

## Novel Macrocyclic Polysulphur Compounds. 7,15,17,19-Tetra-alkoxy-2,3,4,5,10,11,12,13-octathiatricyclo[12,2,2,2<sup>6,9</sup>]eicosa-6,8,14,16,17,19-hexaenes and 2,3,7,8-Tetra-alkoxythianthrens; Products of the Catalysed Reaction of Aromatic Ethers and Sulphur Monochloride

By Z. S. Ariyan,\* Pharmaceutical Chemicals Research, Uniroyal, Naugatuck, Connecticut 06770  
R. L. Martin, Department of Chemistry, State University of New York at Binghamton, New York 13901

The preparation of 7,15,17,19-tetra-alkoxy-2,3,4,5,10,11,12,13-octathiatricyclo[12,2,2,2<sup>6,9</sup>]eicosa-6,8,14,16,17,19-hexaenes (I), sulphur analogues of paracyclophane, is reported. Catalytic hydrogenation of these novel sulphur macrocycles yielded the 2,5-dialkoxybenzene-1,4-dithiols, whilst aqueous chlorination at room temperature yielded the corresponding 2,5-dialkoxybenzene-1,4-disulphonyl dichlorides. Thianthren has now been prepared from chlorodithiobenzene.

OUR earlier report<sup>1</sup> of novel polysulphur compounds of type (I) has initiated considerable interest in this field. There is no example in the literature of two aromatic rings attached together in the *para* positions by two sets of polysulphide bridges such as the replacement of the methylenes in the paracyclophane system by sulphur atoms. Recently, Fehér and his co-workers<sup>2</sup> reported three isomeric hexathia[3,3]cyclophanes (II) by reacting

sulphur monochloride (S<sub>2</sub>Cl<sub>2</sub>) and sulphur dichloride (SCL<sub>2</sub>). The report<sup>5,6</sup> of an oxidation product (V) from *ortho*-benzenedithiol remains unresolved. Here, we report the preparation of novel macrocyclic polysulphur compounds (I), isolated while investigating the possibility of synthesis in the thianthren (VI) series.

Whilst the uncatalysed reactions of dialkoxybenzenes with sulphur monochloride (S<sub>2</sub>Cl<sub>2</sub>) in inert solvents yield linear sulphides,<sup>7</sup> the same reactants in the presence of anhydrous aluminium chloride or an acid-clay catalyst (*cf.* Experimental section) in carbon disulphide or 1,2-dichloroethane yield very different sulphur heterocycles. Under catalytic conditions both *ortho*-dimethoxy- and -diethoxy-benzenes gave 2,3,7,8-tetrasubstituted thianthrens (VI; R<sup>1</sup> = OMe, R<sup>2</sup> = H, m.p. 175°; R<sup>1</sup> = OEt, R<sup>2</sup> = H, m.p. 129–130°). In the case of the *para* substituted dialkoxybenzene under similar catalytic conditions, unexpected novel crystalline large ring polysulphides (I) were obtained with relatively high sulphur content. We report first compounds of type (I), in which both methylene bridges in paracyclophane may be considered to have been replaced by tetrasulphide linkages. Attempts so far to synthesise the unsubstituted parent compound have been unsuccessful since apparently electron-donating groups, in particular *para*-alkoxy-groups, seem an important electronic factor in our synthesis. The parent compound may possibly be prepared by the decomposition of the intermediate *para*-bis(chlorodithio)benzene recently reported.<sup>2</sup> Decomposition of chlorodithio-compounds to tetrasulphides are well known.<sup>8</sup>

*Thianthrens* (VI).—Although thianthren (VI; R<sup>1</sup> = R<sup>2</sup> = H) may readily be prepared by the aluminium chloride-catalysed treatment of benzene with sulphur monochloride, the synthesis has not been readily extended to derivatives of thianthren, and alternative routes were sought. For example, the five-stage synthesis of 2,3,7,8-tetramethoxythianthrens (VI; R<sup>1</sup> = OMe, R<sup>2</sup> = H) in poor yield has been described.<sup>9,10</sup> We

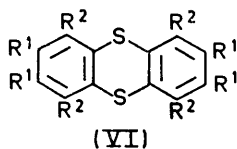
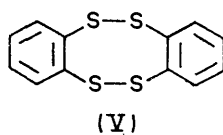
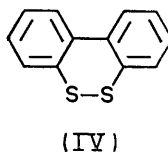
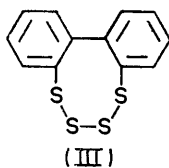
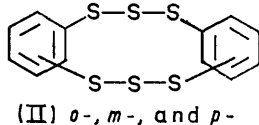
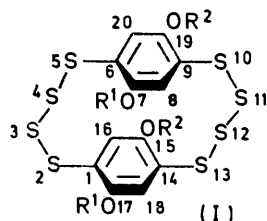
<sup>6</sup> L. Field, W. D. Stephens, and E. L. Lippert, jun., *J. Org. Chem.*, 1961, **26**, 4782.

