Synthesis of Novel Macrocyclic Compounds Containing Sulphur or Oxygen in the Ring: Thia- and Oxa-cyclophanes. Mass Spectral and Other Studies

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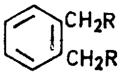
The synthesis of a number of large-ring heterocyclic compounds containing two or four sulphur atoms in the ring is described. The compounds include 2,2′-bridged biphenyls having 7—11-membered heterocyclic rings; and 7-, 8-, 9-, 14-, 16-, 18-, and 24-membered heterocyclic systems containing *o*-xylylene bridges. Oxygen analogues of the former series are also described. The ^1H n.m.r. and mass spectra of the compounds are discussed.

Most of the sulphur macrocycles are derivatives of *o*-xylene-αα′-dithiol (Ia) or biphenyl-2,2′-dithiol; improved syntheses of the latter compounds are described, together with certain reactions of their simple derivatives including complex formation with palladium(II) and platinum(II) bromides.

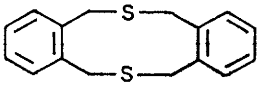
Biphenyl-2,2′-bisdialkylsulphonium di(methyl sulphates) when heated undergo a novel reaction to give dibenzothiophen.

ortho-XYLENE-αα′-DITHIOL (Ia) and αα′-dibromo-*o*-xylene (Ib) are useful intermediates in the synthesis of sulphur macrocycles; their value arises both from the ‘ benzylic ’ reactivity of the dibromide, and from the fact that the functional groups are held in a favourable orientation for cyclisation in both intermediates.

Autenrieth and Brüning[1] first demonstrated the use of the *o*-xylylene bridge in syntheses of macrocyclic sulphur compounds, when they treated the disodium salt of the dithiol (Ia) with αα′-dibromo-*o*-xylene (Ib) to obtain the 10-membered heterocycle dibenzodithiecin (II).



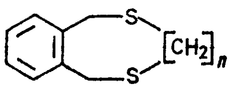
(I) a; R = SH
b; R = Br



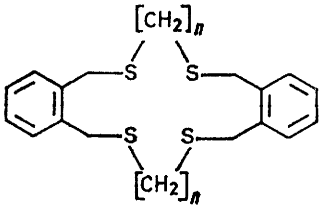
(II)

Although the seven-[2] and eight-[3] membered dithia-systems benzodithiepin (III; $n = 1$) and benzodithiocin (III; $n = 2$) respectively have been described, the corresponding 'dimeric' macrocycles had not been reported.

The dithiol (Ia) was originally prepared by Kötz,[4] but Autenrieth and Hennings[5] were the first workers to describe the synthesis, which involved treating αα′-dibromo-*o*-xylene (Ib) with an ethanolic solution of potassium thiolate to give the dithiol (Ia) in 50% yield. This synthesis is very tedious, and it is difficult to isolate a pure product. We have found the *S*-alkylisothiouronium salt method (as adapted by Fletcher and Pan[6]) to be applicable to this preparation and to be a much superior method, giving the dithiol (Ia) in almost quantitative yield.



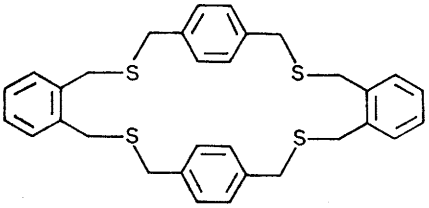
(III)



(IV)

In the present work we have found that the dithiol (Ia) and αα′-dibromo-*o*-xylene (Ib) react with di-iodomethane and with alkane-αω-dithiols respectively, to yield both 'monomeric' and 'dimeric' cyclic systems. Thus the disodium salt of the dithiol (Ia) on treatment with di-iodomethane in alcoholic media, gave the 7-membered dithia-heterocycle (III; $n = 1$) (15%) together with the 14-membered tetrathia-macrocycle (IV; $n = 1$) (3%). In a similar reaction with αα′-dibromo-*p*-xylene the 24-membered tetrathia-compound (V) was isolated as the only crystalline product, in 10% yield. By treating αα′-dibromo-*o*-xylene with the disodium salts of ethanedithiol and propanedithiol certain higher homologues, *i.e.* the 8- and 9-membered dithia-heterocycles (III; $n = 2$ and 3), and the 16- and 18-membered tetrathia-macrocycles (IV; $n = 2$ and 3) respectively were obtained. The yield of both the latter compounds was *ca.* 5%.

An interesting difference between the monomeric and dimeric sulphur heterocycles is shown in the aromatic region of their p.m.r. spectra. For the monomeric heterocycles (III; $n = 1$—3) and the 24-membered heterocycle (V), the aromatic protons of the *o*-xylylene bridges all give sharp singlets in the p.m.r. spectra, showing the aromatic protons for a given system to have similar chemical shifts. For the dimeric macrocycles (IV; $n = 1$—3) however, the aromatic absorption signals occur as A_2B_2 multiplets. This effect has been reported by Shoulders and Smith[7] for 9,10-dihydroanthracene; they postulate that it is due to the ring current effect of one aromatic ring upon the protons in the other aromatic ring, made possible because of the 'butterfly wing' shape of the molecule. Since the related disulphide (II) also exhibits a similar effect, we suggest that the methylene-bridged macrocycles (IV; $n = 1$—3) are sufficiently flexible to allow the aromatic rings to approach one another and cause a similar effect to that described for 9,10-dihydroanthracene. It is interesting to note that for the 24-membered heterocycle (V) no such interaction is observed, perhaps due to a more sterically rigid system with the two *o*-xylylene units well separated.



(V)

The mass spectra of these compounds were determined primarily to establish the molecular weight of the molecules, especially important for distinguishing between the 'monomeric' and 'dimeric' heterocycles. In addition it has proved of interest to examine some of the mass spectra in more detail and to suggest possible mechanisms for some of the fragmentation processes.

A feature of the mass spectra of these sulphur heterocycles is the presence of a very abundant ion of mass 135. In most of the compounds examined, including some αα′-dialkylthio-*o*-xylene compounds, this ion is the base peak in the spectra, and in other cases it had a very high abundance relative to the base peak.

The mass spectra of the dithia-heterocycles (III; $n = 1$—3) are characterised by two abundant ions of mass 104 and 135, and the molecular ion. That the ion of mass 135 is formed directly from a molecular ion in each case is confirmed by the presence of the appropriate metastable ions in the spectra. Two possible

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[1] W. Autenrieth and A. Brüning, *Ber.*, 1903, **36**, 183.

[2] W. Autenrieth and R. Hennings, *Ber.*, 1902, **35**, 1388.

[3] W. Kiessling, J. Peschel, U. Schmidt, and W. Schroth, *Z. Chem.*, 1964, **4**, 302.

[4] A. Kötz, *Ber.*, 1900, **33**, 729.

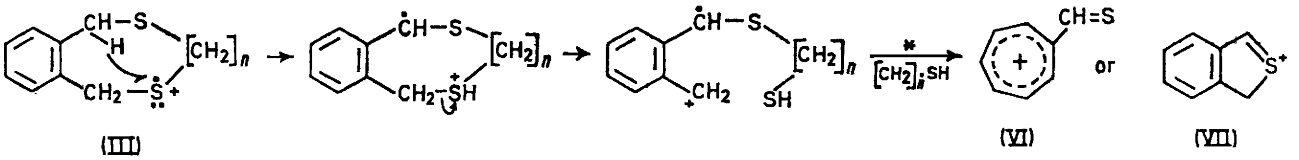
[5] W. Autenrieth and R. Hennings, *Ber.*, 1901, **34**, 1772.

[6] T. L. Fletcher and H. Pan, *Chem. and Ind.*, 1968, 546.

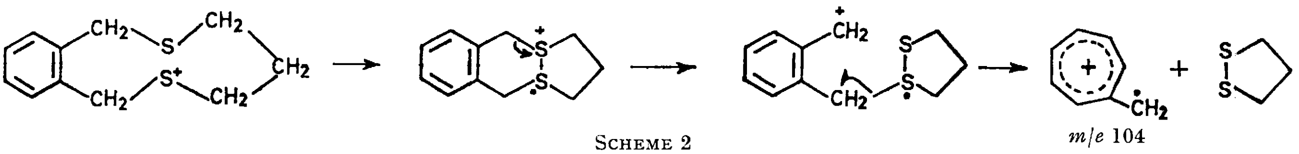
[7] B. A. Shoulders and W. B. Smith, *J. Phys. Chem.*, 1965, **69**, 2022.

structures for the ion of mass 135 are the substituted tropylium ion (VI) and the cyclic sulphonium ion (VII) which may be formed by the path shown in Scheme 1. Since it has been observed that both benzyl and tropylium type ions are preferentially stabilised according to the substituents on the aromatic ring,[8] one cannot say which species is the more stable in these cases.

The formation of the ion of mass 104 is particularly favourable for the dithia-heterocycle (III; $n = 3$) which has this ion as its base peak. A suggested fragmentation path which involves the elimination of a neutral molecule of dithiolan, is shown in Scheme 2. As will be shown later a *m*-xylylene group also produces an abundant ion at *m*/*e* 104 and therefore the tropylium structure is preferred to the alternative *o*-quinodimethylene structure. On the other hand the smaller mono- and di-methylene bridges hold the sulphur atoms further apart, making such a cyclisation reaction less probable, thus reducing the occurrence of the ion *m*/*e* 104.

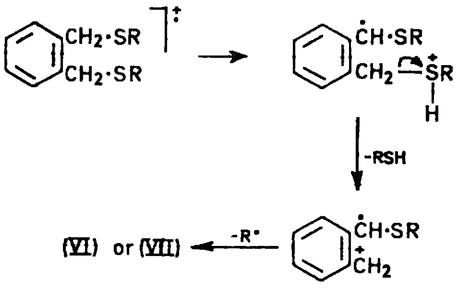


Scheme 1 (* = metastable ion observed)



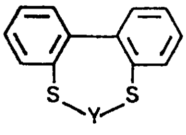
Scheme 2

The 'acyclic' compounds, αα′-diethylthio- or αα′-dimethylthio-*o*-xylene also fragment to the stable ion at *m*/*e* 135. A single-step process does not appear to occur since the required metastable ions are absent. It is possible that the acyclic compounds degrade in a similar way to that suggested for the dithia-heterocycles, the fragmentation now being a two-step process as follows:

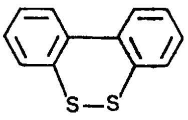


The previously-known sulphur compounds of skeletal type (VIII) are limited to the 7-membered ring system [VIII; $Y = \cdot(\mathrm{C}{<})\cdot$], and the 6-membered cyclic disulphide (IX).[9] Biphenyl-2,2′-dithiol (X) was first synthesised by Barber and Smiles in 1928.[9] They diazotised orthanilic acid, and treated the solution with iodide; the resulting sodium *o*-iodobenzenesulphonate was converted into disodium biphenyl-2,2′-disulphonate by boiling an aqueous solution with copper bronze. Subsequent reaction with phosphorus pentachloride gave the biphenyl-2,2′-bis(sulphonyl chloride), which on reduction with zinc and hydrochloric acid in ethanol gave the dithiol (X) in 35% overall yield.

