solvent.

(*b*) To a solution of 9-chlorodithioanthracene (5·5 g., 0·02 mole) in chloroform (50 ml.), the amine (0·04 mole) was added and the mixture shaken for ½ hr. and left overnight. Neutralisation with sodium hydroxide and removal of the aqueous layer yielded the mixed disulphide which crystallised on storage or removal of the solvent.

(*c*) To a solution of 9-chlorodithioanthracene (5·5 g., 0·02 mole) in chloroform (50 ml.), indene (5·0 g., 0·04 mole) was added and the mixture refluxed for ½ hr. On cooling, the mixed disulphide separated.

(*d*) To a solution of 9-chlorodithioanthracene (5·5 g., 0·02 mole) in chloroform (50 ml.) was added potassium thiocyanate (2·9 g., 0·03 mole). The mixture was shaken for 3 days. Filtration from inorganic materials and evaporation of some of the solvent yielded the red, crystalline disulphide.

(*e*) To a stirred solution of 9-chlorodithioanthracene (11 g., 0·04 mole) in chloroform (100 ml.), zinc dust and concentrated hydrochloric acid were added until the orange solution became yellow. The mixture was then refluxed for ½ hr. and filtered. Removal of the solvent and steam-distillation gave anthracene-9-thiol.

Di-(10-*chloro*-9-*anthryl*) *Tetrasulphide* (IV).—(*a*) Sulphur monochloride (13·5 g., 0·1 mole) was added to a suspension of anthracene (8·9 g., 0·05 mole) in benzene (25 ml.). The mixture was warmed on a water-bath until the anthracene dissolved and an initial evolution of hydrogen chloride was complete. Some of the solvent was then removed under reduced pressure and the mixture again heated; a second evolution of hydrogen chloride occurred. A gum was obtained on removal of the remainder of the solvent, and recrystallisation from pyridine gave a pale orange *tetrasulphide*, m. p. 223° (65%) (Found: C, 61·0; H, 3·0; Cl, 12·6; S, 23·2. $C_{28}H_{16}Cl_2S_4$ requires C, 60·7; H, 3·3; Cl, 12·8; S, 23·2%).

(*b*) Sulphur monochloride (1·3 g., 0·01 mole) and 9-chloroanthracene[12] (2·1 g., 0·01 mole) in benzene (5 ml.) were heated until evolution of hydrogen chloride ceased. Half the solvent was then removed under reduced pressure; giving dark orange crystals, m. p. 185°. This compound, believed to be 9-chloro-10-chlorodithioanthracene, was unstable. Re-warming the filtrate for ½ hr., removal of the solvent, and re-crystallisation from pyridine gave an orange solid, m. p. 223°. This compound had the infrared spectrum of the tetrasulphide and there was no depression in the mixed m. p. determination.

10-*Chloroanthracene*-9-*thiol* (V).—Di-(10-chloro-9-anthryl) tetrasulphide (5·5 g., 0·01 mole) in chlorobenzene (200 ml.) was stirred and refluxed with zinc and concentrated hydrochloric acid. The orange chlorobenzene layer soon became pale yellow. The aqueous layer was concentrated. Golden-yellow needles crystallised, soluble in sodium hydroxide solution and giving a blue fluorescence in benzene. After recrystallisation from benzene–light petroleum (b. p.

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[12] Nonhebel, *Proc. Chem. Soc.*, 1961, 307.

60—80°) this *thiol* had m. p. 205° (60%) (Found: C, 68·4; H, 3·7; Cl, 14·8; S, 13·3. $C_{14}H_9ClS$ requires C, 68·7; H, 3·7; Cl, 14·5; S, 13·1%).

Di-(10-*chloro*-9-*anthryl*) *Disulphide* (VI).—40% Aqueous ferric chloride (10 ml.) was added to the thiol (V) (2·4 g., 0·01 mole) in dioxan, and the mixture refluxed for ½ hr. An orange *disulphide*, insoluble in alkali, was obtained, having m. p. 226° (decomp.) (from benzene or benzene–alcohol) (Found: C, 69·0; H, 3·3; Cl, 14·6; S, 13·35. $C_{28}H_{16}Cl_2S_2$ requires C, 69·0; H, 3·3; Cl, 14·9; S, 13·2%).