<sup>7</sup> Z. S. Ariyan and L. A. Wiles, *J. Chem. Soc.*, 1962, 4709.

<sup>8</sup> Z. S. Ariyan and L. A. Wiles, *J. Chem. Soc.*, 1962, 1725; 1969, 755.

<sup>9</sup> K. Fries, H. Koch, and H. Stockenbrock, *Annalen*, 1929, **468**, 162.

<sup>10</sup> E. Vinkler and J. Szabo, *Magyar Kém. Lapja*, 1949, **4**, 708, (*Chem. Abs.*, 1953, **46**, 8120).



aromatic dithiols with bis(chlorodithio)benzenes (Cl-S<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-S<sub>2</sub>-Cl). Field and Engelhardt<sup>3</sup> reported a series of interesting dithiols as possible intermediates to compounds of type (I). In an attempt to synthesise bridged bistetrasulphides linking aromatics, Millar and his co-workers<sup>4</sup> recently prepared compounds (III) and (IV) by reacting biphenyl-2,2'-dithiol with

<sup>1</sup> Z. S. Ariyan and R. L. Martin, *Chem. Comm.*, 1969, 847 (*cf. Chem. Eng. News*, 1969, **47**, 40; Ger.P. 2,010,787/1970; U.S.P. 3,621,032/1971).

<sup>2</sup> F. Fehér, K. Glinka, and F. Malcharek, *Angew. Chem. Internat. Edn.*, 1971, **10**, 413.

<sup>3</sup> L. Field and P. R. Engelhardt, *J. Org. Chem.*, 1971, **35**, 3647.

<sup>4</sup> D. W. Allen, P. N. Braunton, I. T. Millar, and J. C. Tebby, *J. Chem. Soc. (C)*, 1971, 3454.

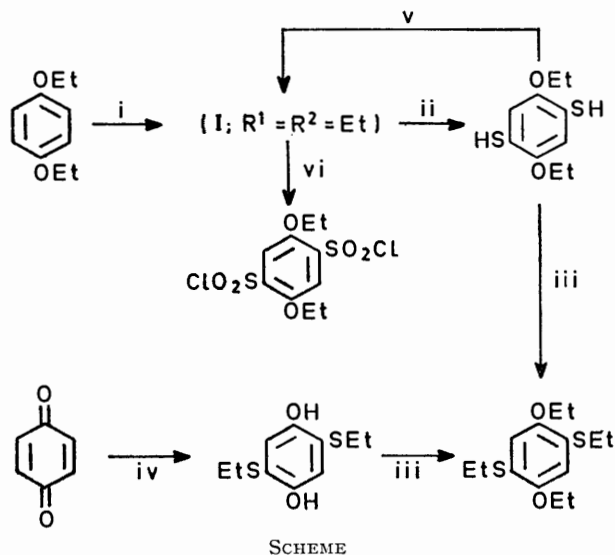
<sup>5</sup> P. C. Guha and M. N. Chakladar, *J. Indian Chem. Soc.*, 1952, **2**, 318 (*Chem. Abs.*, 1926, **20**, 1797).

have prepared both tetra-alkoxythianthrens (VI;  $R^1 = \text{OMe}$  and  $\text{OEt}$ ,  $R^2 = \text{H}$ ), although also in poor yields, by the direct action of sulphur monochloride on the *ortho*-dialkoxybenzenes in the presence of aluminium chloride. The products in both cases were accompanied by polymeric oils, from which the thianthrens crystallised out on standing. There is at present little information about thianthren formation from sulphur monochloride and benzene. It has been postulated only but not substantiated experimentally, that thianthrens could well result from a sulphenyl chloride intermediate.<sup>11</sup> In connection with mechanistic considerations, we also mention that we have prepared thianthren (VI;  $R^1 = R^2 = \text{H}$ ) from the intermediate chlorodithiobenzene<sup>12</sup> ( $\text{PhS}\cdot\text{S}\cdot\text{Cl}$ ) in benzene, catalysed by aluminium chloride. This further supports earlier postulates of chlorodithio-intermediates<sup>8</sup> in sulphur monochloride reactions. Sulphur monochloride is polarized, ( $\delta^+$ ) $\text{S}_2\text{Cl}-\text{Cl}(\delta^-)$ , and the chlorodithio-cation is an electrophilic substituent.<sup>13</sup>

