Intramolecular Free-radical Substitution at the Sulphur Atom in Sulphides

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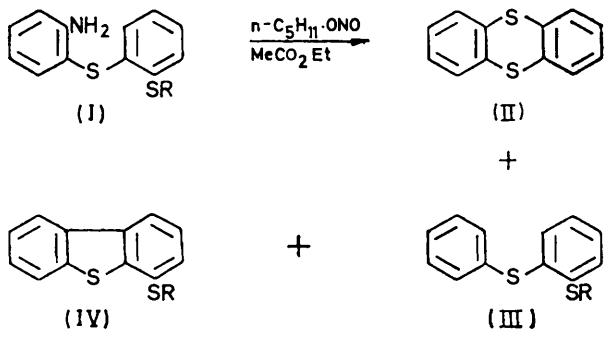
Aprotic diazotization of 2-aminophenyl 2-phenylthiophenyl (Ia), and of 2-aminophenyl 2-methylthiophenyl sulphide (Ib) in ethyl acetate gives rise to the corresponding deaminated products (III), dibenzothiophen derivatives (IV), and thianthren (II). Reactions carried out in anisole and nitrobenzene afforded a mixture of *o*-, *m*-, and *p*-methoxy- and -nitro-biphenyls; the isomer ratios were similar to those obtained in the phenylation of the same substrates with benzoyl peroxide. The same reaction carried out on 2-aminophenyl 2-phenylthiophenyl ether (VI) led to phenoxathiin and phenyl 2-phenylthiophenyl ether (VIII). A mechanism is proposed to explain the formation of the products; thianthren and phenoxathiin are assumed to form through an S_Hi reaction at the sulphur atom.

SEVERAL studies have demonstrated that homolytic substitution at sulphur take place particularly easily when sulphur is linked to another sulphur atom;[1] thus the relatively weak S–S bond of disulphides can be broken both by carbon and thiyl radicals.[2] Carbon radicals also promote homolytic fission of the S–S bond of thiosulphonates.[3] On the other hand, homolytic substitutions at the sulphur atom of sulphides are seldom encountered; these, however, do take place when the leaving radical forms a weak bond with sulphur:[1] Schmidt *et al.*[4] showed that attack of the 3-chlorobenzyl radical on dibenzyl sulphide led to benzyl 3-chlorobenzyl sulphide; Bentrude and Martin[5] presented kinetic results which demonstrated anchimeric assistance by the sulphur atom of sulphides in homolytic decompositions of peresters; and lastly Kampmeir and Evans[6] reported evidence of the involvement of the sulphur atom in the 2'-methylthiobiphenyl-2-yl radical; the formation of dibenzothiophen from this radical represents the only example known of an S_Hi reaction at the sulphur atom of a sulphide.

During our investigation[7] on the behaviour of 1,2,3-benzothiadiazole towards free radicals we encountered other examples of this type of reaction, and we now report these.

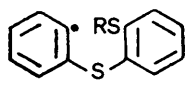
Aprotic diazotization, with n-pentyl nitrite in ethyl acetate, of 2-aminophenyl 2-phenylthiophenyl sulphide (Ia) afforded thianthren (II) as the major product, and phenyl 2-phenylthiophenyl sulphide (IIIa) and 4-phenylthiodibenzothiophen (IVa). Similarly, 2-aminophenyl 2-methylthiophenyl sulphide (Ib) gave thianthren (II) as the major product, and 2-methylthiophenyl phenyl sulphide (IIIb) and 4-methylthiodibenzothiophen (IVb).

The formation of the three products can be explained by assuming the intervention of the substituted phenyl radical (V) as a common intermediate; this can abstract hydrogen from the solvent to afford (IIIa and b) or effect an intramolecular aromatic substitution on the adjacent benzene ring to give (IVa and b). The formation of thianthren from (V) can be explained as a result of an intramolecular homolytic substitution, S_Hi, on the



a, R = Ph, b, R = Me

sulphur atom of the phenylthio- or methylthio-group linked to the adjacent aromatic nucleus.