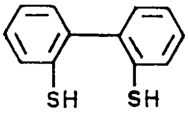
Biphenyl-2,2′-dithiol was found to condense with the carbonyl function of aldehydes and ketones in the presence of an acid catalyst to give the 7-membered ring system (VIII; $Y = \mathrm{CMe_2}$, CHPh, or $\mathrm{CPh_2}$).[9] Another derivative of this cyclic system (VIII; $Y = \mathrm{C{=}O}$) was formed when the disodium salt of the dithiol was treated with phosgene in toluene.[9] Barber and Smiles also tried to form the 8-membered ring system by treatment of the disodium salt of the dithiol (X) with oxaloyl chloride and 1,2-dibromoethane but without success.



(VIII)



(IX)



(X)

A later preparation of the dithiol (X) by Armarego and Turner[10] failed at the Ullmann stage in the synthesis, and so they modified the Ullmann reaction by using the phenyl ester of *o*-iodobenzenesulphonic acid. This brought the number of synthetic stages to six without increasing the original yield. In our work we

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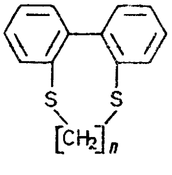
[8] H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Interpretation of Mass Spectra of Organic Compounds,' Holden-Day Inc., San Francisco, 1964, ch. 9.

[9] H. J. Barber and S. Smiles, *J. Chem. Soc.*, 1928, 1141.

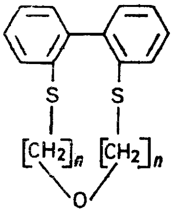
[10] W. L. F. Armarego and E. E. Turner, *J. Chem. Soc.*, 1956, 1665.

have successfully repeated the original synthesis by using activated copper bronze [11] in the Ullmann reaction.

We have found the disodium salt of the dithiol (X) to undergo reactions in dilute alcoholic solution with a variety of reactive αω-dihalogenoalkanes, di(halogenoalkyl) ethers, αα′-dibromo-*o*- and -*m*-xylenes, to give a range of 2,2′-bridged biphenyl dithia-heterocycles in good yields. Thus di-iodomethane and dibromo-methane, -ethane, -propane, -butane, and -pentane, gave a homologous series of dithia-heterocycles of general formulae (XI; $n = 1$—5). Surprisingly, the yields (35—70%) did not diminish as the longer bridges were employed; on the contrary, the highest yields (60—70%) were achieved using the two longest bridges.

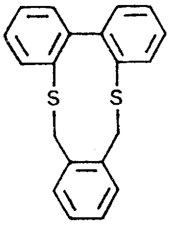


(XI)

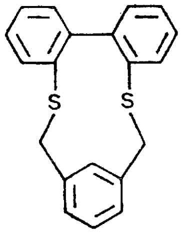


(XII)

In a similar reaction, di(chloromethyl) ether and di-(2-bromoethyl) ether gave the two dithia-oxa heterocyclic compounds (XII; $n = 1$ and 2) both in 60% yield. Also, αα′-dibromo-*o*- and -*m*-xylene gave the 10- and 11-membered ring heterocycles (XIII) and (XIV) respectively, in this reaction, in 70% and 50% yields. In contrast, αα′-dibromo-*p*-xylene in this reaction gave a polymeric solid.



(XIII)

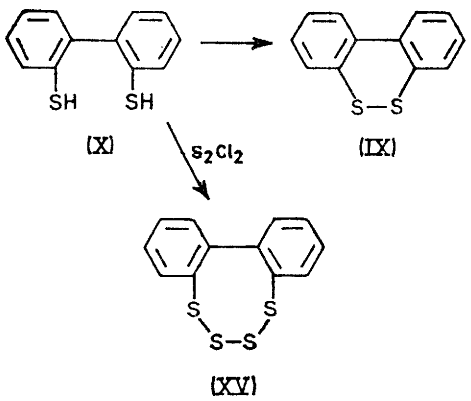


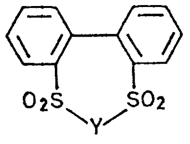
(XIV)

On treating the dithiol with sulphur dichloride (SCl_2) or ' sulphur monochloride ' (S_2Cl_2) in benzene, the novel cyclic tetrasulphide (XV) was isolated in both cases.

With sulphur dichloride the tetrasulphide (XV) and the cyclic disulphide (IX) were isolated in a 1 : 1 ratio, whereas with sulphur monochloride (S_2Cl_2) the major product was the cyclic tetrasulphide. The isolation of a mixture when the former reagent is used is in accord with some disproportionation of the sulphur dichloride: $2SCl_2 \longrightarrow S_2Cl_2 + Cl_2$. The liberated chlorine would be removed readily by the dithiol (X).

Each of the dithia-heterocycles was oxidised to the corresponding disulphone, using hydrogen peroxide in acetic acid, to give a second series of heterocycles of general structure (XVI).





(XVI)

The p.m.r. spectrum of 9,10-dihydrophenanthrene shows two multiplets in the aromatic region at τ 2·31 (2H) and 2·80 (6H). The low field resonance has been attributed to deshielding of the 6,6′ protons by the aromatic ring opposite each proton.[12] In the p.m.r. spectra of the 2,2′-bridged dithia-biphenyls (XI; $n = 1$—5), the aromatic protons are partially split into two multiplets, which become completely separated in the case of the dimethylene bridged disulphide (XI; $n = 2$). The multiplets for the aromatic protons of this compound at τ 2·2 and 2·7 integrate for two and six protons respectively, and it appears that this is another example of the type of deshielding effect observed for 9,10-dihydrophenanthrene. It is noteworthy that integration of the partially separated aromatic proton multiplets in the other compounds gave roughly the same ratio of protons as in the case of the disulphide (XI; $n = 2$). The p.m.r. spectra of all the disulphone analogues show the aromatic protons to be generally deshielded, but again split into two multiplets integrating for two and six protons. The two-proton multiplet is shifted downfield relative to the six-proton multiplet. This extra deshielding effect is the result of diamagnetic deshielding of the aromatic protons *ortho* to the sulphonyl group; the situation is similar to the deshielding which occurs with the carbonyl group in benzaldehyde.

The mass spectra of the bridged and unbridged dithiabiphenyls have been recorded and qualitatively interpreted. The mass spectrum of dibenzothiophen, which is an important fragment ion in the spectra of these compounds, has been discussed by Danby and Eland.[13]

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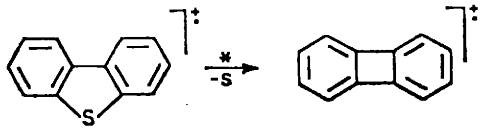
[11] R. Adams and E. C. Kleiderer, *J. Amer. Chem. Soc.*, 1933, **55**, 4219.

[12] M. A. W. Glass, H. B. Hopps, K. Mislow, E. Simon, and G. H. Wahl, *J. Amer. Chem. Soc.*, 1964, **86**, 1710.

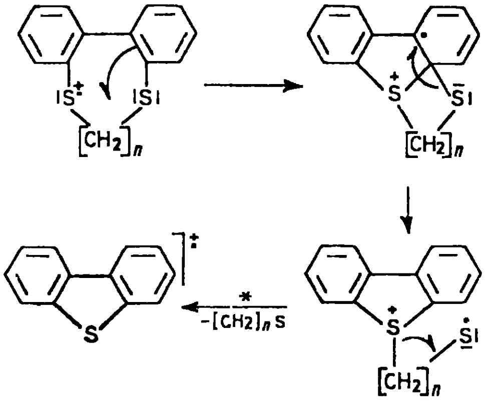
[13] C. D. Danby and J. H. D. Eland, *J. Chem. Soc.*, 1965, **5935**.

The mass spectra of the 2,2′-bridged dithiabiphenyls are such that they are best considered by examining these compounds in separate classes.

The formally similar polymethylene-bridged and methylene ether-bridged compounds have mass spectra which are dominated by the base peak at *m/e* 184. The fragmentation pattern below this ion closely resembles that of dibenzothiophen. The peak is, therefore, attributed to the very stable dibenzothiophen ion. An ion at *m/e* 152 and a metastable ion at *m/e* 125·5 occur in all the spectra and are attributed to the formation of the biphenylene ion from dibenzothiophen.[1,3]

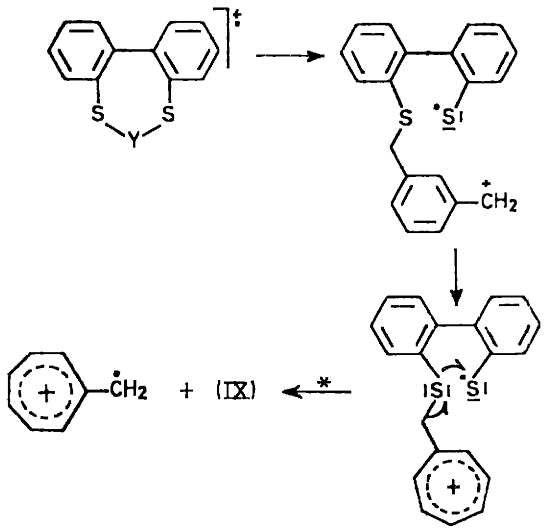


The molecular ions of all these heterocycles give an ion corresponding to dibenzothiophen in one fragmentation step, the process being verified by their metastable ions. The path by which the rearrangement takes place may occur as shown in Scheme 3. Support for the structure of the rearranged molecular ion which fragments is obtained from the mass spectra of the dithiol (X) and its alkylated derivatives (see later). The larger polymethylene and 5-membered ether-bridged biphenyls [*i.e.* (XI) and (XII); $n = 2$] show a small peak at *m/e* 216 which corresponds to the cyclic disulphide (IX).



Scheme 3

When the bridge is replaced by an *o*-xylylene group the mass spectrum closely resembles those of the corresponding compounds with the polymethylene bridges. The usual ions of mass 104 and 135 derived from the *o*-xylylene group are also present. Dreiding models suggest that the *o*-xylylene bridged biphenyl (XIII) is quite flexible and there is little steric hindrance to the formation of the dibenzothiophen ion by the process previously described. In contrast the *m*-xylylene bridge forces the sulphur atoms apart to a transoid configuration, which will clearly prohibit a mechanism such as that suggested for the other bridged biphenyls (*i.e.* Scheme 3). The dibenzothiophen ion at *m/e* 184 is reduced to a peak of modest intensity, the base peak appearing at *m/e* 104. The appearance of a metastable ion at *m/e* 34 indicates that the ion of mass 104 is formed directly from the molecular ion which is in accord with the path shown in Scheme 4. An ion of low abundance corresponding to the disulphide (IX) (*m/e* 216) is also observed in the spectra of the *o*- and *m*-xylylene-bridged compounds.