**Polysulphur Macrocylic Compounds (I).**—In the 1,4-dialkoxybenzenes, the conjugation with the nucleus is diminished since negative charges will be formed on neighbouring carbon atoms. Dimethoxybenzene is attacked only slowly by the reagent ( $\text{S}_2\text{Cl}_2$ ) in boiling benzene.<sup>7</sup> We have found that the catalysed reaction of *p*-diethoxybenzene and sulphur monochloride yields unexpected, crystalline, large ring polysulphides [ $M$  (ebullioscopic in benzene), 541; required  $M$ , 584] with relatively high sulphur content. In the reaction of 1,4-diethoxybenzene with sulphur monochloride in aluminium chloride in carbon disulphide, a red oil was obtained, which on cooling gave small quantities (6%) of orange crystals of the macrocycle (I;  $R^1 = R^2 = \text{Et}$ ). After several attempts to refine this reaction it was found that sulphur monochloride and hydroquinone dialkyl ethers react very smoothly in 1,2-dichloroethane or carbon tetrachloride in the presence of an acid-clay catalyst, with yields up to 60%. An oil invariably results, from which, on closer study, a variety of products was isolated. Our postulated structure<sup>1</sup> (I) has been fully verified by X-ray crystallography<sup>14</sup> and further substantiates the nature of the reduction products. Reduction of the macrocycle (I;  $R^1 = R^2 = \text{Et}$ ) yields an aromatic dithiol (VII;  $R^1 = R^2 = \text{OEt}$ ) for which the 1,4-position for the thiol groups has been assigned. Starting from *p*-benzoquinone and ethanethiol, the bisethylthio-derivative was prepared (see Scheme).

Ricci and Bernal<sup>14</sup> have shown that the lengths of the sulphur-carbon bonds indicate the presence of 'double-bond' character and that there is an alternation of bond lengths in both independent  $\text{S}_4$  chains. Recently, Sullivan<sup>15</sup> has shown by e.s.r. studies that the unpaired electron in the cation radical is completely

delocalised over the whole molecule. This further substantiates the X-ray studies, indicating that the polysulphide chains are part of the conjugated system. The u.v. absorption maximum in ( $\text{CHCl}_3$ ) occurs at 372 nm ( $\log \epsilon$  4.05) which is considerably higher than other polysulphides [ $\text{RS}_x\text{R}$  ( $x = 1-4$ )] whose broad absorption occurs at 290–320 nm.<sup>16-18</sup> The intense bright colouration of these novel macrocycles may well be due to the delocalisation of the



Reagents: i,  $\text{S}_2\text{Cl}_2$ -catalyst; ii,  $\text{Pt}_2\text{S}-\text{C}-\text{H}_2$ ; iii,  $(\text{EtO})_2\text{SO}_2-\text{NaOH}$ ; iv,  $\text{EtSH}$ -autoclave; v,  $\text{S}_2\text{Cl}_2$  or  $\text{S}\cdot\text{Cl}_2$ ; vi,  $\text{Cl}_2-\text{aq. AcOH}$

electrons of the phenyl rings through the tetrasulphide chains. We had earlier ascribed this bathochromic shift to an  $\text{S}\cdots\text{O}$  contact.<sup>1,14</sup>

TABLE I  
Macrocylic polysulphides (I)

$R^1$	$R^2$	Yield (%)	M.p. ( $^\circ\text{C}$ )
Me	Me	52	210–215 <sup>a</sup>
Me	Et	54	156–160 <sup>b</sup>
Et	Et	60	185–187 <sup>c</sup>

Recrystallisation solvents: <sup>a</sup> toluene; <sup>b</sup> benzene; <sup>c</sup> chloroform.

Table 1 lists the crystalline macrocylic polysulphides (I) isolated, whilst Table 2 lists aromatic dithiols (VII), which were obtained in good yield by controlled hydrogenation. These dithiols are all well-defined, stable, crystalline solids which undergo typical reactions. Table 3 lists a series of bis(mono-, di-, and tri-sulphides) (VIII) obtained by reaction with alkyl halides, sulphenyl chlorides ( $\text{RS}\cdot\text{Cl}$ ), and a chlorodithio-derivative ( $\text{RS}_2\text{Cl}$ ), respectively. On passing chlorine through a solution

<sup>15</sup> P. D. Sullivan, *J. Amer. Chem. Soc.*, in the press.