(V)

a, R = Ph, b, R = Me

This explanation [(V) ⟶ (II) + R·] implies that methyl or phenyl radicals are contemporaneously generated in the reaction mixture; we have demonstrated their intervention, and hence the validity of the proposed mechanism, by carrying out the reaction in the presence of aromatic substrates which can be attacked by these radicals to afford a mixture of isomeric substitution products. The aprotic diazotization of (Ia) in anisole and in nitrobenzene gave mixtures containing methoxy- and nitro-biphenyls respectively; the substitution ratios were almost identical with those obtained when other sources of phenyl radicals, *e.g.* benzoyl peroxide,[8] were employed. The results are compared in the Table.

[1] K. U. Ingold and B. P. Roberts, 'Free-radical Substitution Reactions,' Wiley-Interscience, New York, 1971, p. 200.

[2] I. Degani and A. Tundo, *Ann. Chim.* (*Italy*), 1961, **51**, 543; I. Degani, M. Tiecco, and A. Tundo, *Gazzetta*, 1962, **92**, 1213; W. A. Pryor and P. K. Platt, *J. Amer. Chem. Soc.*, 1963, **85**, 1496; W. A. Pryor and H. Guard, *ibid.*, 1964, **86**, 1150; W. A. Pryor and K. Smith, *ibid.*, 1970, **92**, 2731; see also ref. 1.

[3] I. Degani, S. Ghersetti, and A. Tundo, *Ann. Chim.* (*Italy*), 1961, **51**, 461; I. Degani, M. Tiecco, and A. Tundo, *ibid.*, p. 550.

[4] U. Schmidt, A. Hochrainer, and A. Nikiforov, *Tetrahedron Letters*, 1970, 3677.

[5] W. C. Bentrude and J. G. Martin, *J. Amer. Chem. Soc.*, 1962, **84**, 1561.

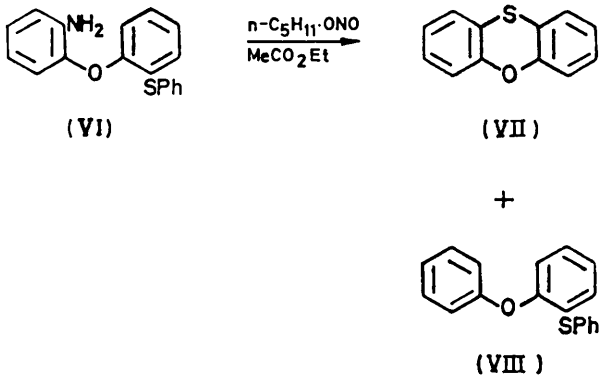
[6] J. A. Kampmeier and T. R. Efans, *J. Amer. Chem. Soc.*, 1966, **88**, 4096.

[7] L. Benati, A. Tundo, and G. Zanardi, *J.C.S. Chem. Comm.*, 1972, 590.

[8] G. H. Williams, 'Advances in Free-radical Chemistry,' Academic Press, New York, 1967, pp. 66, 124.

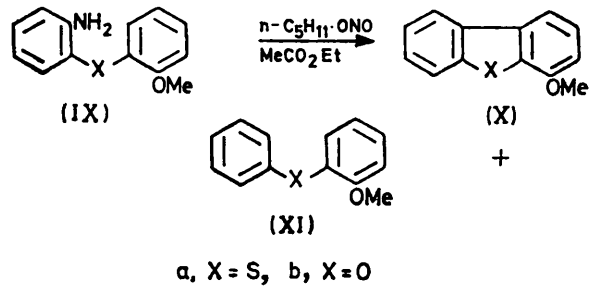
Source of phenyl radicals	Reaction in $PhNO_2$ Nitrobiphenyls (%)			Reaction in PhOMe Methoxybiphenyls (%)		
	o-	*m*-	*p*-	*o*-	*m*-	*p*-
(Ia) + n-C_5H_{11}·ONO	60	9	31	73	14	13
(VI) + n-C_5H_{11}·ONO				72	13	15
Bz_2O_2 [8]	62·8	9·7	25·7	69·8	14·7	15·6

The same reaction occurs with 2-aminophenyl 2-phenylthiophenyl ether (VI) which afforded a mixture



(VI) (VII) + (VIII)

of phenoxathiin (VII) and phenyl 2-phenylthiophenyl ether (VIII).



