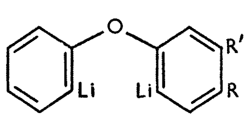
913. *The Preparation and Properties of* 10 : 10-*Disubstituted Phenoxsilanes.*

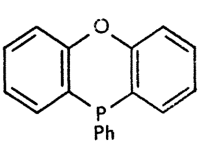
By Christopher H. S. Hitchcock, Frederick G. Mann, and A. Vanterpool.

The preparation, properties, and stereochemistry of certain 10 : 10-disubstituted phenoxsilanes and of *spiro*bis-10-phenoxsilane are discussed. Although this spirocyclic compound is readily prepared and stable, attempts to synthesise methyl-substituted derivatives failed, the products being stable silanols in which the hydroxyl group undergoes strong intramolecular hydrogen bonding.

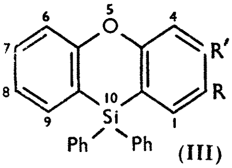
It has been shown by Mann and Millar [1] that 2 : 2′-dilithiodiphenyl ether (I; R = R′ = H), prepared by the action of *n*-butyl-lithium on the 2 : 2′-dibromo-ether, reacts with dichlorophenylphosphine, $PhPCl_2$, to form 10-phenylphenoxphosphine (II) in 63% yield. This reaction, showing the marked predominance of cyclisation over linear condensation, indicated that other reagents having two reactive chlorine atoms might also give the corresponding cyclic derivatives in good yield.



(I)



(II)



(III)

This we find to be the case. Dichlorodiphenylsilane, Ph_2SiCl_2, reacts with the dilithio-derivative (I; R = R′ = H) to form 10 : 10-diphenylphenoxsilane (III; R = R′ = H) in 59% yield, and the 10 : 10-dimethyl analogue is similarly formed in 78% yield. Moreover, the dilithio-derivative reacts very readily with silicon tetrachloride to form *spiro*bis-10-phenoxsilane (IV).

These results were obtained in 1953—1954.[2] It has recently been shown by Oita and Gilman [3] that *n*-butyl-lithium reacts directly with diphenyl ether to give the dilithio-derivative (I; R = R′ = H), from which the diphenyl derivative (III; R = R′ = H), its dimethyl analogue, and the spirocyclic derivative (IV) have similarly been prepared.

The stereochemistry of the diphenylphenoxsilane (III; R = R′ = H) and the spirocyclic derivative (IV) is of considerable interest. A tricyclic system consisting of two *o*-phenylene rings linked through two central atoms, such as the oxygen and silicon atoms in the compound (III), will be planar only if the intervalency angles subtended within the central ring by these atoms closely approach 120°.[4] If these angles are appreciably less than 120°, as in the phenoxarsines [5] and 5 : 10-dihydroarsanthrens,[6] the molecule will necessarily be folded about an axis through these central atoms.

No precise information is available regarding the intervalency angles at the silicon and oxygen atoms within the ring in the phenoxsilane system. The C–O–C angle can adjust itself to structural requirements over a wide range: for example, it is 61·6° in ethylene oxide,[7] 108° ± 3° in diethyl ether,[8] 112° ± 5° in 1 : 4-dioxan,[8, 9] 124° ± 5° in diphenyl

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[1] Mann and Millar, *J.*, 1953, 3746.

[2] Vanterpool, Ph.D. Diss., Cambridge, 1954; *Abs. Cambridge Diss.*, 1953—1954, p. 246 (Cambridge Univ. Press, 1956).

[3] Oita and Gilman, *J. Amer. Chem. Soc.*, 1957, **79**, 339.

[4] Campbell, Le Fèvre, Le Fèvre, and Turner, *J.*, 1938, 404.

[5] Lesslie and Turner, *J.*, 1934, 1170.

[6] Chatt and Mann, *J.*, 1940, 1184.

[7] Cunningham, Boyd, Myers, Gwinn, and Le Van, *J. Chem. Phys.*, 1951, **19**, 676.

[8] Cf. Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.

[9] Hassel and Viervoll, *Acta Chem. Scand.*, 1947, **1**, 149, give 108° ± 5°.

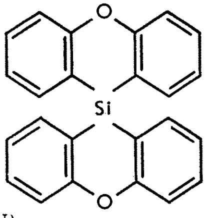
ether,[10] and 123° ± 1° in di-*p*-bromodiphenyl ether [11] and its iodo-analogue.[12] In spite of these values for free diphenyl ethers, the C–O–C angle in the phenoxsilane ring system might be less than 120°, particularly if there is a strong tendency for the C–Si–C angle to attain 109°; consequently the molecule might be folded about the O–Si axis.