<sup>16</sup> J. Tsurugi and T. Nakabayashi, *J. Org. Chem.*, 1959, **24**, 807.

<sup>17</sup> T. Nakabayashi, J. Tsurugi, and T. Yabuta, *J. Org. Chem.*, 1964, **29**, 1236.

<sup>18</sup> 'Sulphur Bonding,' eds. C. C. Price and S. Oae, The Ronald Press Company, New York, 1962, p. 42.

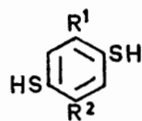
<sup>11</sup> K. Fries, *Ber.*, 1912, **45**, 2965.

<sup>12</sup> F. Fehér and W. Kruse, *Chem. Ber.*, 1958, **91**, 2528.

<sup>13</sup> P. Hope and L. A. Wiles, *J. Chem. Soc. (Supplement I)*, 1964, 5679, 5837.

<sup>14</sup> J. S. Ricci, jun., and I. Bernal, *Chem. Comm.*, 1969, 1453; *J. Chem. Soc. (B)*, 1971, 1928.

TABLE 2

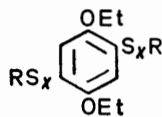


(VII)

R <sup>1</sup>	R <sup>2</sup>	Yield (%)	M.p. (°C)
OMe	OMe	68	122 <sup>a</sup>
OMe	OEt	49	69 <sup>a</sup>
OEt	OEt	73	117 <sup>a</sup>
OBu	OBu	43	77—78 <sup>b</sup>

Recrystallisation solvents: <sup>a</sup> cyclohexane; <sup>b</sup> light petroleum.

TABLE 3



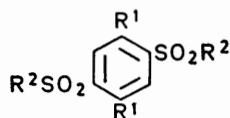
(VIII)

R	x	M.p. (°C)
Me	1	109—111 <sup>a</sup>
Et	1	78—78.5 <sup>a</sup>
Pr <sup>n</sup>	1	78—78.5 <sup>a</sup>
Pr <sup>i</sup>	1	71—72 <sup>a</sup>
Bu <sup>n</sup>	1	78—79 <sup>a</sup>
Bu <sup>s</sup>	1	17—18 <sup>a</sup>
n-Pentyl	1	56—57 <sup>a</sup>
n-Hexyl	1	37—39 <sup>a</sup>
Cyclohexyl	1	78—79 <sup>a</sup>
4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	1	205—206 <sup>b</sup>
Bz	1	180—181 <sup>b</sup>
Cl <sub>3</sub> C	2	119—120 <sup>a</sup>
2-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	2	165 <sup>c</sup>
Cl <sub>3</sub> C <sub>6</sub>	2	205—206 <sup>d</sup>
2,4-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	2	198—199 <sup>c</sup>
4-Cl-2-NO <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	2	207—208 <sup>c</sup>
9-Anthryl	3	165—166 <sup>b</sup>

Recrystallisation solvents: <sup>a</sup> ethanol; <sup>b</sup> benzene-cyclohexane; <sup>c</sup> benzene-ethanol; <sup>d</sup> chloroform-light petroleum.

of the macrocyclic polysulphides (I) in 92% acetic acid<sup>19</sup> at room temperature, the corresponding 1,4-disulphonyl chlorides were obtained. Table 4 lists chlorinolysis

TABLE 4



(IX)

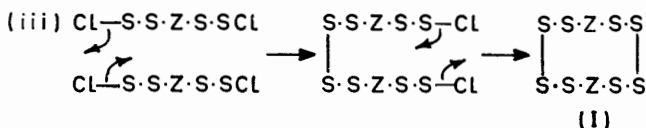
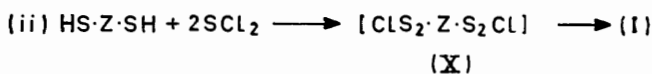
R <sup>1</sup>	R <sup>2</sup>	Yield (%)	M.p. (°C)
OMe	Cl	83	214—215 <sup>a</sup>
OEt	Cl	89	190—191 <sup>b</sup>
OMe	NH <sub>2</sub>	96	300 <sup>c</sup>
OEt	Bu <sup>n</sup> NH	53	167—168 <sup>d</sup>
OEt	CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>4</sub> -CH-NH	62	255—256 <sup>e</sup>

<sup>a</sup> From tetrahydrofuran. <sup>b</sup> Cyclohexane. <sup>c</sup> Product is extremely insoluble, successively worked-up with water and ethanol. <sup>d</sup> From ethanol. <sup>e</sup> From dioxan.