(IX) (X) + (XI)

a, X = S, b, X = O

If the reaction is carried out in anisole a mixture of methoxybiphenyls, in the ratio reported in the Table, can be detected; the similarity of the isomer ratios indicates that phenyl radicals are also involved in this reaction and that the mechanism of formation of (VII) is similar to that of thianthren from (Ia). The product of intramolecular aromatic substitution, *i.e.* the 4-phenylthiodibenzofuran was not found in this reaction; this is not very surprising in the light of other results which demonstrated that intramolecular aromatic arylation leading to a dibenzofuran was always more difficult than that affording a dibenzothiophen.[8]

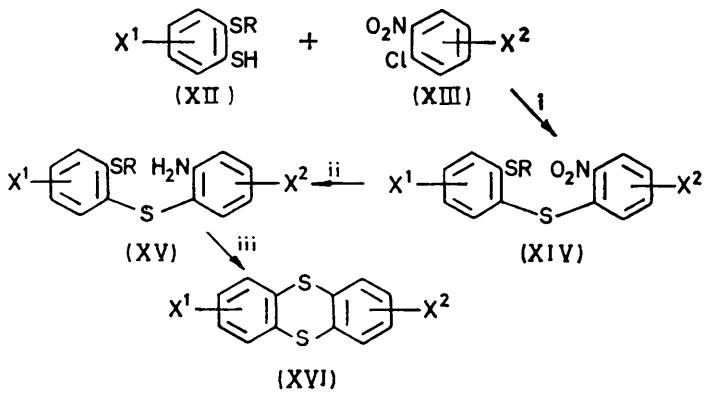
It thus seems that this intramolecular S_Hi reaction occurs easily whenever a sulphur atom is attacked to afford a stable compound such as thianthren and phenoxathiin in the present cases or the dibenzothiophen in the example reported by Kampmeir and Evans.[6] Substitution of oxygen for sulphur totally suppresses this kind of reaction; thus aprotic diazotization of 2-aminophenyl 2-methoxyphenyl sulphide (IXa) and of 2-aminophenyl 2-methoxyphenyl ether (IXb) produced neither the phenoxathiin (VII) nor the phenoxin respectively; the products in these cases were (Xa and b) (trace only) derived from intramolecular arylation and (XIa and b) from hydrogen abstraction.

Aprotic diazotization of amines such as (I) can be conveniently used as a synthetic route to thianthren derivatives (XVI) which cannot be easily obtained in other ways. The overall process is shown in the Scheme and was applied to the syntheses of the following thianthren derivatives (XVI), with yields ranging from 45 to 50%; 2-methyl-, 2-methoxy-, 2,7-dichloro-, and 2,8-dichloro-thianthren.

EXPERIMENTAL

G.l.c. analyses were carried out with a Varian model 1440/1 instrument, equipped with a 5% FFAP on Varaport column. The reaction products were identified by mixed m.p.s with prepared authentic specimens, and by comparison of their i.r. (Perkin-Elmer 257) and n.m.r. (JEOL 60 MHz) spectra.

Phenyl 2-phenylthiophenyl sulphide (IIIa),[9] 2-aminophenyl 2-phenylthiophenyl ether (VI),[10] 2-methylthiophenyl phenyl sulphide (IIIb),[11] phenoxathiin (VII),[12] phenyl 2-phenylthiophenyl ether (VIII),[13] 2-aminophenyl