Apart from *X*-ray crystal analysis, evidence for this folding could be sought in two directions, chemical and physical. First, a derivative of the phenoxsilane (III) having a substituent in one of the *o*-phenylene rings should be resolvable into optically active forms if the ring system is stably folded. We have, therefore, prepared 2-methyl-10 : 10-diphenylphenoxsilane (III; R = Me, R′ = H) (55% yield) by interaction of 2 : 2′-dilithio-4-methyldiphenyl ether (I; R = Me, R′ = H) and dichlorodiphenylsilane, and converted it with *N*-bromosuccinimide into the 2-bromomethyl derivative (III; R = CH_2Br, R′ = H). Attempts to convert the bromomethyl group into an acidic or basic group for optical resolution proved, however, unsatisfactory. The bromomethyl compound (III; R = CH_2Br, R′ = H) gave no decisive product when brought into reaction with ethyl sodiomalonate or potassium cyanide, or hexamethylenetetramine with subsequent hydrolysis of the crude hexaminium salt.[13] and it failed to react with ammonia under various conditions or with potassium phthalimide. The 2-dibromomethyl derivative (III; R = $CHBr_2$, R′ = H) resisted normal hydrolysis, but with silver nitrate in aqueous 2-ethoxyethanol solution, gave the 2-aldehyde (III; R = CHO, R′ = H), which did not crystallise and was identified solely as its 2 : 4-dinitrophenylhydrazone. Work on these lines was therefore abandoned.

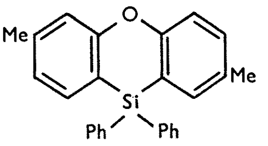
Secondly, it appeared that evidence for the folded structure might be obtained by comparing the dipole moments of 10 : 10-diphenylphenoxsilane (III; R = R′ = H) and its 2 : 7-dimethyl derivative (V). Mr. E. W. Randall and Dr. L. E. Sutton, who have kindly investigated our compounds, find that these two derivatives in benzene solution have dipole moments of 0·97 ± 0·03 and 1·01 ± 0·03 D respectively. They report:

" It is not possible to form any definite conclusions regarding the angle between the aromatic ring planes because (i) the total moments are small, and the precision of the measurements is, therefore, relatively poor; moreover, error due to neglect of atom polarisation may be considerable; (ii) the substitution moments due to the methyl groups are small, so the change in total moment is insensitive to change in interplanar angle.

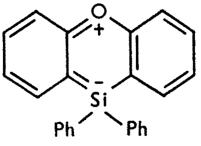
" If, however, the total moments are taken at their face value and reasonable assumptions (see below) are made concerning bond lengths and bond moments, the interplanar angle is calculated as 165—158° for (III; R = R′ = H) and as 158—154° for (V).



(IV)



(V)



(IIIA)

These angles would be considerably larger if the $_AP$ terms were appreciable. The effect of contributions from structures such as (IIIA) upon the calculations would be to make the angles smaller, although on physical grounds one expects such contributions to make the tricyclic system planar.

" The assumptions made are: (i) That the O–C bond moment is 1·16 D. This is

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[10] Coop and Sutton, *J.*, 1938, 1869.

[11] Toussaint, *Mem. Soc. roy. Sci. Liège*, 1952, **12**, 1.

[12] Toussaint, *Bull. Soc. Sci. Liège*, 1946, **15**, 86.

[13] Cf. Angyal, Morris, Tetaz, and Wilson, *J.*, 1950, 2141; Wood, Tung, Perry, and Gibson, *J. Amer. Chem. Soc.*, 1950, **72**, 2992.

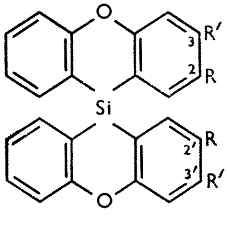
derived from the value, 1·16 D, for the moment of diphenyl ether[14] and an assumed C–O–C angle of 120°;[10,15] (ii) that the methyl substitution moment is 0·40 D;[16] (iii) that the contributions of the Si–C bond moments can be ignored because of the approximate symmetry of the bonds around the silicon and the probable small magnitude of the moment;[17] (iv) that the bond lengths are 1·84 Å for Si–C, 1·40 Å for C–C, and 1·40 Å for C–O.[18]

" A simple stereochemical calculation based on the above bond lengths, and values of 120° and 109° respectively for the oxygen and silicon bond angles, shows that the model with the least angular strain has an interplanar angle of 150°.