products and some derivatives (IX). On treating the dithiol (VII; R<sup>1</sup> = R<sup>2</sup> = OEt) with either sulphur

\* For details of Supplementary publications, see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 10 pp. are supplied as full-size copies).

monochloride or sulphur dichloride, the macrocycle (I; R<sup>1</sup> = R<sup>2</sup> = Et) was obtained. We expected the macrocycle from the sulphur monochloride reaction (i); however, in the case of sulphur dichloride (ii) we hoped to isolate an intermediate bis(chlorodithio)-derivative. The resultant ruby red solution readily decomposed during work-up to yield the macrocycle (I). It is reported that mono- and bis-chlorodithio-compounds have been isolated by treating mono- and di-thiols with sulphur dichloride.<sup>2,12</sup> Undoubtedly the sulphur dichloride intermediate is the unstable bis-1,4-(chlorodithio)-2,5-diethoxybenzene (X). Apparently (X) is sterically favourable for cyclisation to the macrocycle (I) through an electrophilically assisted displacement process (iii). We have, earlier, reported on the ready formation of tetrasulphides from chlorodithio-compounds, 2ArS<sub>2</sub>Cl → ArS<sub>4</sub>Ar + Cl<sub>2</sub>.<sup>9</sup>



Z = 2,5-diethoxy-1,4-phenylene

During the preparation of the macrocycle (I; R<sup>1</sup> = R<sup>2</sup> = Me), we isolated small amounts of bis-(3-chloro-2,5-dimethoxyphenyl) mono- and di-sulphides and we believe these arise through the decomposition of a bis(chlorodithio)-intermediate (X). Mono-, di-, and poly-sulphides are obtained from the S<sub>2</sub>Cl<sub>2</sub> reaction with aromatic ethers.<sup>7</sup>

From the foregoing results we conclude that chlorodithio-derivatives are intermediates in our reactions. The preparation of thianthren from chlorodithiobenzene (PhS<sub>2</sub>Cl) supports our conclusions, about these compounds, which are now frequently reported and quite reactive.<sup>8</sup> Moreover, chlorodithio-compounds have also been postulated as intermediates in the reaction of aliphatic amides with sulphur monochloride and in the reaction of aniline with S<sub>2</sub>Cl<sub>2</sub> (the Herz reaction<sup>13,20a-c</sup>). Such intermediates readily account for the production of the macrocyclic polysulphur compounds (I) reported in this paper.

#### EXPERIMENTAL

Satisfactory analytical data were obtained for all the compounds listed in Tables 1—4. The data are listed in Supplementary Publication No. SUP 20368 (6 pp., 1 microfiche).\*

<sup>19</sup> H. Kwart and L. J. Miller, *J. Amer. Chem. Soc.*, 1958, **80**, 884.

<sup>20</sup> (a) 'Advances in Heterocyclic Chemistry,' eds. A. R. Katritzky and A. J. Boulton, Academic Press, London, 1968, vol. 9, p. 121; (b) P. Hope and L. A. Wiles, *Chem. and Ind.*, 1966, 32; (c) P. Hope and L. A. Wiles, *J. Chem. Soc. (C)*, 1966, 1283.

**Reagents.**—Commercial sulphur monochloride was purified as described previously.<sup>21</sup> However, it was found that a freshly-opened bottle was just as good a reagent for our catalysed reactions. The acid-clay catalyst referred to as catalyst in the text was 'Montmorillonite catalyst, K series,' (Chemical Products Division of Chemitron Corporation, Louisville, Kentucky, 40201). Sulphenyl chlorides were prepared by the conventional methods.

**Spectra.**—U.v. absorption spectra were measured in chloroform with a Beckman 505 recording spectrophotometer and i.r. spectra with a Perkin-Elmer high resolution grating spectrophotometer, model 421. The aromatic dithiols showed the thiol absorption as a sharp band (SH stretching at 2560 cm<sup>-1</sup>). N.m.r. spectra were recorded with a Varian 60 MHz instrument with tetramethylsilane as internal standard and CDCl<sub>3</sub> as solvent.

The novel macrocyclic polysulphur compounds of type (I) did not have sharp m.p.s and vitrification usually occurs over a short range. Whilst after several recrystallisations and column chromatography, excellent analytical results were obtained, no improvement of m.p. was achieved.