SCHEME Reagents: i, MeO^-; ii, H_2/Pd–C; iii, n-C_5H_{11}·ONO–$MeCO_2Et$

[9] J. R. Campbell, *J. Org. Chem.*, 1964, **29**, 1830.
[10] F. Bottino and N. Marziano, *Boll. Sed. Acc. Gioenia Sci. Nat. Catania (Italy)*, 1962, [4], 6(7), 441.
[11] N. Marziano and G. Montaudo, *Boll. Sed. Acc. Gioenia Sci. Nat. Catania (Italy)*, 1961, [4], 6, n.ro 239, 160.
[12] C. M. Suter, J. P. McKenzie, and C. E. Maxwell, *J. Amer. Chem. Soc.*, 1936, **58**, 717.
[13] N. Marziano and G. Montaudo, *Ricerca sci.*, Sez. A1, n.ro 1, 1961, 87.

2-methoxyphenyl ether (IXb),[14] 2-methoxyphenyl phenyl sulphide (XIa),[15] 4-methoxydibenzothiophen (Xa),[16] 2-methoxyphenyl phenyl ether (XIb),[17] and 4-methoxydibenzofuran (Xb),[18] were prepared as described in the literature.

2-Aminophenyl 2-Phenylthiophenyl Sulphide (Ia).—A solution of 2-mercaptophenyl phenyl sulphide [19] (0·02 mol) in 20% aqueous NaOH (0·02 mol) was added to 2-nitrochlorobenzene (0·02 mol) in ethanol (10 ml) and refluxed for 1 h. The mixture was poured on water and extracted with ether and the extract was dried and evaporated. The residue was chromatographed on a silica gel column using a mixture of n-pentane–ether (95 : 5) as eluant. After small quantities of unidentified products, *2-nitrophenyl 2-phenylthiophenyl sulphide*, m.p. 87—88°, [from pentane–ether (1 : 1)], was collected (Found: C, 63·7; H, 3·95; N, 4·05; S, 18·75. $C_{18}H_{13}NO_2S_2$ requires C, 63·7; H, 3·85; N, 4·05; S, 18·9%). A solution of this compound (2 g) in ether (20 ml) was hydrogenated over Pd–C. The product obtained after filtration and evaporation of the solvent was purified by column chromatography on Florisil (60—100 mesh; Sigma Chemical Co.) using pentane–ether (98 : 2) as eluant. The *sulphide* (Ia), m.p. 84—85° (from pentane), was collected pure (Found: C, 69·9; H, 4·7; N, 4·75; S, 20·55. $C_{18}H_{15}NS_2$ requires C, 69·85; H, 4·9; N, 4·55; S, 20·55%).

2-Aminophenyl 2-Methylthiophenyl Sulphide (Ib).—This *product* was prepared by hydrogenation over Pd–C of 2-methylthiophenyl 2-nitrophenyl sulphide,[20] and had m.p. 60—61° [from light petroleum (b.p. 100—120°)] (Found: C, 63·15; H, 5·2; N, 5·6; S, 25·8. $C_{13}H_{13}NS_2$ requires C, 63·1; H, 5·3; N, 5·65; S, 25·9%).

2-Aminophenyl 2-Methoxyphenyl Sulphide (IXa).—This *compound* was prepared by hydrogenation over Pd–C of 2-methoxyphenyl 2-nitrophenyl sulphide,[21] and had m.p. 97—98° [from light petroleum (b.p. 100—120°)] (Found: C, 67·5; H, 5·6; N, 6·0; S, 13·6. $C_{13}H_{13}NOS$ requires C, 67·5; H, 5·6; N, 6·05; S, 13·85%).