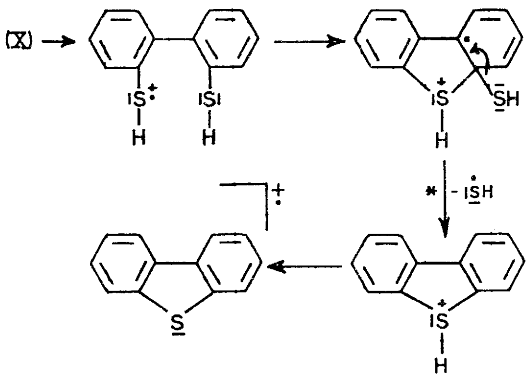
Scheme 4

When the bridge consists of two or four atoms of sulphur only, the spectra are again quite characteristic. For example the cyclic disulphide (IX), has a very stable molecular ion (which is the base peak), which breaks down to the slightly less abundant dibenzothiophen ion by loss of a sulphur atom.

The cyclic tetrasulphide (XV) is not flat and the molecular ion readily fragments to the lower cyclic sulphides. The molecular ion loses two sulphur atoms to form the cyclic disulphide ion which then eliminates a further sulphur atom to give the dibenzothiophen ion, which is also the base peak in the spectrum. A strong metastable peak at *m/e* 156 confirms the fragmentation of the disulphide ion (*m/e* 216) to the dibenzothiophen ion. Thus, one fragmentation path would appear to be a stepwise degradation process in which two, three, and four atoms of sulphur are successively eliminated.

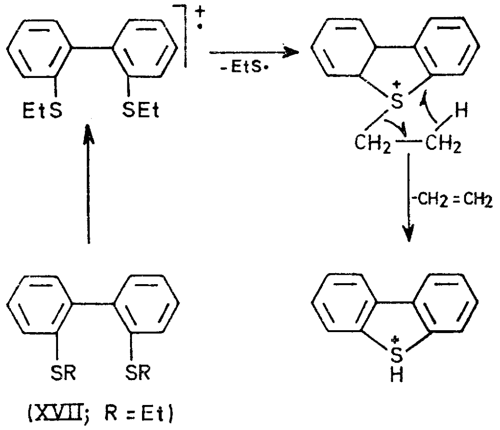
The last class of compounds to be discussed are the ' acyclic ' 2,2′-biphenyl derivatives. The fragmentation patterns are all similar to those described earlier. The dithiol (X) fragments to an ion at *m/e* 185, which is of equal intensity to that of the dibenzothiophen ion at *m/e* 184. These two ions are joint base peaks. The metastable ion at *m/e* 157 shows that the ion of mass 185 is formed directly from the molecular ion (see Scheme 5).

The methyl and ethyl derivatives of the dithiol (X) fragment in a very similar way; in each case the alkyl sulphonium derivative of the dibenzothiophen ion is formed.



Scheme 5

The mass spectrum of 2,2′-dimethylthiobiphenyl (XVII; R = Me) is very similar to that of biphenyl-2,2′-dithiol (X); in this case a methylated dibenzothiophen ion is produced in place of the protonated species. Metastable ions indicate that one path involves a two-step process as shown for the dithiol (X). In contrast, 2,2′-diethylthiobiphenyl (XVII; R = Et) fragments by a modification of the process described. The ethyl sulphonium ion of dibenzothiophen is formed in the usual manner but eliminates ethylene to give the protonated dibenzothiophen as the base peak of the spectrum (see Scheme 6). The protonated dibenzothiophen presumably eliminates a hydrogen atom to give the dibenzothiophen ion as before.

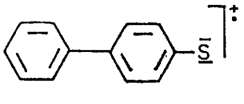


Scheme 6

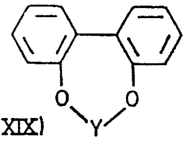
In contrast with its 2,2′-isomer, 4,4′-diethylthiobiphenyl fragments in an entirely different way. The molecular ion is the base peak in the spectrum, probably because the molecule cannot easily rearrange to give a stable heterocyclic ion as is the case for the 2,2′-biphenyl dithia compounds. The second most abundant ion represents loss of an ethyl radical from the molecular ion. A peak at *m*/*e* 184 is probably the biphenylylene ion (XVIII) rather than the dibenzothiophen ion because a peak corresponding to the biphenylylene ion (*m*/*e* 152) is present in much greater abundance than is observed in the spectrum of dibenzothiophen.

The 2,2′-bridged biphenyls so far described contain the bulky sulphone and smaller sulphide groups and it was thought that the synthesis of the ether analogues would be of interest. As the oxygen atom is much smaller than sulphur, this would give three series of 2,2′-bridged biphenyls with a graded steric effect between the series.

The 2,2′-bridged dioxa-biphenyl system of structure type (XIX) was first synthesised by Bibergeil and Diels in 1902.[14] Thus on heating biphenyl-2,2′-diol, potassium hydroxide, water, and dibromoethane at 150° for 16 h, the 8-membered ring system (XIX; Y = $[CH_2]_2$) was isolated in unspecified yield. Di-iodomethane and dibromopropane in the same reaction gave polymeric solids. In 1965 Hewgill and Hewitt synthesised the smallest bridged diethers of this type by acid-catalysed condensation of biphenyl-2,2′-diol with various ketones.[15] Thus with acetone the dioxepin (XIX; Y = CMe_2) was obtained in 30% yield.

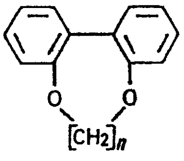


(XVIII)

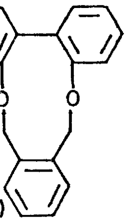


(XIX)

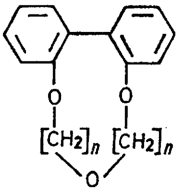
A difficulty in synthesising these ether heterocycles is the low reactivity of disodium biphenyl-2,2′-dioxide, even under reflux. Thus, use of a similar procedure to that for the synthesis of the sulphur heterocycles fails. We find that this problem is solved by use of aqueous dimethyl sulphoxide as solvent. Thus biphenyl-2,2′-diol, sodium hydroxide, and the appropriate reactive αω-dihalogenoalkane, di(halogenoalkyl) ether, or αα′-dibromoxylene, were heated in aqueous dimethyl sulphoxide for 24 h. We have found that a range of heterocycles can be obtained in good yield by this method. Treatment of the disodium salt of biphenyl-2,2′-diol with di-iodomethane or dibromo-ethane, -propane, -butane, or -pentane gave the novel heterocycles (XX; *n* = 1—5). Dibromo-*o*-xylene in this reaction gave the 10-membered ring system (XXI), but only polymer was formed when dibromo-*m*-xylene was used. Finally di(chloromethyl) and di(2-bromoethyl) ether in this reaction yielded the heterocycles (XXII; *n* = 1 and 2).



(XX)



(XXI)



(XXII)

Yields of heterocycles are not strictly comparable since a number of these reactions were carried out under

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[14] O. Diels and A. Bibergeil, *Ber.*, 1902, **35**, 302.

[15] F. R. Hewgill and D. G. Hewitt, *J. Chem. Soc.*, 1965, 1536.

a variety of conditions in order to improve the yields. The conditions used to prepare the trimethylene bridged heterocycle (XX; $n = 3$) gave good results, although more dilute solutions and a slower addition of the dibromopropane might give even better yields.

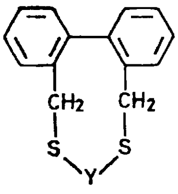
The oxygen heterocycles were synthesised mainly in order to examine their u.v. spectra (see following papers); however, the p.m.r. spectra and mass spectra of the compounds also show some interesting features.

On examination of the p.m.r. spectrum of the methylene-bridged compounds (XX; $n = 1$) the aromatic protons appear as two separate multiplets centred at τ 2·4 and 2·85 and integrate for two and six protons respectively. A similar observation has been made earlier with regard to the sulphur analogues, and the phenomena could similarly be attributed to the deshielding of the 6,6′ protons. Interestingly, the partial separation of the aromatic multiplets observed in the 2,2′-bridged dithia-biphenyls does not occur to the same extent in the corresponding ethers.

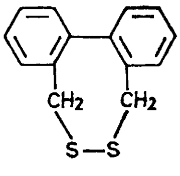
The mass spectra of the bridged and unbridged diethers have been recorded, to determine their molecular weights. Although the spectra have not been examined in detail, some preliminary comments are appropriate.

From the spectra of the ethers it is clear that cyclisation reactions to form the dibenzofuran ion (m/e 168) occur only to a limited extent. The molecular ion is the base peak in the spectrum of the 2,2′-biphenyl diethers, which is surprising when one considers the apparent ease with which the sulphur analogues fragment to the dibenzothiophen ion. The spectra of the diethers are much more complex than those of the sulphur compounds and interpretation is more difficult.

We have also prepared a number of sulphur heterocycles of the general formulae type (XXIII), mainly to study their optical (*i.e.* conformational) stability and to compare this with the optical stability of isomeric sulphur compounds.



(XXIII)



(XXIV)

One member of this series, the 8-membered cyclic disulphide (XXIV), was synthesised by Hess, Lüttringhaus, and Rosenbaum.[16] Thus 2,2′-bis(bromomethyl)-biphenyl on treatment with potassium thioacetate gave the di(thioacetoxymethyl) derivative, which on oxidation with ferric chloride in ether and acetic acid gave the cyclic disulphide (XXIV) in 50% yield. The same workers obtained 2,2′-bis(mercaptomethyl)biphenyl by hydrolysis of 2,2′-di-(thioacetoxymethyl)biphenyl with methanolic sodium methoxide, in *ca.* 50% yield.[16]

We have found very simple syntheses of both the cyclic disulphide (XXIV) and of 2,2′-bis(mercaptomethyl)biphenyl. The disulphide (XXIV) may be obtained in 50% yield by treatment of 2,2′-bis(bromomethyl)biphenyl with sodium disulphide (' Na_2S_2 ') in aqueous methanol. This simple one-step procedure gave a good yield of the required product. 2,2′-Bis(mercaptomethyl)biphenyl was obtained by use of the general procedure described for the synthesis of *o*-xylenedithiol (Ia), in 90% yield.

We find that 2,2′-bis(mercaptomethyl)biphenyl condenses with acetone in the presence of hydrochloric acid, to give the 9-membered cyclic heterocycle (XXIII; $Y = CMe_2$). When the disodium salt of 2,2′-bis-(mercaptomethyl)biphenyl is treated with di-iodomethane in alcohol another 9-membered ring (XXIII; $Y = CH_2$) is produced in good yield. Also αα′-dibromo-*m*-xylene in the same reaction gave the 15-membered heterocycle (XXIII; $Y = m\text{-}CH_2{\cdot}C_6H_4{\cdot}CH_2$) in good yield.

These heterocycles have been examined with regard to their optical stability and will be discussed elsewhere.

In addition to the heterocyclic systems a number of compounds were prepared in which the hetero-atom is not part of a ring, in order to compare them with the heterocyclic compounds. The compounds are *S*- or *O*-alkylated (or benzylated) derivatives of *o*-xylenedithiol, biphenyl-2,2′-diol, and biphenyl-2,2′-dithiol. In general these compounds were synthesised in a similar manner to the related heterocycles, except that dilution problems associated with intra- and inter-molecular cyclisation do not arise.