**2,3,7,8-Tetramethoxythianthren.**—*o*-Dimethoxybenzene (33.2 g, 0.2 mol) and sulphur monochloride (13.5 g, 0.1 mol) in carbon disulphide (200 ml) were kept cool in an ice bath with stirring. Anhydrous aluminium chloride (13.3 g, 0.1 mol) was gradually added and a green complex soon formed with evolution of HCl. After complete addition of the catalyst the mixture was heated under reflux for 24 h. Addition of conc. hydrochloric acid-ice and subsequent extraction of the product yielded an oily material. Purification (chromatography) gave the desired product, a white solid, m.p. 180–181° (lit.,<sup>8</sup> 175–176). Oxidation with hydrogen peroxide-acetic acid gave the disulphone, m.p. 300–301° (lit.,<sup>10</sup> 296).

**2,3,7,8-Tetraethoxythianthren.**—To a mixture of *o*-diethoxybenzene (33.2 g, 0.2 mol) and sulphur monochloride (13.5 g, 0.1 mol) in carbon disulphide (200 ml) was slowly added anhydrous aluminium chloride (13.3 g, 0.2 mol) with cooling. A deep blue-green colour developed and HCl evolved copiously. The solution was heated under reflux until no more HCl evolved. Breakdown of the complex in the usual manner gave a thick brown oil, which was chromatographed on alumina with benzene as eluant. The resulting golden oil did not crystallise; dissolution in ethanol-1,2-dichloroethane led to precipitation of white crystals (4 g) on standing, m.p. 129–130° (from cyclohexane) (Found: C, 61.5; H, 6.1; S, 16.1. C<sub>20</sub>H<sub>24</sub>O<sub>4</sub>S<sub>2</sub> requires C, 61.2; H, 6.15; S, 16.35%), δ 7.0 p.p.m. (s, ArH), and an integrated ratio of aliphatic to aromatic protons of 4:8:1.

**Thianthren via Chlorodithiobenzene Intermediate.**—Chlorodithiobenzene (prepared according to Fehér and Kruse)<sup>12</sup> (35.2 g, 0.2 mol) was added to dry benzene (200 ml). Anhydrous aluminium chloride (18.8 g, 0.15 mol) was added in portions with stirring. The solution assumed an intense purple colouration, characteristic of this reaction. The mixture was heated under reflux until all gas evolution ceased. The complex was then treated with cold conc. hydrochloric acid. The aqueous mass was then extracted with chloroform, dried, and the solvent was evaporated. The tan residue was taken up in hot ethanol, the solution was treated with charcoal, filtered, and cooled to give thianthren (18 g), m.p. 159° (no depression with an authentic sample of thianthren, m.p. 158–159°).

**7,15,17,19-Tetramethoxy-2,3,4,5,10,11,12,13-octathiatri-cyclo[12,2,2,2,2<sup>6,9</sup>]eicosa-6,8,14,16,17,19-hexaene** (I; R<sup>1</sup> = R<sup>2</sup> = Me).—1,4-Dimethoxybenzene (27.6 g, 0.2 mol), dichloromethane (200 ml), sulphur monochloride (27 g, 0.2 mol), and catalyst (0.5 g), were mixed and heated with efficient stirring on a steam-bath. A green colouration developed and the heating continued until no more HCl gas evolved (ca. 6 h). The orange product-catalyst was extracted (Soxhlet) with toluene to give the orange crystalline *macrocycle* (I; R<sup>1</sup> = R<sup>2</sup> = Me) (52.2%), m.p. 210–212° (with vitrification), λ<sub>max</sub> 372 nm (log ε 3.98). The mother liquor was evaporated and chromatographed on alumina with benzene as eluant. Some more product (I; R<sup>1</sup> = R<sup>2</sup> = Me) was isolated as a thin orange band, m.p. 212–214° (with vitrification). From the larger, main, yellow band we isolated (by repeated fractional recrystallisation from cyclohexane) two products: bis-(3-chloro-2,5-dimethoxyphenyl) monosulphide (4%), m.p. 144–145° (Found: C, 51.35; H, 4.35; Cl, 18.85; S, 8.9. C<sub>16</sub>H<sub>16</sub>Cl<sub>2</sub>O<sub>4</sub>S requires C, 51.2; H, 4.3; Cl, 18.9; S, 8.55%) and 2,5-dichloro-1,4-dimethoxybenzene (6%), m.p. and mixed m.p. 130–131° (lit.,<sup>22</sup> 130). This compound had its i.r. spectrum identical to an authentic sample.