4-Phenylthiodibenzothiophen (IVa).—To a solution of dibenzothiophen-4-yl-lithium [prepared from dibenzothiophen [16] (0·11 mol) in ether], cooled at −70 °C, a solution of diphenyl disulphide (0·11 mol) in ether (50 ml) was added dropwise. The solution was then allowed to warm gradually to room temperature, stirred for 24 h, and then poured on water. The organic layer was washed with 3% NaOH solution and then with water, and evaporated. The residue was chromatographed on a silica gel column using light petroleum (b.p. 40—70°) as eluant. After a few fractions containing unchanged diphenyl disulphide, the *dibenzothiophen* (IVa), m.p. 70—71° [from light petroleum (b.p. 100—120°)] was collected (Found: C, 73·85; H, 4·1; S, 21·7. $C_{18}H_{12}S_2$ requires: C, 73·9; H, 4·1; S, 21·9%). A solution of this compound (0·2 g) in acetic acid (10 ml) was oxidized with 30% H_2O_2 (0·2 ml) at 50 °C. The mixture was poured on water and the precipitate gave *4-phenylsulphonyldibenzothiophen 5,5-dioxide*, m.p. 270° (from acetic acid) (Found: C, 60·7; H, 3·45; S, 17·75. $C_{18}H_{12}O_4S_2$ requires C, 60·65; H, 3·4; S, 18·0%).

4-Methylthiodibenzothiophen (IVb).—To an ethereal solution of dibenzothiophen-4-yl-lithium [16] [prepared from dibenzothiophen (0·11 mol)] cooled at −60 °C, sulphur (0·11 mol) was added in small portions. The mixture was then stirred at room temperature for 4 h and poured on dilute aqueous NaOH. The organic layer was discarded and the alkaline solution, containing 4-mercaptodibenzothiophen, was directly treated with dimethyl sulphate (0·2 mol). The mixture was extracted with ether, and the extract was dried and evaporated. The residue, after crystallization from light petroleum (b.p. 100—120°), afforded the pure *dibenzothiophen* (IVb), m.p. 60—61° (Found: C, 68·6; H, 4·7; S, 27·6. $C_{13}H_{11}S_2$ requires C, 67·5; H, 4·7; S, 27·7%).

4-Phenylthiodibenzofuran.—To an ethereal solution of dibenzofuran-4-yl-lithium [prepared from dibenzofuran (0·042 mol) as described in the literature [18]], a solution of diphenyl disulphide (0·042 mol) in ether (50 ml) was added dropwise. The mixture was stirred at room temperature for 1 h and then poured on water. The organic layer was dried and distilled; the residue was purified by column chromatography on silica gel, with light petroleum (b.p. 40—70°) as eluant. After a few fractions containing unchanged diphenyl disulphide, *4-phenylthiodibenzofuran*, m.p. 62—63° [from light petroleum (b.p. 100—120°)], was collected (Found: C, 78·2; H, 4·7; S, 11·6. $C_{18}H_{12}OS$ requires C, 78·2; H, 4·4; S, 11·8%). A solution of this compound in acetic acid was treated at 50 °C with an excess of 30% H_2O_2. The mixture was poured on water and the precipitate filtered off; crystallization from acetic acid gave pure *4-phenylsulphonyldibenzofuran*, m.p. 190—191° (Found: C, 69·95; H, 4·1; S, 10·1. $C_{18}H_{12}O_3S$ requires C, 70·1; H, 3·9; S, 10·4%).

Aprotic Diazotizations.—(a) *The sulphide* (Ia).—Amyl nitrite (0·015 mol) was added to solution of the sulphide (Ia) (0·01 mol) in ethyl acetate (50 ml). The mixture was kept at 50° for 5 h and then the solvent was evaporated off. G.l.c. analysis of the residue showed the presence of thianthren (II) (53%), 4-phenylthiodibenzothiophen (IVa) (8%), and phenyl 2-phenylthiophenyl sulphide (IIIa) (5%). The yields were based on the starting amine. The three products were also separated by column chromatography on silica gel using n-pentane as eluant. They were identified by mixed m.p.s with authentic specimens and by comparison of i.r. and n.m.r. spectra.

The same reaction was carried out in anisole and in nitrobenzene; beside the products described above a mixture of *o*-, *m*-, and *p*-methoxy- and nitro-biphenyls, respectively, was found by g.l.c. The yields of the various isomers are reported in the Table.

(b) *The sulphide* (Ib).—The reaction was carried out as described above for (Ia). By column chromatography on silica gel the following products were eluted in order; thianthren (II) (58%), 4-methylthiodibenzothiophen (IVb) (4%), and 2-methylthiophenyl phenyl sulphide (IIIb) (7%).