2,2′-Dialkylthiobiphenyls react with dimethyl sulphate to give the disulphonium salts in good yield. Thus 2,2′-dimethylthiobiphenyl and its ethyl analogue when heated with dimethyl sulphate gave the corresponding disulphonium salts [as (XXV; $X = MeSO_4^-$)]. Some of the 2,2′-bridged dithia-heterocycles when heated with dimethyl sulphate, gave black tars, which could not be purified.

The thermal decomposition of the disulphonium di(methyl sulphates) (XXV; $X = MeSO_4^-$) is of interest, since it proceeds in a manner which is novel in sulphur chemistry. Thus thermal decomposition of the di-(methyl sulphate) (XXV; $R = Me$, $X = MeSO_4^-$) gave 2,2′-dimethylthiobiphenyl and dibenzothiophen. On the other hand the di(methyl sulphate) of 2,2′-diethylthiobiphenyl on decomposition gave the two possible di(alkyl sulphides) (XVII; $R = Me$, Et), dibenzothiophen, and probably the ' mixed alkyl ' compound. It is significant that in the non-heterocyclic products of the last decomposition reaction, the di(methyl sulphide) was the most abundant and the di(ethyl sulphide) the least abundant product, in accord with the greater ease with which an ethyl group is generally ejected in such reactions. We have found the amount of dibenzothiophen produced in these thermal decomposition reactions is dependent on the temperature, and below

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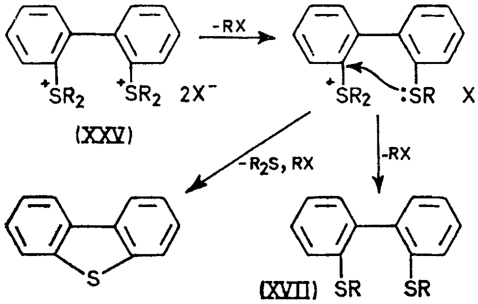
[16] A. Lüttringhaus, U. Hess, and H. J. Rosenbaum, *Z. Nat.*, 1967, **22*b***, 1296.

200° the product is, in some cases, free from dibenzothiophen.

Analogous thermal decomposition reactions are known for comparable nitrogen, phosphorus, and arsenic compounds,[17-19] and the thermal decompositions described here appear to be additional examples of this type of reaction. The production of dibenzothiophen is thought to take place *via* an internal nucleophilic displacement (S_Ni) reaction as follows:



The dialkyl and dibenzyl derivatives of *o*-xylenedithiol (Ia) and biphenyl-2,2′-dithiol (X), have sulphide groups suitably disposed to act as novel chelate ligands. We have prepared some 1 : 1 co-ordination compounds, by heating representative *S*-alkyl derivatives of the dithiols (Ia) and (X) with potassium tetrabromopalladite or potassium tetrabromoplatinite in aqueous ethanol. The results of molecular-weight determination by the vapour pressure–thermistor method in CH_2Cl_2 show that the complexes are probably monomeric and moderately dissociated in this solvent.

EXPERIMENTAL

Compounds are colourless unless otherwise stated. M.p.s were measured on a Kofler hot stage apparatus. I.r. absorption spectra were obtained using a Perkin-Elmer 257 grating spectrophotometer. N.m.r. spectra were recorded in deuteriochloroform (unless otherwise stated) on a Perkin-Elmer 60 MHz instrument. Mass spectra were recorded on a Perkin-Elmer–Hitachi R.M.U.-6 spectrometer. Molecular weights were determined by mass spectrometry, or with a Mechrolab 301A vapour-pressure osmometer. V.p.c. analyses were carried out using a Pye model 64 gas chromatograph, fitted with a 6 ft. spiral glass column packed with Chromosorb P coated with 5% S.E.30 silicone oil: a flame ionisation detector was used. All operations involving alkaline solutions of dithiols were performed under nitrogen.

o-*Xylene-αα′-dithiol* (Ia).—This compound was prepared by modification of a method by Fletcher and Pan.[6] αα′-Dibromo-*o*-xylene (Ib) (13·2 g) and thiourea (8·4 g) were stirred overnight in dimethyl sulphoxide (150 g) at room temperature. The *S*-alkyl isothiouronium salt solution was hydrolysed by stirring it for $\frac{1}{2}$ h with aqueous 10% sodium hydroxide (600 ml). Ice and concentrated hydrochloric acid were then added to the solution at such a rate as to keep the solution at room temperature, until it became acidic. The milky solution was extracted with ether (3 × 300 ml), and the ether extract was then washed with water and dried (Na_2SO_4). The ether was removed to leave a colourless oil, which on cooling gave the crystalline dithiol (8·2 g, 96%), m.p. 45° (lit.,[5] m.p. 44—46°).

Tetrathia Macrocycles with o-*Xylylene Bridges*

(a) 4,7,11,14-*Tetrahydrodibenzo*[e,l][1,3,8,10]*tetrathiacyclotetradecene* (IV; $n = 1$).—Di-iodomethane (17·4 g) was added to a stirred solution prepared from sodium (3·0 g) in ethanol (500 ml) and the dithiol (Ia) (11·0 g). The solution was stirred for 1 h, refluxed for a further 2 h, and then filtered whilst hot to remove polymer. As the solution cooled a white solid was obtained, which crystallised from ethanol to give an impure crystalline product. The mixture was chromatographed on preparative t.l.c. plates with a 1 : 1 benzene/60°—80° light petroleum as eluant, to give two bands on the plate. The higher band was removed and extracted with ethanol to give dihydrobenzo[*e*][1,3]-dithiepin (III; $n = 1$) (needles from ethanol) (15%), m.p. 157—159° (lit.,[2] m.p. 152—153°); τ 2·6 (s, 4 ArH), 5·9 (s, 4 CH_2), and 6·0 (s, 2 CH_2).

Extraction of the lower band yielded the macrocyclic *dimer* (IV; $n = 1$) (needles from ethanol) (3%), m.p. 198—200° (Found: C, 59·0; H, 5·5. $C_{18}H_{20}S_4$ requires C, 59·3; H, 5·5%), *m/e* 364 (M^+); τ 2·5 (A_2B_2 multiplet, 8 ArH), 5·75 (s, 8 CH_2), and 5·95 (s, 4 CH_2).

(b) 2,3,5,8,10,11,13,16-*Octahydrodibenzo*[f,n][1,4,9,12]-*tetrathiacyclohexadecene* (IV; $n = 2$).—Finely powdered dibromo-*o*-xylene (13·2 g) was added to a stirred solution prepared from sodium (2·3 g) in ethanol (300 ml) and ethanethiol (4·7 g) during 10 min. The reaction mixture was refluxed for 1 h, and then filtered. The filtrate, on cooling, yielded a pale precipitate, which crystallised from benzene as fine needles to give the *dimer* (IV; $n = 2$) (5%), m.p. 142—144° (Found: C, 60·9; H, 6·2. $C_{20}H_{24}S_4$ requires C, 61·2; H, 6·2%), *m/e* 392 (M^+); τ 2·55 (A_2B_2 multiplet, 8 ArH), 6·0 (s, 8 CH_2), and 7·1 (s, 8 CH_2). On addition of water to the residual filtrate a mass of crystals of tetrahydrobenzo[*f*][1,4]dithiocin (III; $n = 2$) was deposited (40%), m.p. 94—96° (lit.,[3] m.p. 93°); τ 2·6 (s, 4 ArH), 6·1 (s, 4 CH_2), and 7·1 (s, 4 CH_2).

(c) 2,3,6,9,11,12,15,18-*Octahydrodibenzo*[g,p][1,5,10,14]-*tetrathiacyclo-octadecene* (IV; $n = 3$).—Powdered dibromo-*o*-xylene (13·2 g) was added to a stirred solution prepared from sodium (2·3 g) in ethanol (500 ml) and propane-1,3-dithiol (5·4 g). After the addition of the dibromide, the solution was refluxed for 2 h, and the clear solution decanted. The alcoholic solution was diluted with 2—3 volumes of water to yield a solid, which crystallised from 95% ethanol in needles to give the *benzo*[g][1,5]*dithionin* (III; $n = 3$) (40%), m.p. 85° (Found: C, 63·1; H, 6·65. $C_{11}H_{14}S_2$ requires C, 62·85; H, 6·7%), *m/e* 210 (M^+); τ 2·55 (s, 4 ArH), 6·15 (s, 4 CH_2), 7·35 (t, 4 CH_2), and 8·1 (m, 2 CH_2). The residual polymer was extracted with hot benzene, which on cooling yielded crystals of the *dimer* (IV; $n = 3$) (5%), m.p. 208—210° (Found: C, 62·9; H, 6·8. $C_{22}H_{28}S_4$ requires C, 62·85; H, 6·7%), *m/e* 420 (M^+); τ 2·55 (A_2B_2 multiplet, 8 ArH), 6·05 (s, 8 CH_2), 7·3 (t, 8 CH_2), and 8·0 (q, 4 CH_2).

(d) 2,5,7,12,14,17,19,24-*Octahydro*-8(11),20(23)-*dietheno-dibenzo*[c,o][1,6,13,18]*tetrathiacyclotetracosene* (V).—A solution of dibromo-*o*-xylene (8·6 g) in boiling ethanol (200 ml)

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[17] H. Heaney, D. M. Heinekey, F. G. Mann, and I. T. Millar, *J. Chem. Soc.*, 1958, 3838.

[18] D. W. Allen, F. G. Mann, and I. T. Millar, *J. Chem. Soc.* (*C*), 1967, 1869.

[19] D. W. Allen and I. T. Millar, *J. Chem. Soc.* (*C*), 1968, 2406.

was quickly added to a stirred solution prepared from sodium (1·5 g) in ethanol (250 ml) and *o*-xylenedithiol (Ia) (5·2 g). The mixture was set aside overnight, and then the alcohol was decanted and the residue extracted with hot benzene. After many recrystallisations from benzene the *tetracosene* was obtained as large rhombs (10%), m.p. 183—184° (Found: C, 70·7; H, 5·85. $C_{32}H_{32}S_4$ requires C, 70·6; H, 5·9%), *m/e* 544 (M^+); τ 2·62 (s, 8 ArH), 2·67 (s, 8 ArH), and 6·4 (two s, 16 CH_2).

(e) 2,5,7,10-*Tetrahydrodibenzo*[c,h][1,6]*dithiecin* (II).—This compound was prepared according to the method due to Autenrieth and Brüning [1] in 50% yield; τ 2·3 and 2·6 (A_2B_2 multiplets, 8 ArH) and 6·55 (s, 8 CH_2).

*αα'-Dibenzylthio-*o*-xylene.*—A solution prepared from sodium (0·46 g) in ethanol (50 ml) and toluene-α-thiol (2·5 g) and dibromo-*o*-xylene (2·64 g) was stirred for 2 h. The mixture was diluted with an equal volume of water to precipitate a solid which crystallised from aqueous ethanol to give αα'-dibenzylthio-*o*-xylene (3·4 g, 95%), m.p. 48—50° (lit.,[2] isolated as an oil).