**7,15-Diethoxy-17,19-dimethoxy-2,3,4,5,10,11,12,13-octathiatri-cyclo[12,2,2,2,2<sup>6,9</sup>]eicosa-6,8,14,16,17,19-hexaene** (I; R<sup>1</sup> = Me, R<sup>2</sup> = Et).—4-Ethoxyanisole (76 g, 0.5 mol), chloroform (125 ml), sulphur monochloride (67 g, 0.5 mol), and catalyst (5 g) were mixed and stirred at room temperature for 4 h. Hydrogen chloride gas evolved and the mixture was then heated on a steam bath for 1 h until no more evolution of gas was noticed. The hot solution was filtered and the condensed filtrate was chromatographed on alumina with chloroform. The bright yellow main fraction was evaporated and the orange residue, which possessed a strong odour of 4-ethoxyanisole, was washed with diethyl ether to leave fine orange crystals (54%), m.p. 156–158° (with vitrification), λ<sub>max</sub> 372 nm (log ε 4.07).

**7,15,17,19-Tetraethoxy-2,3,4,5,10,11,12,13-octathiatri-cyclo-[12,2,2,2,2<sup>6,9</sup>]eicosa-6,8,14,16,17,19-hexaene** (I; R<sup>1</sup> = R<sup>2</sup> = Et).—1,4-Diethoxybenzene (332 g, 2.0 mol), dichloromethane (500 ml), sulphur monochloride (268 g, 2.0 mol), and catalyst were stirred for 16 h. The reaction became exothermic after several min, and much hydrogen chloride was evolved. The bright deep green colouration disappeared at the end of reaction. After 16 h the mixture was warmed to 40 °C for 1 h and filtered hot. The orange solution, on standing overnight, yielded orange crystals (I; R<sup>1</sup> = R<sup>2</sup> = Et) (144 g; 59%), m.p. 185–187° (with vitrification; after several recrystallisations from chloroform there was no change in m.p.), δ (60 MHz; CDCl<sub>3</sub>) 7.23 (s, ArH), 4.03 (m, CH<sub>2</sub>), and 1.47 p.p.m. (t, Me).

**Controlled Hydrogenation of Tetra-alkoxyoctathiatri-cyclo-eicosa-hexaenes** (I). **Preparation of 2,5-Dialkoxybenzene-1,4-dithiols** (VII).—The reductions were carried out in Magne-Dash autoclaves under controlled hydrogenation conditions with platinum sulphide-carbon in benzene or toluene for an average period of 4 h at 200 °C and 900–1300 lb in<sup>-2</sup>. Filtration and distillation yielded the desired dithiols (VII) (see Table 2) as white solids.

**Reaction of Sulphur Monochloride or Dichloride with 2,5-Diethoxybenzene-1,4-dithiol** (VII; R<sup>1</sup> = R<sup>2</sup> = OEt).—The

<sup>21</sup> Z. S. Ariyan and L. A. Wiles, *J. Chem. Soc.*, 1961, 4510.

<sup>22</sup> G. B. Marini-Bettolo and F. S. Trucco, *Gazzetta*, 1943, **73**, 300.

dithiol (2 g, 0.01 mol) was dissolved in ether (100 ml) and cooled to 0 °C with stirring. Gradual addition of either sulphur monochloride (1.35 g, 0.01 mol) or sulphur dichloride (2.04 g, 0.02 mol) gave a yellow solution which deepened to orange on further addition of the sulphur halides, with evolution of HCl. Gentle removal of solvent in either case gave the macrocycle (I;  $R^1 = R^2 = Et$ ), m.p. 185—187°, in good yield.

*General Method for the Preparation of Bis-(alkythio)- or -(aryllthio)-derivatives* (VIII;  $x = 1$ ).—Typically, the aromatic dithiol (VII) (0.05 mol) was added to a 20% sodium hydroxide solution (25 ml) and stirred well until a paste resulted. To this disodium salt, the alkylating agent (the alkyl halide, alkyl sulphate, or aryl halide) (0.1 mol) was added in ethanol (20 ml) and heated under reflux for 1 h and then cooled in an ice bath. The bis-sulphides (Table 3) were obtained by filtration and recrystallisation.

*General Method for the Preparation of Bis-(alkyldithio) or -(aryldithio)-derivatives* (VIII;  $x = 2$ ).—To the appropriate sulphenyl chloride<sup>23</sup> (1 mol) in carbon tetrachloride (50 ml), the dithiol (0.5 mol) was added in carbon tetrachloride (20 ml) with stirring. Hydrogen chloride soon evolved gently and the reaction was complete after heating under reflux for 0.5 h. On cooling and addition of light petroleum the bis(dithio)-derivative precipitated. In the case of trichloromethanesulphenyl chloride, glacial acetic acid was used instead of carbon tetra chloride.