(c) *The ether* (VI).—The reaction was carried out as described above for (Ia). By column chromatography on silica gel the following products were eluted in order;

[14] J. Inobuschi and K. Nomura, *Yakugaku Zasshi*, 1962, **82**, 696.
[15] G. E. Hilbert and T. B. Johnson, *J. Amer. Chem. Soc.*, 1929, **51**, 1526.
[16] H. Gilmann and A. L. Jacoby, *J. Org. Chem.*, 1939, **3**, 108.
[17] F. Ullman and A. Stein, *Ber.*, 1906, **39**, 622.
[18] H. Gilmann and R. V. Young, *J. Amer. Chem. Soc.*, 1935, **57**, 1121.
[19] N. Marziano, *Boll. Sed. Acc. Gioenia Sci. Nat. Catania (Italy)*, 1961, **6**, 80.
[20] G. Cordella and R. Passerini, *Boll. sci. Fac. Chim. ind. Bologna*, 1956, **14**, 104.
[21] D. R. Hogg, J. H. Smith, and P. W. Vipond, *J. Chem. Soc. (C)*, 1968, 2713.

phenoxathiin (VII) (45%), phenyl 2-phenylthiophenyl ether (VIII) (traces), and small quantities of an unidentified product. 4-Phenylthiodibenzofuran was not present.

The reaction was also carried out in anisole, and besides the products identified in ethyl acetate, *o*-, *m*- and *p*-methoxybiphenyls were formed. The isomer ratios are reported in the Table.

(d) *The sulphide* (IXa).—The reaction was carried out as described above for (Ia). Column chromatography of the reaction mixture on silica gel, using light petroleum (b.p. 40—70°)–ether (96 : 4) as eluant, afforded 4-methoxydibenzothiophen (Xa) and an oil. The oil was further chromatographed on alumina, using pentane as eluant to give 2-methoxyphenyl phenyl sulphide (XIa).

(e) *The ether* (IXb).—The reaction was carried out as described above for (Ia). By column chromatography on silica gel, using pentane as eluant, 2-methoxyphenyl phenyl ether (XIb) and traces of 4-methoxydibenzofuran (Xb) could be separated.

5-Methyl-2-phenylthiophenyl 2-Nitrophenyl Sulphide (XIV; R = Ph, X^1 = 5-Me, X^2 = H).—2-Amino-4-methylphenyl phenyl sulphide [22] (20 g) in diluted (1 : 1) hydrochloric acid (110 ml) was diazotized with sodium nitrite (8 g) in water (20 ml). The diazonium salt was added dropwise to an aqueous solution of ethyl potassium xanthate (25 g) at 40°; the mixture was warmed at 80° for 30 min and then cooled and extracted with ether. The extract was dried and concentrated to 100 ml, and added dropwise to a stirred suspension of $LiAlH_4$ (3·8 g) in ether (50 ml) at −10 °C. The mixture was kept at room temperature for 12 h, and after hydrolysis with dilute HCl, the organic layer was separated, dried, and evaporated. The residue was crude 2-mercapto-4-methylphenyl phenyl sulphide (XII; R = Ph, X^1 = 4-Me) which was dissolved in 1M-sodium methoxide (100 ml) without further purification. A solution of *o*-chloronitrobenzene (15·7 g) in methanol (100 ml) was added and the resulting mixture refluxed for 2 h. The solvent was distilled off and the residue purified by column chromatography on silica gel, using light petroleum (b.p. 40—60°)–ether (95 : 5) as eluant. The pure *sulphide* (XIV; R = Ph, X^1 = 5-Me, X^2 = H), m.p. 78—79° (from light petroleum), was obtained (Found: C, 64·65; H, 4·4; N, 3·95; S, 18·25. $C_{19}H_{15}NO_2S_2$ requires C, 64·55; H, 4·3; N, 3·95; S, 18·15%).