9,10-*Dichloroanthracene* (IX).—Sulphur monochloride (2·7 g., 0·02 mole) was added to anthracene (1·8 g., 0·01 mole) in 1,2,4-trichlorobenzene (50 ml.), and the mixture was refluxed for 2 hr. in a stream of dry nitrogen. Removal of half of the solvent gave dark brown crystals which had an intense blue fluorescence in benzene. Recrystallisation from 50% benzene–alcohol or carbon tetrachloride gave a yellow solid (60%), m. p. 210° alone or mixed with 9,10-dichloroanthracene (correct infrared spectrum) [Found: C, 68·2; H, 3·45; Cl, 28·8%; *M* (Rast), 208. Calc. for $C_{14}H_8Cl_2$: C, 68·0; H, 3·3; Cl, 28·7%; *M*, 247].

Reaction of 9-*Chlorodithioanthracene and* 2-*Naphthol.*—9-Chlorodithioanthracene (13 g., 0·05 mole) and 2-naphthol (7 g., 0·05 mole) were dissolved in chloroform (150 ml.) and left at room temperature for 24 hr. A white precipitate recrystallised from light petroleum (b. p. 100—120°) in needles, m. p. 218° (25%) alone or mixed with 2,2′-dihydroxy-1,1′-binaphthyl. The chloroform solution was evaporated, giving a yellow solid. This was extracted with absolute alcohol to remove 2,2′-dihydroxy-1,1′-binaphthyl. The yellow residue, recrystallised from benzene, gave 9,9′-dianthryl tetrasulphide, m. p. 190° (36%).

9-*Chlorodithio*-9,10-*dihydroanthracene.*—Sulphur monochloride (1·4 g., 0·01 mole) was poured on 9,10-dihydroanthracene (0·9 g., 0·005 mole) and the mixture was gently warmed until the evolution of hydrogen chloride ceased. The orange *chlorodithio*-compound crystallised on cooling, and after being washed with light petroleum (b. p. 40—60°) had m. p. 104—105° (70%) (Found: C, 60·6; H, 3·4; Cl, 12·5; S, 23·55. $C_{14}H_{11}ClS_2$ requires C, 60·3; H, 4·0; Cl, 12·7; S, 23·0%).

Di-(10-*bromo*-9-*anthryl*) *Trisulphide.*—Sulphur monochloride (1·3 g., 0·01 mole) was added to 9-bromoanthracene (2·6 g., 0·01 mole) and benzene (5 ml.). The mixture was heated on a water-bath until the evolution of hydrogen chloride was complete. Treatment of the product as for the corresponding chloro-compound gave an orange *trisulphide* which, recrystallised three times from pyridine, had m. p. 214—215° (52%) (Found: C, 55·0; H, 2·6; Br, 26·7; S, 16·1. $C_{28}H_{16}Br_2S_3$ requires C, 55·3; H, 2·65; Br, 26·3; S, 15·8%).

Naphthacene 5,6:11,12-*Bisdisulphide* (XI).—Sulphur monochloride (4·1 g., 0·03 mole) was added to naphthacene (2·2 g., 0·01 mole). A vigorous reaction gave 5,11-di(chlorodithio)-naphthacene[6] which was washed free from sulphur monochloride with hexane. 1,2,4-Trichlorobenzene (50 ml.) was added and the mixture was boiled for 2 hr. in a stream of dry nitrogen. The green crystals which separated were washed free from trichlorobenzene with alcohol and dried; they had m. p. 337—340° (vac.; decomp.) (Found: C, 61·3; H, 2·5; S, 36·2. Calc. for $C_{18}H_8S_4$: C, 61·4; H, 2·3; S, 36·4%).

Action of Sulphur Monochloride on Dehydroviolanthrene (XII).—Sulphur monochloride (4·05 g., 0·03 mole) was added to dehydroviolanthrene[13] (2·14 g., 0·005 mole) in trichlorobenzene (50 ml.), and the mixture was boiled in a stream of dry nitrogen until evolution of hydrogen chloride ceased. The purple *product*, when washed with light petroleum (b. p. 60—80°) and alcohol, had m. p. >360° (70%) (Found: C, 49·3; H, 0·9; Cl, 18·0; S, 31·6. $C_{34}H_6S_8Cl_4$ requires C, 50·35; H, 0·7; Cl, 17·5; S, 31·7%). Use of equimolar quantities of sulphur monochloride and dehydroviolanthrene gave a dark brown solid which it was not possible to purify. Treatment of this solid with excess of sulphur monochloride gave the purple compound.

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[13] Parkyns and Ubbelohde, *J.*, 1960, 4188.