*Bis(anthracen-9-yl) 2,5-Diethoxy-1,4-phenylene Bistrisulphide* (VIII;  $R = anthracen-9-yl$ ;  $x = 3$ ).—To a solution of 2,5-diethoxybenzene-1,4-dithiol (6.9 g) in chloroform (100 ml), 9-chlorodithioanthracene<sup>21</sup> (16.6 g) in chloroform (100 ml) was added and the mixture was heated under reflux for 0.5 h. Hydrogen chloride evolved and the heating was maintained until all evolution of HCl gas had ceased. Evaporation and chromatography (alumina; benzene) gave the orange product (see Table 3), m.p. 165—166° (from cyclohexane-benzene).

*2,5-Dialkoxybenzene-1,4-sulphonyl Dichlorides* (IX;  $R^2 = Cl$ ).—The procedure involved is essentially that of Kwart and Miller.<sup>19</sup> Into the tetraethoxyoctathiatricycloicosahexaene (I;  $R^1 = R^2 = Et$ ) (4 g) in glacial acetic acid (100 ml) to which water was added (10 ml), chlorine gas was bubbled and the temperature was kept below 45 °C. After 75 min of chlorination, straw coloured crystals of the disulphonyl dichloride (3.5 g) appeared. Recrystallisation from cyclohexane gave pale yellow crystals, m.p. 190—191°.

The corresponding dimethoxy-derivative was prepared from the tetramethoxy-compound (I;  $R^1 = R^2 = Me$ ).

The disulphonyl chloride had m.p. 214—215° (from tetrahydrofuran).

*2,5-Dimethoxybenzene-1,4-disulphonamide*.—The corresponding disulphonyl chloride was heated under reflux in water with an excess of ammonia (*d* 0.880). The insoluble white sulphonamide was filtered and washed successively with water and ethanol and had m.p. 300°,  $\nu_{max}$  3360 and 3250 (NH stretch) and 1160  $cm^{-1}$  ( $SO_2$  stretch).

*NN'-Dicyclohexyl-2,5-diethoxybenzene-1,4-sulphonamide*.—2,5-Diethoxybenzene-1,4-disulphonyl dichloride (3.6 g, 0.01 mol) in benzene (100 ml) was gradually added to cyclohexylamine (3.6 g, 0.04 mol) with shaking at room temperature. The reaction was slightly exothermic. The product was heated under reflux for 30 min and left overnight. After washing with water and separation, the benzene was removed. The white crystalline disulphonamide (4 g) was recrystallised from dioxan, m.p. 255—256°,  $\nu_{max}$  3290 (NH stretch) and 1163  $cm^{-1}$  ( $SO_2$  stretch).

*2,5-Diethoxy-NN'-di-n-butylbenzene-1,4-disulphonamide*.—Similarly, this was prepared from 2,5-diethoxybenzene-1,4-disulphonyl dichloride (7.2 g, 0.02 mol) in benzene (200 ml) and n-butylamine (2.8 g). The benzene solution was washed, separated, and evaporated to leave needles, m.p. 167—168° (from ethanol),  $\nu_{max}$  3290 (NH stretch) and 1160  $cm^{-1}$  ( $SO_2$  stretch.).

*1,4-Diethoxy-2,5-bis(ethylthio)benzene*.—*p*-Benzoquinone (0.5 mol) and ethanethiol (1.5 mol) in benzene (125 ml) were heated for 1 h at 195 °C at 1240—1360 lb in<sup>-2</sup> in a 600 ml MagneDash autoclave in presence of 5% rhenium sulphide-carbon catalyst (2.8 g). Filtration yielded an oily product, which after evaporation and removal of quinhydrone, gave a product with strong hydroxy-bands in the i.r. spectrum. Treatment of this undistilled oil with diethyl sulphate in alkali and subsequent chromatography (alumina; benzene) gave a pale yellow solid, m.p. 78—78.5 °C. This product was identical (i.r., m.p. and mixed m.p.) with that from ethylation of the aromatic dithiol [cf. Table 3; (VIII;  $R = Et$ ,  $x = 1$ )].

We suggest 'parathiacyclophane' as a trivial name for the basic unsubstituted tricyclic structure (I; H for  $OR^1$  and  $OR^2$ ).

We thank Dr. Harold Greenfield for carrying out all high-pressure reactions, and Professor H. Kwart for stimulating discussions.

[2/152 Received, 24th January, 1972]

<sup>23</sup> Stauffer Chemical Co., U.S.P. 2,929,820/1960.