2-Aminophenyl 5-Methyl-2-phenylthiophenyl Sulphide (XV; R = Ph, X^1 = Me, X^2 = H).—This *product* was obtained by hydrogenation over Pd–C of the foregoing 2-nitrophenyl sulphide. It was purified by chromatography on alumina using light petroleum (b.p. 40—60°)–ether (95 : 5) as eluant, m.p. 78—79° (from light petroleum) (Found: C, 70·5; H, 5·35; N, 4·4; S, 19·55. $C_{19}H_{17}NS_2$ requires C, 70·5; H, 5·3; N, 4·35; S, 19·8%).

2-Methylthianthren (XVI; X^1 = Me, X^2 = H).—Amyl nitrite (0·034 mol) was added to a solution of the foregoing 2-aminophenyl sulphide (0·034 mol) in ethyl acetate (40 ml). The mixture was kept at 50° for 5 h, then evaporated, and the residue was chromatographed over a silica gel column using n-pentane as eluant. The first product eluted was *2-methylthianthren*, m.p. 70—71° (45% yield) (Found: C, 67·5; H, 4·8; S, 27·5. $C_{13}H_{10}S_2$ requires: C, 67·8; H, 4·4; S, 27·85%).

5-Methoxy-2-phenylthiophenyl 2-Nitrophenyl Sulphide (XIV; R = Ph, X^1 = 5-OMe, X^2 = H).—2-Amino-4-methoxyphenyl phenyl sulphide [23] (18 g) in dilute (1 : 1) hydrochloric acid (50 ml) was diazotized with sodium nitrite (7 g) in water (10 ml). The diazonium salt was added dropwise to an aqueous solution (40 ml) of ethyl potassium xanthate (19·6 g) at 40°; the resulting mixture was then kept at 80° for 30 min. After cooling, ether was added and the organic layer was separated, dried, and concentrated to 100 ml. This solution was added in portions to a suspension of $LiAlH_4$ (3·04 g) in ether (50 ml) at −10°, and left at room temperature for 12 h. Dilute hydrochloric acid was added and the ethereal layer separated and evaporated. The crude 2-mercapto-4-methoxyphenyl phenyl sulphide (XII; R = Ph, X^1 = 4-OMe) was dissolved in a 1M-sodium methoxide (80 ml). A solution of *o*-chloronitrobenzene (12·5 g) in methanol (80 ml) was added and the mixture was refluxed 2 h. The solvent was distilled off and the residue was chromatographed on a silica gel column using light petroleum (b.p. 40—60°)–ether (95 : 5) as eluant. The sulphide (XIV; R = Ph, X^1 = 5-OMe, X^2 = H) was obtained as a yellow oil which was hydrogenated without further purification.

2-Aminophenyl 5-Methoxy-2-phenylthiophenyl Sulphide (XV; R = Ph, X^1 = OMe, X^2 = H).—This *product* was obtained from the hydrogenation over Pd–C of the foregoing nitro-derivative, and had m.p. 85—86° [from light petroleum (b.p. 80—120°)] (Found: C, 67·25; H, 5·2; N, 4·3; S, 18·65. $C_{19}H_{17}NOS_2$ requires C, 67·2; H, 5·05; N, 4·15; S, 18·9%).

2-Methoxythianthren (XVI; X^1 = 2-OMe, X^2 = H).—This *product* was obtained from the aprotic diazotization of the foregoing amino-sulphide under the usual conditions, and was purified by column chromatography on silica gel using n-pentane as eluant, m.p. 79—80° (yield 45%) (Found: C, 63·2; H, 4·3; S, 25·65. $C_{13}H_{10}OS_2$ requires C, 63·4; H, 4·1; S, 26·05%).