*αα'-Dimethylthio-*o*-xylene.*—A solution of *o*-xylenedithiol (Ia) (4·0 g), methyl iodide (5·9 g), and potassium hydroxide (2·6 g) in ethanol (100 ml) was stirred for 1 h. The solution was diluted with twice its volume of water, and extracted with ether. Distillation of the ether gave αα'-dimethylthio-*o*-xylene (3·0 g, 65%), b.p. 114°/1·0 mmHg (Found: C, 60·6; H, 7·0. $C_{10}H_{14}S_2$ requires C, 60·6; H, 7·1%); τ 2·7 (s, 4 ArH), 6·1 (s, 4 CH_2), and 8·1 (s, 6 CH_3).

*Biphenyl-*2,2'*-dithiol* (XVII).—This compound was prepared by modification of Barber and Smiles [9] procedure, as follows. (a) *Sodium* o*-iodobenzenesulphonate.* A solution of orthanilic acid (73 g), sodium hydroxide (16·8 g), and sodium nitrite (28 g) in water (600 ml) at 0° was added dropwise to a stirred solution of concentrated sulphuric acid (75 ml) in water (200 ml) at 0°, during 10 min. After the mixture had been stirred for a further 10 min, potassium iodide (94 g) in water (200 ml) was added to the stirred suspension. The mixture was gradually heated on a steam-bath until most of the nitrogen was evolved. The solution was then evaporated to *ca.* 500 ml (sulphurous acid being added as necessary during the evaporation to reduce the liberated iodine); the crystalline product was deposited as the solution cooled. It was filtered off, and washed with saturated brine; yield of damp product, 130—140 g.

(b) *Disodium biphenyl-*2,2'*-disulphonate.* A solution of sodium *o*-iodobenzenesulphonate (350 g) and saturated aqueous copper sulphate (10 ml) in boiling water (2 l) was stirred vigorously under reflux with activated copper-bronze [11] (300 g) for 24 h. The hot solution was separated from excess of copper-bronze, *etc.*, by filtration, and evaporated to give the crude grey product (*ca.* 150 g after drying at 150°).

(c) *Biphenyl-*2,2'*-bis*(*sulphonyl chloride*). Phosphorus pentachloride (300 g) and dry disodium biphenyl-2,2'-disulphonate (180 g) were intimately mixed; the mixture rapidly becoming warm and mobile. The mixture was heated under reflux at 150° for 1 h and then cooled at 0°. The product was stirred with ice (1 kg) until the excess of phosphorus pentachloride was hydrolysed. The dense sludge-like product was filtered off, and washed with water, to yield biphenyl-2,2'-bis(sulphonyl chloride) (100 g).

(d) *Biphenyl-*2,2'*-dithiol* (X). Concentrated hydrochloric acid (200 ml) was added in small portions to a stirred suspension of crude biphenyl-2,2'-bis(sulphonyl chloride) (100 g), zinc dust (150 g), and 95% ethanol (200 ml), the temperature being kept below 20°. When the acid had been added, the solution was carefully boiled, and more acid and ethanol were added at intervals until all the zinc had dissolved. The hot solution was quickly filtered and diluted with water to give, on cooling, copious needles of almost pure biphenyl-2,2'-dithiol (50 g). The overall yield was *ca.* 40%.

*Reactions of Biphenyl-*2,2'*-dithiol with Reactive αω-Dihalides to give Dithia-heterocycles*

(a) *Dibenzo*[d,f]*dithiepin* (XI; $n = 1$).—A solution of di-iodomethane (13·4 g) in methylated spirit (200 ml) was added dropwise during 0·5 h to a stirred solution from sodium (2·3 g) in methylated spirit (1 l) and the dithiol (X) (11 g). The solution was stirred for 2 h, refluxed for 15 min, and then filtered whilst hot. The alcoholic solution was evaporated to 400 ml, and diluted with 2—3 volumes of water to give a pale yellow solid. The solid was dissolved in the minimum of benzene and eluted down a column containing 200 g of 'Woelm' neutral alumina (activity 1) with 1 : 1 light petroleum (60—80°)–benzene. Evaporation of the first fractions of eluant yielded crystals of the *dithiepin* (XI; $n = 1$) which recrystallised from 95% ethanol as prisms (4·5 g, 39%), m.p. 95—96° (Found: C, 67·7; H, 4·3. $C_{13}H_{10}S_2$ requires C, 67·8; H, 4·4%); τ 2·4 (m, 2 ArH), 2·65 (m, 6 ArH), and 5·8 (s, 2 CH_2). A sample (0·3 g) was dissolved in hot glacial acetic acid (5 ml) and mixed with hydrogen peroxide (100 vol) (5 ml). The mixture was set aside for 24 h when crystals of *dibenzo*[d,f]-[1,3]*dithiepin* SSS'S'*-tetraoxide* had been deposited, m.p. 254—255° (from aqueous acetic acid) (Found: C, 53·5; H, 3·3. $C_{13}H_{10}O_4S_2$ requires C, 53·1; H, 3·4%); $\nu_{max.}$ (mull) 1325 and 1150 cm^{-1} [S(=O)$_2$].

(b) 6,7-*Dihydrodibenzo*[e,g][1,4]*dithiocin* (XI; $n = 2$).—A solution of 1,2-dibromoethane (9·4 g) in methylated spirit (600 ml) was added dropwise overnight to a stirred solution prepared from sodium (2·3 g) in methylated spirit (1 l), and the dithiol (X) (10·9 g). The solution was evaporated to *ca.* 400 ml, and diluted with 2—3 volumes of water to give a pale yellow solid. The solid was dissolved in benzene, boiled with charcoal, and then evaporated to give colourless crystals, which when recrystallised from 95% ethanol gave the *dithiocin* (XI; $n = 2$) (5·0 g, 41%), m.p. 179—180° (Found: C, 69·0; H, 4·7. $C_{14}H_{12}S_2$ requires C, 68·8; H, 4·9%), *m/e* 244 (M^+); τ 2·2 (m, 2 ArH), 2·7 (m, 6 ArH), and 6·98 (A_2B_2, m, 4 CH_2). A sample was oxidised to give the SSS'S'*-tetraoxide* as prisms from acetic acid, m.p. 234—236° (Found: C, 54·8; H, 3·7. $C_{14}H_{12}O_4S_2$ requires C, 54·6; H, 3·9%); $\nu_{max.}$ (mull) 1320 and 1160 cm^{-1} [S(=O)$_2$]; τ 1·85 (m, 2 ArH), 2·5 (m, 6 ArH), and 6·4 (m, A_2B_2, 4 CH_2).

(c) 6,7-*Dihydrodibenzo*[f,h][1,5]*dithionin* (XI; $n = 3$).—This compound was prepared as in (b) using 1,3-dibromopropane (4·6 g) in methylated spirit (500 ml), and sodium (1·05 g) in methylated spirit (1 l) with the dithiol (X) (5·0 g). Chromatography on an alumina column to remove polymer [see preparation (a)] gave colourless crystals of the *dithionin* (XI; $n = 3$); recrystallisation from 95% ethanol gave needles (2·3 g, 36%), m.p. 69—70° (Found: C, 69·5; H, 5·3. $C_{15}H_{14}S_2$ requires C, 69·8; H, 5·5%), *m/e* 258 (M^+); τ 2·3—2·9 (m, 8 ArH), 7·3 (t, 4 CH_2), and 7·9 (m, 2 CH_2). Oxidation of a sample gave the SSS'S'*-tetraoxide* (prisms from acetic acid), m.p. 256—258° (Found: C, 56·0;

H, 4·2. $C_{15}H_{14}O_4S_2$ requires C, 55·9; H, 4·4%); $\nu_{max.}$ (mull) 1305 and 1120 cm^{-1} [S(=O)$_2$].

(d) 6,7,8,9-*Tetrahydrodibenzo*[b,d][1,6]*dithiecin* (XI; n = 4).—This compound was prepared as in (b) using 1,4-dibromobutane (7·2 g) in methylated spirit (500 ml), and sodium (1·54 g) in methylated spirit (1 l) with the dithiol (X) (7·4 g). The crude white solid gave needles (from 95% ethanol) of the *dithiecin* (XI; n = 4) (6·0 g, 66%), m.p. 143—144° (Found: C, 70·4; H, 5·8. $C_{16}H_{16}S_2$ requires C, 70·6; H, 5·9%), m/e 272 (M^+); τ 2·35 (m, 2 ArH), 2·7 (m, 6 ArH), 7·8 (m, 4 CH$_2$), and 8·6 (4 CH$_2$).

A sample was oxidised to the SSS′S′-*tetraoxide* which gave prisms from acetic acid, m.p. >300° (Found: C, 57·3; H, 4·7. $C_{16}H_{16}O_4S_2$ requires C, 57·1; H, 4·8%); $\nu_{max.}$ (mull) 1305 and 1130 cm^{-1} [S(=O)$_2$].

(e) 6,7,8,9-*Tetrahydrodibenzo*[b,d][1,6]*dithiacycloundecene* (XI; n = 5).—This compound was prepared as in (b) using 1,5-dibromopentane (6·9 g) in methylated spirit (500 ml), and sodium (1·4 g) in methylated spirit (1 l) with the dithiol (X) (6·5 g). The crude crystalline product was purified by percolation through an alumina column as in preparation (a), to give needles of the *cycloundecene* (XI; n = 5) (from 95% ethanol) (7·0 g, 81%), m.p. 121—122° (Found: C, 71·6; H, 6·4. $C_{17}H_{18}S_2$ requires C, 71·3; H, 6·35%), m/e 286 (M^+); τ 2·6 (m, 2 ArH), 2·85 (m, 6 ArH), 7·4 (m, 4 CH$_2$), and 8·6 (m, 6 CH$_2$). A sample was oxidised to give the SSS′S′-*tetraoxide* as needles from acetone, m.p. >300° (Found: C, 58·8; H, 5·1. $C_{17}H_{18}O_4S_2$ requires C, 58·3; H, 5·2%); $\nu_{max.}$ (mull) 1300 and 1150 cm^{-1} [S(=O)$_2$].