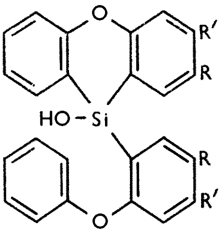
" From these two sets of calculations it would appear that the interplanar angle is between 150° and 160°."

It is clear, therefore, that dipole studies of this type require phenoxsilanes containing substituents, such as chlorine, which are more polar than methyl groups, but the synthesis of these chloro-derivatives presents considerable difficulties.

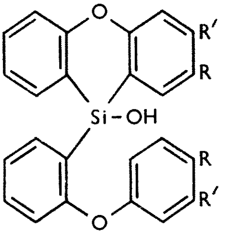
The investigation of the stereochemistry of the spirocyclic system in *spiro*bis-10-phenoxsilane (IV) has revealed an unexpected factor. If each phenoxsilane unit in this compound is folded about the O–Si axis, and the silicon atom has the usual tetrahedral angle, the compound is dissymmetric and should be capable (if the folding is stable) of existing in optically active forms. If a substituent group is inserted in two corresponding positions in the molecule, giving for example the 2 : 2′-dimethyl derivative (VI; R = Me, R′ = H) or the 3 : 3′-dimethyl derivative (VI; R = H; R′ = Me), these products should each exist in two racemic forms.



(VI)



(VII)



(VIII)

We have attempted to prepare such substituted compounds both by direct substitution in the compound (IV), and by synthesis, whereby the positions of the substituents would be clearly defined.

The compound (IV) possesses considerable stability. This is shown by the fact that 2 : 2′-dilithiodiphenyl ether (I; R = R′ = H), when treated even with one molecular equivalent of silicon tetrachloride, forms the spirocyclic derivative (IV), apparently to the exclusion of 10 : 10-dichlorophenoxsilane. Further, we have recovered the spiro-compound (IV) unchanged after it had been treated with fuming nitric acid in hot acetic anhydride solution, with bromine in boiling chloroform solution, and with *N*-bromo-succinimide and benzoyl peroxide in boiling carbon tetrachloride solution. The use of more vigorous conditions appeared to cause extensive rupture of the cyclic system, and no decisive products could be isolated. This high stability of the compound (IV) makes the direct preparation of substituted derivatives apparently impracticable.

In view of the ready formation of 2-methyl-10 : 10-diphenylphenoxsilane (III; R = Me, R′ = H) in 55% yield of purified material by the interaction of dichlorodiphenylsilane and

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[14] Hampson, Farmer, and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **143**, 147.

[15] Maxwell, Hendricks, and Mosley, *J. Chem. Phys.*, 1935, **3**, 699.

[16] Everard and Sutton, *J.*, 1951, 2807.

[17] Freiser, Eagle, and Speier, *J. Amer. Chem. Soc.*, 1953, **75**, 2821.

[18] " Table of Interatomic Distances and Molecular Configurations," forthcoming Special Publication of the Chemical Society.

2 : 2′-dilithio-4-methyldiphenyl ether (I; R = Me, R′ = H), we treated the latter with silicon tetrachloride in order to obtain 2 : 2′-dimethyl*spiro*bis-10-phenoxsilane (VI; R = Me, R′ = H). Thorough purification of the crude product yielded, however, solely (17% yield) 10-hydroxy-2-methyl-10-(5-methyl-2-phenoxyphenyl)phenoxsilane (VII; R = Me, R′ = H) or its 10-*o*-(*p*-tolyloxy)phenyl isomer (VIII; R = Me, R′ = H). Consequently the desired spirocyclic system had apparently not been formed, in marked contrast to the ready formation of the unsubstituted spiran (IV).

We find similarly that, although 2 : 2′-dilithio-5-methyldiphenyl ether (I; R = H, R′ = Me) reacts with dichlorodiphenylsilane to give 3-methyl-10 : 10-diphenylphenoxsilane (III; R = H, R′ = Me) in 43% yield, it reacts with silicon tetrachloride to give a crude product from which the silanol (VII; R = H, R′ = Me) or its isomer (VIII; R = H, R′ = Me) has been isolated in low yield.