4-Chloro-2-nitrophenyl 4-Chloro-2-phenylthiophenyl Sulphide (XIV; R = Ph, X^1 = X^2 = 4-Cl).—2-Amino-5-chlorophenyl phenyl sulphide [24] (9·2 g) in dilute (1 : 1) hydrochloric acid (60 ml) was diazotized with sodium nitrite (3 g) in water (10 ml). The diazonium salt was added dropwise to an aqueous solution (15 ml) of ethyl potassium xanthate (9·8 g) at 40°; the temperature was raised to 80° and maintained for 30 min. The cooled mixture was extracted with ether, and the extract was dried and concentrated to 100 ml. This solution was added in portions to a suspension of $LiAlH_4$ (1·5 g) in ether at −10° and left at room temperature for 12 h. Dilute hydrochloric acid was added and the organic layer separated. Evaporation gave the crude 5-chloro-2-mercaptophenyl phenyl sulphide (XII; R = Ph, X^1 = 5-Cl), and this was dissolved in 1M-sodium methoxide (40 ml). A solution of 1,4-dichloro-2-nitrobenzene (7·7 g) in methanol (60 ml) was added and the mixture refluxed for 2 h. The residue from evaporation was chromatographed on silica gel using light petroleum (b.p. 40—60°)–ether (95 : 5) as eluant to give the *sulphide* (XIV; R = Ph, X^1 = X^2 = 4-Cl), m.p. 119—120° (Found: C, 53·55; H, 3·0; Cl, 17·05; N, 3·4; S, 15·4. $C_{18}H_{11}Cl_2NO_2S_2$ requires: C, 52·95; H, 2·7; Cl, 17·35; N, 3·45; S, 15·7%).

5-Chloro-2-nitrophenyl 4-Chloro-2-phenylthiophenyl Sulphide (XIV; R = Ph, X^1 = 4-Cl, X^2 = 5-Cl).—This compound was similarly prepared by the condensation of

[22] M. Nakaniski and T. Otsuka, *Jap. P.* 6120/1959 (*Chem. Abs.*, 1960, **54**, 14,276).

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5-chloro-2-mercaptophenyl phenyl sulphide (XII; R = Ph, X^1 = 4-Cl) with 2,4-dichloro-1-nitrobenzene. The *product*, purified by column chromatography under the same conditions, has m.p. 138—140° (Found: C, 53·55; H, 2·8; Cl, 17·1; N, 3·3; S, 15·6%).

2-*Amino*-3-*chlorophenyl* 4-*Chloro*-2-*phenylthiophenyl Sulphide* (XV; R = Ph, X^1 = 4-Cl, X^2 = 3-Cl).—This compound was obtained as an *oil* from the hydrogenation over Pd–C of the corresponding nitro-derivative (Found: C, 57·4; H, 3·55; Cl, 18·5; N, 3·7; S, 16·65. $C_{18}H_{13}Cl_2NS_2$ requires C, 57·15; H, 3·45; Cl, 18·75; N, 3·7; S, 16·9%).

2-*Amino*-5-*chlorophenyl* 4-*Chloro*-2-*phenylthiophenyl Sulphide* (XV; R = Ph, X^1 = 4-Cl, X^2 = 5-Cl).—This *compound* was obtained from the hydrogenation over Pd–C of the corresponding nitro-derivative, m.p. 77—78° [from light petroleum (b.p. 40—60°)–ether] (Found: C, 57·6; H, 3·55; Cl, 18·6; N, 3·7; S, 16·6%).

2,7-*Dichlorothianthren* (XVI; X^1 = 2-Cl, X^2 = 7-Cl).—This compound was obtained from the aprotic diazotization of the foregoing sulphide with amyl nitrite, m.p. 185—187° (lit.,[25] 185—186°) (Found: C, 51·2; H, 2·15; Cl, 24·6; S, 22·2. Calc. for $C_{12}H_6Cl_2S_2$: C, 50·55; H, 2·2; Cl, 24·5; S, 22·5%).

2,8-*Dichlorothianthren* (XVI; X^1 = 2-Cl, X^2 = 8-Cl).—This *compound* was obtained from the aprotic diazotization of the sulphide (XV; R = Ph, X^1 = X^2 = 4-Cl) with amyl nitrite as described for 2-methylthianthren, m.p. 176—177° (Found: C, 50·55; H, 2·2; Cl, 24·7; S, 22·1%).

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