Reactions of Biphenyl-2,2′-*dithiol* (X) *with* αω-*Dihalogeno-ethers to give Dithiaoxa-heterocycles*

(a) *Dibenzo*[d,f][1,3,8]*oxadithionin* (XII; n = 1).—Di-(chloromethyl) ether (3·83 g) in methylated spirit (500 ml) was added overnight to a stirred solution prepared from sodium (1·53 g) in methylated spirit (1 l) and the dithiol (X) (7·4 g). The solution was evaporated, and diluted with water to give a white solid, which gave the *oxadithionin* (from 95% ethanol) (5·1 g, 59%), m.p. 150—152° (Found: C, 64·5; H, 4·5. $C_{14}H_{12}OS_2$ requires C, 64·6; H, 4·65%), m/e 260 (M^+); τ 2·7 (m, 8 ArH), 5·15 (AB doublets, J_{AB} 11·3 Hz, $\Delta\nu_{AB}$ = 15·6 Hz, 4 CH$_2$). Oxidation of a sample gave the SSS′S′-*dioxide* as needles from acetic acid, m.p. 250° (Found: C, 52·1; H, 3·6. $C_{14}H_{12}O_5S_2$ requires C, 51·9; H, 3·7%), $\nu_{max.}$ (mull) 1300 and 1150 cm^{-1} [S(=O)$_2$]; τ 1·9 (m, s ArH), 2·5 (m, 6 ArH), and 5·35 (AB doublets, J_{AB} 12·5 Hz, $\Delta\nu_{AB}$ = 18·8 Hz, 4 CH$_2$).

(b) 6,7,9,10-*Tetrahydrodibenzo*[e,g][1,4,9]*oxadithiacycloundecene* (XII; n = 2).—Bis-(2-bromoethyl) ether (7·7 g), the dithiol (X) (7·3 g) and sodium (1·53 g) were heated in alcohol as in the previous preparation to give a white solid, which crystallised from 95% ethanol to give the *oxadithiacycloundecene* (XII; n = 2) (6·4 g, 67%), m.p. 129° (Found: C, 67·1; H, 5·6. $C_{16}H_{16}OS_2$ requires C, 66·7; H, 5·6%), m/e 288 (M^+); τ 2·6 (m, 8 ArH), 6·5 (m, 4 CH$_2$), and 7·0 (m, 4 CH$_2$). A sample on oxidation gave the SSS′S′-*tetraoxide* as crystals from acetic acid, m.p. 250° (Found: C, 54·8; H, 4·8. $C_{16}H_{16}O_5S_2$ requires C, 54·6; H, 4·6%); $\nu_{max.}$ (mull) 1310 and 1120 cm^{-1} [S(=O)$_2$].

Reactions between Biphenyl-2,2′-*dithiol* (X) *and* αα′-*Dibromo*-o-*xylene to give Dithia-heterocycles*

(a) *Tribenzo*[b,d,h][1,6]*dithiecin* (XIII).—Dibromo-*o*-xylene (8·8 g), the dithiol (X) (7·3 g), and sodium (1·63 g) were heated in methylated spirit as above to give a yellow solid, which crystallised from 95% ethanol to give the *dithiecin* (XIII) (7·3 g, 69%), m.p. 102—103° (Found: C, 75·3; H, 4·8. $C_{20}H_{16}S_2$ requires C, 75·0; H, 5·0%), m/e 320 (M^+); M 302 by osmometry; τ 2·5 (m, 2 ArH), 2·8 (m, 10 ArH), and 6·37 (AB doublets, J_{AB} 14·5 Hz, $\Delta\nu_{AB}$ = 9 Hz, 4 CH$_2$). Oxidation of a sample gave the SSS′S′-*tetraoxide* as crystals from acetic acid, m.p. 285° (Found: C, 62·4; H, 3·8. $C_{20}H_{16}O_4S_2$ requires C, 62·5; H, 4·2%); $\nu_{max.}$ (mull) 1310 and 1130 cm^{-1} [S(=O)$_2$]; τ 1·95 (m, 2 ArH), 2·5 (m, 10 ArH), and 5·7 (AB doublets, J_{AB} 15 Hz, $\Delta\nu_{AB}$ = 20 Hz, 4 CH$_2$).

(b) 6,7-*Dihydro*-7(11)-*methenodibenzo*[b,d][1,6]*dithiatridecene* (XIV).—A solution of αα′-dibromo-*m*-xylene (8·8 g) in warm methylated spirit was added overnight to a stirred solution prepared from sodium (1·53 g) in methylated spirit (1 l) and the dithiol (X) (7·3 g). Water (1 l) was added to the solution, and the resulting yellow solid was crystallised from boiling acetone to give the *dithiatridecene* (XIV) (6·1 g, 57%), m.p. 164—165° (Found: C, 75·3; H, 4·7. $C_{20}H_{16}S_2$ requires C, 75·0; H, 5·0%), m/e 320 (M^+); τ 2·3—3·4 (m, 12 ArH), and 6·15 (AB doublets, J_{AB} 14 Hz, $\Delta\nu_{AB}$ = 12·8 Hz, 4 CH$_2$). A sample on oxidation gave the SSS′S′-*tetraoxide* as crystals from acetic acid, m.p. 304° (Found: C, 62·6; H, 4·2. $C_{20}H_{16}O_4S_2$ requires C, 62·5; H, 4·2%); $\nu_{max.}$ (mull), 1310 and 1150 cm^{-1} [S(=O)$_2$]; τ 1·9—3·0 (m, 12 ArH) and 5·6 (s, 4 CH$_2$).

(c) When αα′-dibromo-*p*-xylene was heated with the disodium salt of the dithiol (XV) it gave a white polymer. It had low solubility in common solvents and melted over a wide temperature range. No crystalline product was isolated from the reaction.

The Reaction between Biphenyl-2,2′-*dithiol* (X) *and the Lower Sulphur Chlorides to give Polysulphide Heterocycles*

(a) *Reaction with Sulphur Dichloride* (SCl_2).—Sulphur dichloride (1·03 g) was added to a stirred solution of the dithiol (X) (2·18 g) in dry benzene (500 ml). A solution of triethylamine (2·0 g) in benzene (250 ml) was then added to the solution during 1 h. The resulting emulsion was shaken with water, and the benzene solution was separated, dried, and evaporated to yield a yellow solid. This solid was extracted with boiling acetone to yield the disulphide (IX) (1·05 g), m.p. 110—112° (lit.,[9] m.p. 113°). The residual solid from the acetone extraction was extracted with boiling chloroform to yield pale yellow rhombs of *dibenzo*[e,g][1,2,3,4]*tetrathiocin* (XV) (1·0 g), m.p. 200° (Found: C, 51·5; H, 3·1. $C_{12}H_8S_4$ requires C, 51·4; H, 2·9%), m/e 280 (M^+); τ 2·1 (m, 2 ArH) and 2·6 (m, 8 ArH).

(b) *Reaction with Sulphur Monochloride* (S_2Cl_2).—The dithiol (X) (2·8 g), sulphur monochloride (1·7 g), and trimethylamine (2·6 g) were mixed as in the above preparation. The benzene solution on evaporation yielded a yellow solid, which crystallised from chloroform as pale yellow rhombs of the tetrathiocin (XV) (2·5 g), m.p. 200°. In this reaction none of the cyclic disulphide (IX) was isolated.

Dialkyl and Dibenzyl Derivatives of the Dithiol (X)

(a) 2,2′-*Dimethylthiobiphenyl*.—Methyl iodide (2·82 g) was added to a stirred solution of the dithiol (X) (2·18 g) and sodium hydroxide (0·8 g) in ethanol (20 ml). After being set aside for 1 h, the solution was diluted with two volumes of water to yield a solid, which crystallised from 95%

ethanol to give dimethylthiobiphenyl (2·2 g, 85%), m.p. 155—157° (lit.,[20] m.p. 155°). A sample was oxidised to the SSS'S'-*tetraoxide*, m.p. 170—172° (Found: C, 54·5; H, 4·5. $C_{14}H_{14}O_4S_2$ requires C, 54·2; H, 4·55%), τ 1·9 (m, 2 ArH), 2·5 (m, 6 ArH), and 7·07 (s, 6 CH_3).

(b) 2,2'-*Diethylthiobiphenyl*.—Ethyl iodide (2·0 g) was added to a stirred solution of the dithiol (X) (2·2 g) and sodium hydroxide (0·8 g) in ethanol (20 ml). The solution was boiled under reflux for 2 h and then diluted with water and extracted with ether. Evaporation of the dried extracts gave a white solid, which crystallised from 95% ethanol to give needles of 2,2'-*diethylthiobiphenyl* (2·1 g, 77%), m.p. 54—55° (Found: C, 69·7; H, 6·4. $C_{16}H_{18}S_2$ requires C, 70·0; H, 6·6%), τ 2·8 (m, 8 ArH), 7·2 (q, 4 CH_2), and 8·8 (t, 6 CH_3). A sample was oxidised to the SSS'S'-*tetraoxide*, m.p. 175° (Found: C, 56·6; H, 5·3. $C_{16}H_{18}O_4S_2$ requires C, 56·8; H, 5·4%), τ 1·9 (m, 2 ArH), 2·5 (m, 6 ArH), 6·95 (q, 4 CH_2), and 8·8 (t, 6 CH_3).

(c) 2,2'-*Di-isopropylthiobiphenyl*.—A solution of isopropyl bromide (2·46 g), the dithiol (X) (2·2 g), and sodium hydroxide (0·8 g) in ethanol (50 ml) was refluxed overnight. The solution was diluted with water, and extracted with ether to yield an oil, which was bulb-distilled to give 2,2'-*di-isopropylthiobiphenyl* (Found: C, 71·8; H, 7·3. $C_{18}H_{22}S_2$ requires C, 71·5; H, 7·3%), τ 2·8 (m, 8 ArH), 6·8 (heptuplet, 2 aliphatic H), and 8·8 (d, CH_3).

(d) 2,2'-*Dibenzylthiobiphenyl*.—Benzyl chloride (2·5 g) was added to a solution of the dithiol (X) (2·2 g) and potassium hydroxide (1·1 g) in ethanol (50 ml). After 1 h the solution was heated to boiling; water was then added and as the solution cooled crystals of 2,2'-*dibenzylthiobiphenyl* were deposited (from 95% ethanol) (3·4 g, 85%), m.p. 116° (Found: C, 78·7; H, 5·4. $C_{26}H_{22}S_2$ requires C, 78·4; H, 5·6%), τ 2·9 (m, 18 ArH) and 6·1 (s, 4 CH_2). A sample was oxidised to the SSS'S'-*tetraoxide*, m.p. 233—235° (Found: C, 68·0; H, 4·7. $C_{26}H_{22}O_4S_2$ requires C, 67·5; H, 4·8%), τ 1·8—3·2 (m, 18 ArH) and 5·4 (s, 4 CH_2).