The presence of a methyl group in 2 : 2′-dilithiodiphenyl ether appears, therefore, to inhibit the formation of the spirocyclic system, while not affecting that of the initial phenoxsilane ring system. Other examples are known of the influence of nuclear methyl substituents on heterocyclic-ring formation in entirely different systems, such as Mole and Turner's quantitative study of the effect of such groups on the cyclisation of 2-dichloroarsinodiphenyl ether derivatives to the corresponding phenoxarsines,[19] but complete inhibition of ring formation by a nuclear methyl group which is not exerting steric obstruction is rare.

We have investigated in some detail the properties of the silanol (VII or VIII; R = Me, R′ = H), which is the more readily obtained. This silanol also has considerable stability. When first isolated, it was thought to be the spiran (VI; R = Me, R′ = H) and that the persistent low carbon content was due to analytical difficulties. It was, therefore, converted into the bromomethyl compound (VII; R = CH_2Br, R′ = H) and thence into the aldehyde compound (VII; R = CHO, R′ = H). All three compounds gave analytical results in accordance with the silanol structure, which had apparently been unaffected by these reactions. Further, the silanol sublimes with some charring at 380°/760 mm., and the sublimate on recrystallisation yields the unchanged silanol: in contrast, triphenylsilanol at 280° yields hexaphenyldisiloxane.

In experiments designed to give evidence for the hydroxyl group, the silanol was recovered after treatment with thionyl chloride, with ethanolic zinc chloride, and with *n*-butyl-lithium followed (in separate experiments) by methyl iodide, benzoyl chloride, and toluene-*p*-sulphonyl chloride.

To determine whether the two silanols were of type (VII) or (VIII), their infrared spectra have been studied. These spectra appeared to show decisively that both silanols are of the type (VIII), for neither shows a band at 13·5 μ characteristic of a monosubstituted benzene ring, but both show a strong band at 13·2 μ characteristic of an *o*-phenylene group, and in this respect resemble the spiran (IV). These results are in marked contrast to those of 10 : 10-diphenylphenoxsilane and its 2- and 3-methyl derivatives, which do show both these bands (cf. Table).

Benzene substitution bands in Nujol mull.

	13·2 μ region	13·5 μ region
Silanol (VII–VIII; R = Me, R′ = H)	13·25	—
Silanol (VII–VIII; R = H, R′ = Me)	13·2	—
10 : 10-Diphenylphenoxsilane (III; R = R′ = H)	13·15	13·5
2-Methyl-10 : 10-diphenylphenoxsilane (III; R = Me, R′ = H)	13·2	13·5
3-Methyl-10 : 10-diphenylphenoxsilane (III; R = H, R′ = Me)	13·1	13·55
Spiran (IV)	13·2	—

This apparently sharp differentiation of the two classes may, however, be false, for phenol and anisole show bands corresponding to the phenyl group at 753 cm.$^{-1}$ (13·30 μ)

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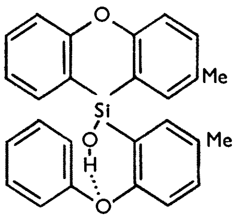
[19] Mole and Turner, *J.*, 1939, 1720.

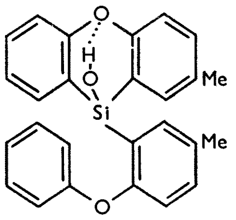
and at 756 cm.$^{-1}$ (13·25 μ) respectively,[20] and diphenyl ether at 748 cm.$^{-1}$ (13·4 μ). This shift of the phenyl band to lower μ values when this group is attached to oxygen means that the silanols might be of type (VII) and that the phenyl band now coincides with the *o*-phenylene band. Hence this structural point remains undecided. For convenience, these silanols will be referred to subsequently as type (VII).

The infrared spectra of the silanols showed, moreover, no indication of a hydroxyl group. Now the silicon atom in silanols has no influence on the O–H stretching vibrations, except when hydrogen bonding occurs. Consequently free $\geqq$Si·OH groups usually absorb strongly in the normal region, 3690—3590 cm.$^{-1}$. Intermolecular hydrogen bonding normally shifts this sharp band to a lower frequency, with increase in the intensity of the band. This type of hydrogen bonding is usually destroyed on dissolution of the silanol, and the normal sharp band appears. Thus triphenylsilanol in carbon tetrachloride solution shows a strong band at 3690 cm.$^{-1}$, but in Nujol mull shows a broad band at 3250 cm.$^{-1}$, indicating intermolecular hydrogen bonding in the solid state.[21]