*The Reaction between Biphenyl-*2,2'*-diol and* αω*-Dihalogenoalkanes*

(a) *Dibenzo*[d,f]*dioxepin* (XX; *n* = 1).—Biphenyl-2,2'-diol (9·3 g) was dissolved in a solution of sodium hydroxide (4 g) in water (100 ml) and added to dimethyl sulphoxide (200 ml). The solution was heated on a steam-bath, and a solution of di-iodomethane (13·5 g) in dimethyl sulphoxide (75 ml) was added during 1 h. The reactants were heated under reflux overnight and then poured into 2—3 volumes of water. The emulsion was extracted with ether (3 × 250 ml) and the combined ether solution was thoroughly shaken with water (3 × 500 ml). Evaporation of the ether solution gave a brown oil, which was stirred and warmed with aqueous 10% sodium hydroxide (100 ml). The residue was washed with water, and boiled with ether and charcoal; evaporation of the filtered and dried ether solution gave a pale yellow oil. This was passed through a column of 'Woelm' neutral alumina with benzene as eluant, to give a colourless crystalline product. A small sample was bulb-distilled to give the *dioxepin* (XX; *n* = 1) (2·5 g, 25%), m.p. 35—36° (Found: C, 79·0; H, 5·05. $C_{13}H_{10}O_2$ requires C, 78·8; H, 5·1%), *m/e* 198 (M^+); τ 2·4 (m, 2 ArH), 2·85 (m, 6 ArH), and 4·5 (s, 2 CH_2). (N.B. In all these reactions between disodium biphenyl-2,2'-diyl oxide and various alkylene, ether, and xylene dihalides, there was always an excess of the oxide at the end of the reaction. The dihalides appear to be partly removed in a side reaction before reaction with the oxide. An excess of dihalide in these reactions may give improved yields of the heterocycles.)

(b) 6,7-*Dihydrodibenzo*[e,g][1,4]*dioxocin* (XX; *n* = 2).—*Method* 1. (By modification of the method due to Claret and Archer.[21]) A solution of biphenyl-2,2'-diol (18·6 g), sodium hydroxide (8 g), and 1,2-dibromoethane (18·6 g) in methylated spirit (500 ml) was refluxed for 24 h. The solution was worked up to give 99% of the original diol and 0·1 g of the desired heterocycle, m.p. 98° (lit.,[14] m.p. 98°).

Method 2. The first method was repeated, and after 24 h, dimethyl sulphoxide (200 ml) was added to the solution, which was then heated on a steam-bath overnight under reflux. Evaporation of the alcohol, followed by dilution with an equal volume of water, gave an emulsion which was extracted with ether (2 × 200 ml). (Evaporation of a sample of the ether solution gave a pale yellow oil. N.m.r. examination of this showed it to be mainly biphenyl-2,2'-diol with a small amount of the desired heterocycle. No dibromoethane remained in the product.) The ether extracts were combined, and thoroughly shaken with aqueous 10% sodium hydroxide (2 × 100 ml), followed by water (2 × 100 ml); evaporation of the dried ether solution gave a pale yellow oil, which crystallised from 95% alcohol to give the dioxocin (XX; *n* = 2) (2·9 g, 13%), m.p. 98° (lit.,[14] m.p. 98°), *m/e* 212 (M^+); τ 2·75 (m, 8 ArH) and 5·8 (collapsed A_2B_2 multiplet, 4 CH_2).

(c) 6,7-*Dihydrodibenzo*[f,h][1,5]*dioxonin* (XX; *n* = 3).—A solution of 1,3-dibromopropane (11 ml) in dimethyl sulphoxide (50 ml) was added during 1·5 h to a hot solution of biphenyl-2,2'-diol (9·3 g), potassium hydroxide (5·6 g), water (75 ml), and dimethyl sulphoxide (50 ml). The solution was heated on a steam-bath for a further 3 h, and then poured into ice-cold aqueous 5% potassium hydroxide (300 ml). The mixture was stirred and the emulsion was extracted with ether (2 × 200 ml); the combined ether extracts were then shaken with water (3 × 400 ml). After being shaken with charcoal and sodium sulphate, the filtered solution was evaporated to give a straw-coloured oil. This was passed down a column packed with 'Woelm' neutral alumina (200 g) with benzene as eluant, to give a colourless oil, which gave the *dioxonin* (XX; *n* = 3) (from aqueous ethanol) (3·1 g, 27%), m.p. 67—69° (Found: C, 80·1; H, 6·3. $C_{15}H_{14}O_2$ requires C, 79·6; H, 6·25%), *m/e* 226 (M^+); τ 2·85 (m, 8 ArH), 5·7 (t, 4 CH_2), and 8·1 (quintuplet, 2 CH_2).

(d) 6,7,8,9-*Tetrahydrodibenzo*[b,d][1,6]*dioxecin* (XX; *n* = 4).—Biphenyl-2,2'-diol (9·3 g) potassium hydroxide (5·6 g), and 1,4-dibromobutane (11 ml) were heated in aqueous dimethyl sulphoxide under the conditions described for preparation (c) to give a pale yellow oily product, which crystallised when cooled and scratched. Recrystallisation from 95% ethanol gave needles of the *dioxecin* (XX; *n* = 4) (4·1 g, 34%), m.p. 110—111° (Found: C, 80·4; H, 6·8. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%), *m/e* 240 (M^+); τ 2·8 (m, 8 ArH), 5·6 (m, 4 CH_2), and 8·1 (m, 4 CH_2).

(e) 6,7,8,9-*Tetrahydrodibenzo*[b,d][1,6]*dioxacycloundecene* (XX; *n* = 5).—Biphenyl-2,2'-diol (9·3 g), potassium hydroxide (5·6 g), and 1,5-dibromopentane (11 ml) were heated together in aqueous dimethyl sulphoxide as described

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[20] K. Brand and O. Stallmann, *J. prakt. Chem.*, 1924, **107**, 358.

[21] A. W. Archer and P. A. Claret, *Chem. and Ind.*, 1969, 171.

in preparation (c), to yield a colourless solid, which crystallised from 95% ethanol to give the *cycloundecene* (XX; $n = 5$) (3·1 g, 24%), m.p. 109—110° (Found: C, 80·3; H, 6·7. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%), *m/e* 254 (M^+); τ 3·0 (m, 8 ArH), 5·9 (broad peak, 4 CH_2), and 8·35 (broad peak, 6 CH_2).

*The Reaction Between Biphenyl-*2,2′*-diol and* αω*-Dihalogeno-ethers to give Trioxa-heterocycles*

(a) *Dibenzo*[f,h][1,3,5]*trioxepin* (XXII; $n = 1$).—A solution of bis(chloromethyl) ether (11·4 g) in dimethyl sulphoxide (50 ml), was rapidly added to a warm solution of biphenyl-2,2′-diol (18·6 g) and sodium hydroxide (8·0 g) in dimethyl sulphoxide (200 ml) and water (200 ml). The solution was heated overnight, diluted with six volumes of water, and acidified with hydrochloric acid. The turbid solution was extracted with ether; the extract after being shaken with water, was dried and evaporated to give an orange oil. This was stirred with aqueous 10% sodium hydroxide (100 ml) to give a white solid, which crystallised from 95% ethanol as small rhombs of the *trioxepin* (XXII; $n = 1$) (1·5 g, 14%), m.p. 144—145° (Found: C, 74·1; H, 5·4. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3%), *m/e* 228 (M^+); τ 2·75 (m, 8 ArH) and 4·7 (s, 4 CH_2).

(b) 6,7,9,10-*Tetrahydrodibenzo*[h,j][1,4,6]*trioxacycloundecene* (XXII; $n = 2$).—Biphenyl-2,2′-diol (9·3 g), potassium hydroxide (5·6 g), and di-(2-bromoethyl) ether (12 ml) in aqueous dimethyl sulphoxide were treated as in preparation (a) above. On dilution of the aqueous dimethyl sulphoxide solution with ice–water a solid was precipitated: this crystallised from carbon tetrachloride as prisms of the *cycloundecene* (XXII; $n = 2$) (3·5 g, 27%), m.p. 190—192° (Found: C, 74·9; H, 6·15. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%), *m/e* 256 (M^+); τ 2·95 (m, 8 ArH), 5·8 (m, 4 CH_2), and 6·2 (m, 4 CH_2).

*The Reaction Between Biphenyl-*2,2′*-diol and* αα′*-Dibromoxylenes*

(a) *Tribenzo*[b,d,h][1,6]*dioxecin* (XXI).—Finely powdered αα′-dibromo-*o*-xylene (13·2 g) was added to a solution of biphenyl-2,2′-diol (9·3 g) and sodium hydroxide (4·0 g) in water (100 ml) and dimethyl sulphoxide (200 ml). During the first hour the reactants were warmed and shaken to dissolve the dibromide, after which the reactants were heated on a steam-bath overnight. The resulting solution was poured onto ice (200 g) and the emulsion was extracted with ether (2 × 250 ml); the combined extracts were shaken with water (3 × 200 ml). Evaporation of the dried ether solution gave an orange gum, which crystallised from 95% ethanol to give needles of the *dioxecin* (XXI) (4·3 g, 30%), m.p. 156—158° (Found: C, 82·9; H, 5·7. $C_{20}H_{16}O_2$ requires C, 83·3; H, 5·6%), *m/e* 288 (M^+); τ 2·8 (m, 12 ArH) and 4·8 (s, 4 CH_2).

(b) αα′-Dibromo-*o*-xylene in a similar reaction, gave a polymeric product only.

2,2′-*Bis*(*mercaptomethyl*)*biphenyl*.—A solution of 2,2′-bis(bromomethyl)biphenyl (17·1 g) and thiourea (8·4 g) in dimethyl sulphoxide (150 ml), was stirred overnight. The solution was then stirred with 10% sodium hydroxide solution (600 ml) for 1 h, and then acidified by the addition of ice and hydrochloric acid, the mixture being kept at room temperature. The acidic solution was then extracted with ether (3 × 250 ml) and the combined extracts were shaken with water (3 × 400 ml). The ether solution was dried ($MgSO_4$) and evaporated at 30° under vacuum to give 2,2′-bis(mercaptomethyl)biphenyl as an almost colourless oil (11·1 g, 90%).

Dibenzo[d,f][1,2]*dithiocin* (XXIV).—Methanol (500 ml) was added to a warm solution of sodium sulphide nonahydrate (12 g) in water (100 ml). Sulphur (1·6 g), was added to the solution which was stirred and heated on a steam-bath to give a yellow solution. A warm solution of 2,2′-bis(bromomethyl)biphenyl (12 g) in methanol (1 l) was added to the stirred solution overnight and at room temperature. The resulting yellow solid was filtered off, and boiled with charcoal and chloroform (40 ml); evaporation of the dried and filtered chloroform solution gave a pale yellow crystalline solid. Recrystallisation from 95% ethanol gave needles of the dithiocin (XXIV) (4·4 g, 51%), m.p. 167° (lit.,[16] m.p. 169°).

Reaction of 2,2′-*Bis*(*mercaptomethyl*)*biphenyl with Di-iodomethane and with* αα′-*Dibromo*-m-*xylene*.—(a) 5,9-*Dihydrodibenzo*[e,g][1,3]*dithionin* (XXIII; Y = CH_2).—A solution of di-iodomethane (5·36 g) in methylated spirit (500 ml) was added overnight to a stirred solution prepared from the dithiol (4·9 g) and sodium (1·0 g) in alcohol (500 ml). The alcoholic solution was evaporated to dryness, and the residue was extracted with chloroform. After evaporation of the chloroform solution to 10 ml, the solution was passed down a column (65 × 3·5 cm) of ‘ Woelm ’ neutral alumina with 1 : 1 benzene–light petroleum as eluant. This gave a colourless oil, which crystallised on cooling to give needles of the *dithionin* (XXIII; Y = CH_2) (from aqueous ethanol) (2·4 g, 46%), m.p. 95—97° (Found: C, 70·0; H, 5·75. $C_{15}H_{14}S_2$ requires C, 69·75; H, 5·45%); τ 2·7 (m, 8 ArH), 6·45 (s, 2 CH_2), and 6·55 (AB doublets, J_{AB} 15 Hz, $\Delta\nu_{AB} = 28$ Hz, 4 CH_2).

(b) 5,7,8,15-*Tetrahydro*-8(12)-*methenodibenzo*[c,e][1,8]*dithiacyclopentadecene* [XXIII; Y = *m*-$(CH_2)_2{\cdot}C_6H_4$].—A solution of dibromo-*m*-xylene (5·3 g) in methylated spirit (1 l) was added overnight to a stirred solution prepared from the dithiol (4·9 g) and sodium (1 g) in ethanol (500 ml). The resulting solution was evaporated to *ca.* 100 ml, diluted with water (200 ml), and the resulting solid separated, and boiled with acetone and charcoal. The acetone solution gave crystals of the *pentadecene* [XXIII; Y = *m*-$(CH_2)_2{\cdot}C_6H_4$] (3·5 g, 50%), m.p. 150—152° (Found: C, 76·0; H, 5·75. $C_{22}H_{20}S_2$ requires C, 75·85; H, 5·8%); τ 2·1—3·6 (complex, m, 12 ArH), 6·5 (s, 4 CH_2), and 6·6 (AB doublets, J_{AB} 16 Hz, $\Delta\nu_{AB} = 37$ Hz, 4 CH_2).

Reaction of 2,2′-*Bis*(*mercaptomethyl*)*biphenyl with Acetone*.—A solution of the dithiol (2·46 g), acetone (1 ml), and concentrated hydrochloric acid (1 ml) in ethanol (15 ml) was set aside overnight. On dilution of the mixture with water a white solid was precipitated, which crystallised from 95% ethanol as needles of 7,7-*dimethyl*-5,9-*dihydrodibenzo*-[e,g][1,3]*dithionin* (XXIII; Y = CMe_2) (1·8 g, 63%), m.p. 97—99° (Found: C, 71·6; H, 5·9. $C_{17}H_{18}S_2$ requires C, 71·3; H, 6·3%); τ 2·75 (m, 8 ArH), 6·3 (s, 4 CH_2), and 8·5 (s, 6 CH_3).

6,6-*Dimethyldibenzo*[d,f][1,3]*dithiepin* (VIII; Y = CMe_2).—This compound was prepared by the method due to Barber and Smiles [9] in 70% yield. A sample was oxidised to the SSS′S′-*tetraoxide*, m.p. 227—229° (Found: C, 55·6; H, 4·3. $C_{15}H_{14}O_4S_2$ requires C, 55·9; H, 4·4%), $\nu_{max.}$ (mull) 1320 and 1050 cm^{-1} [$S(=O)_2$].

6-*Phenyldibenzo*[d,f][1,3]*dithiepin* (VIII; Y = CHPh).—This compound was prepared in 60% yield, by the method due to Barber and Smiles.[9] A sample was oxidised to the

SSS′S′-*tetraoxide*, m.p. 236—238° (Found: C, 62·0; H, 3·8. $C_{19}H_{14}O_4S_2$ requires C, 61·6; H, 3·8%), $\nu_{max.}$ (mull) 1320 and 1050 cm^{-1} [S(=O)$_2$].

Di(phenylthiomethyl) Ether.—A solution of thiophenol (11 g), di(chloromethyl) ether (5·7 g), and potassium hydroxide (5·6 g) in ethanol (250 ml), was refluxed for 2 h. Water (500 ml) was added to the solution, and the product was extracted with ether. Evaporation of the dried extract and distillation gave the *ether* (11 g, 85%), b.p. 134°/0·3 mmHg (Found: C, 64·4; H, 5·15. $C_{14}H_{14}OS_2$ requires C, 64·1; H, 5·4%).

Preparation of Disulphonium Salts

(a) *Biphenyl*-2,2′-*bisdimethylsulphonium Di(methyl sulphate)* (XXV; R = Me, X = $MeSO_4^-$).—2,2′-Di(methylthio)biphenyl (XVII; R = Me) (1·0 g) was heated with dimethyl sulphate (1·0 g) for 4 h at 95°. As the mixture cooled, a crystalline solid was deposited; this was ground with acetone and then recrystallised from ethanol to give colourless prisms (1·4 g, 67%), m.p. 103—108°. After many recrystallisations analytical values were still unsatisfactory, and the ^{1}H n.m.r. spectrum indicated that ethanol was present, even after drying at 60°. The corresponding *dipicrate* was therefore prepared by mixing hot aqueous solutions of the disulphonium salt and sodium picrate: it had m.p. 176° (Found: C, 46·2; H, 3·2; N, 11·3. $C_{28}H_{24}N_6O_{14}S_2$ requires C, 46·1; H, 3·3; N, 11·5%).

(b) *Biphenyl*-2,2′-*bisethylmethylsulphonium Di(methyl sulphate)*.—2,2′-Di(ethylthio)biphenyl (XVII; R = Et) (0·5 g) and dimethyl sulphate (0·6 g) were heated for 4 h at 70°: the mixture was cooled and triturated with acetone to give a colourless solid (0·45 g, 47%), m.p. 160°. The yellow crystalline *dipicrate* was prepared to characterise the disulphonium salt; m.p. 169° (Found: C, 46·9; H, 3·4; N, 10·9. $C_{30}H_{28}N_6O_{14}S_2$ requires C, 47·3; H, 3·7; N, 11·1%).

Thermal Decomposition of Disulphonium Salts

(a) *Biphenyl*-2,2′-*bisdimethylsulphonium Di(methyl sulphate)* (XXV; R = Me, X = $MeSO_4^-$).—The salt (0·1 g) was decomposed by heating it in a bulb tube at 0·2 mm, in an air bath. The distillate was washed from the receiver with ether and the solution was used directly for vapour phase chromatography (v.p.c.) at 200°.

(i) *Decomposition below* 180°. V.p.c. examination of the ether extract showed only one compound to be present; comparison with authentic material showed this to be the bis(methyl sulphide) (XVII; R = Me), R_t 5·6 min.

(ii) *Decomposition between* 240—250°. V.p.c. analysis of the ether extract showed two peaks, with R_t 5·6 and 3·2 min, the second peak being shown to be dibenzothiophen by comparison with authentic material.[9] The ratio of dibenzothiophen to the bis(methyl sulphide) was 2 : 8.

(b) *Biphenyl*-2,2′-*bisethylmethylsulphonium Di(methyl sulphate)*.—The disulphonium salt (0·1 g) was decomposed by heating it at 240°, as above. V.p.c. analysis of an ether extract of the distillate showed the presence of the bis(methyl sulphide) (XVII; R = Me), R_t 3·2; dibenzothiophen, R_t 5·6; the bis(ethyl sulphide) (XVII; R = Et), R_t 7·1; while a peak at 6·3 was probably due to 2-thioethyl-2′-thiomethylbiphenyl. The ratio of dibenzothiophen : bis(methyl sulphide) : bis(ethyl sulphide) : 2-thioethyl-2′-thiomethylbiphenyl was 0·05 : 5 : 1 : 4. On increasing the temperature of the decomposition to 340°, the yield of dibenzothiophen increased to 9%.

Complexes of αα′-*Alkyl-(or aryl-)thio*-o-*xylenes*.—Molecular weights of complexes were determined by the vapour pressure–thermistor method in dichloromethane. The homogeneity of the complexes was established by t.l.c.

(a) *Dibromo-(*αα′-*dimethylthio*-o-*xylene)palladium*(II).— A hot saturated solution of aqueous ethanolic potassium tetrabromopalladite (104 mg) was added to a hot solution of αα′-dimethylthio-*o*-xylene (40 mg) in ethanol (5—10 ml). As the solution cooled fine brown crystals were deposited, which were filtered off and washed with hot ethanol to give the *complex*, decomp. above *ca.* 220° (Found: C, 25·6; H, 2·95. $C_{10}H_{14}Br_2PdS_2$ requires C, 25·8; H, 3·0%).

(b) *Dibromo-(*αα′-*diethylthio*-o-*xylene)palladium*(II). This complex was prepared similarly; orange crystals (from chloroform), m.p. 218—220° (Found: C, 29·4; H, 3·7. $C_{12}H_{18}Br_2PdS_2$ requires C, 29·2; H, 3·7%).

(c) *Dibromo-(*αα′-*dibenzylthio*-o-*xylene)palladium*(II). This complex was prepared similarly; orange crystals, m.p. 186—188° (Found: C, 42·7; H, 3·25%; *M*, 452. $C_{22}H_{22}Br_2PdS_2$ requires C, 42·8; H, 3·6%; *M*, 617).

Complexes of 2,2′-*Bis(alkyl/aryl-thio)biphenyl*.—(a) *Dibromo*-(2,2′-*dimethylthiobiphenyl)palladium*(II).—This complex was prepared under the usual conditions; purple crystals, m.p. 255—257° (from aqueous ethanol) (Found: C, 33·3; H, 2·8. $C_{14}H_{14}Br_2PdS_2$ requires C, 32·9; H, 2·75%).

(b) *Dibromo*-(2,2′-*dimethylthiobiphenyl)platinum*(II). This was prepared by the usual method, using potassium tetrabromoplatinite; orange crystals, m.p. 229—231° (Found: C, 28·2; H, 2·3. $C_{14}H_{14}Br_2PtS_2$ requires C, 27·95; H, 2·35%).

(c) *Dibromo*-(2,2′-*diethylthiobiphenyl)palladium*(II). This complex was prepared similarly, using potassium tetrabromopalladite; orange–red needles, m.p. 245° (decomp.) (Found: C, 36·1; H, 3·1. $C_{16}H_{18}Br_2PdS_2$ requires C, 35·8; H, 3·3%).

(d) *Dibromo*-(2,2′-*diethylthiobiphenyl)platinum*(II). This complex was prepared similarly, using potassium tetrabromoplatinite; fine orange prisms, m.p. 148—150° (decomp.) (Found: C, 30·7; H, 2·6. $C_{16}H_{18}Br_2PtS_2$ requires C, 30·5; H, 2·9%).

(e) *Dibromo*-(2,2′-*dibenzylthiobiphenyl)palladium*(II). This was prepared in the usual way; scarlet needles (from aqueous ethanol), m.p. 206—210° (Found: C, 47·0; H, 3·15%; *M*, 428. $C_{26}H_{22}Br_2PdS_2$ requires C, 46·9; H, 3·3%; *M*, 665).

(f) *Dibromo*-(2,2′-*dibenzylthiobiphenyl)platinum*(II). This complex was made by the usual method; lemon prisms (from aqueous ethanol), m.p. >300° (Found: C, 41·8; H, 2·6%; *M*, 533. $C_{26}H_{22}Br_2PtS_2$ requires C, 41·4; H, 2·95%; *M*, 753).

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