The two silanols (VII; R = Me, R′ = H) and (VII; R = H, R′ = Me) in either Nujol mulls or carbon tetrachloride solution showed no bands between 2500 and 3700 cm.$^{-1}$, except the sharp bands at 2950—3050 cm.$^{-1}$ associated with aromatic C–H stretching. If the silanols possessed $\geqq$SiOH groups, the O–H band is shifted to *ca.* 3000 cm.$^{-1}$ (with weakening of intensity), and is thus masked by these C–H bands. This shift would result only if strong intramolecular bonding occurred, and it appears therefore that, for example, the silanol (VII; R = Me, R′ = H) has the structure (IXA or B).



(IXA)



(IXB)

This intramolecular bonding would persist in solution, and the silanol does give a normal molecular weight in ethylene dibromide and in acetone. It would also account for the high stability of these compounds and in particular the absence of hydroxyl reactions.

The factors which determine the formation of these silanols are necessarily obscure, particularly as each silanol represents solely the one component which has been isolated in a pure condition from the initial crude mixture of products.

The following points regarding the possible mechanism of the reactions are tentatively suggested. The first stage in the formation of the unsubstituted spiran (IV) is the interaction of 2 : 2′-dilithiodiphenyl ether and silicon tetrachloride to form the 2′-lithio-derivative (XA) of trichloro-*o*-phenoxyphenylsilane, a process which occurs essentially by the interaction of the groups $\overset{-}{\text{Cl}}\text{–}\overset{+}{\text{Si}}\leqq$ and $\geqq\overset{-}{\text{C}}\text{–}\overset{+}{\text{Li}}$. The derivative (XA), however, receives some contribution from the polar form (XB), in which the silicon atom gains some negative character at the expense of the *o*-phenylene group and thus of the oxygen atom, and in turn of the 2′-carbon atom, which consequently becomes slightly deactivated. The next stage is thus the reaction of (XA–B) with another molecule of 2 : 2′-dilithiodiphenyl ether, whose carbanion reactivity is still unimpaired, with the formation of the dichlorodilithiosilane (XI), since this reaction is more rapid than the intramolecular reaction of (XA–B) to form 10 : 10-dichlorophenoxsilane. The final stage is the slower reaction of the silicon with the two 2′-carbon atoms in (XI) to give the spiran (IV), this intramolecular reaction being now favoured by the increasingly sterically shielded condition of the silicon atom.

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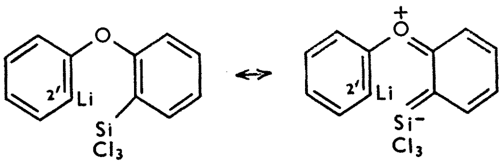
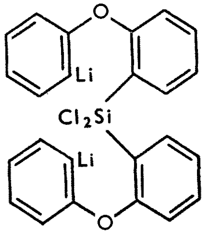
[20] Kross, Fassel, and Margoshes, *J. Amer. Chem. Soc.*, 1956, **78**, 1332.

[21] Richards and Thompson, *J.*, 1949, 124.

When, however, silicon tetrachloride reacts with 2 : 2′-dilithio-5-methyldiphenyl ether (I; R = H, R′ = Me), the methyl group will activate the 2-carbon atom in the *para*-position and facilitate the formation of the initial trichloro-derivative (XIIA). In this compound, the 2′-carbon atom will be slightly deactivated by the polar form of type (XB),



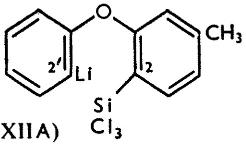
(XA) (XB)



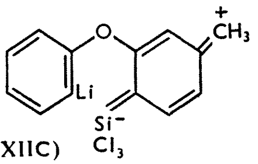
(XI)

and the silicon will have an increased negative contribution by the form (XIIC). Hence, as before, the most rapid reaction of (XII) is with another molecule of 2 : 2′-dilithio-5-methyldiphenyl ether (I; R = H, R′ = Me) to give the dichlorodilithio-derivative (XIII). The much increased negative contribution to the silicon now makes further reaction difficult, and prolonged boiling of the reaction mixture is required to induce some further cyclisation to the monochloro-derivative (XIV), which then undergoes no further cyclisation. There results a mixture of products, from which, during the subsequent working up, the small proportion of the monochloro-derivative (XIV) becomes hydrolysed to the silanol (VII; R = H, R′ = Me).

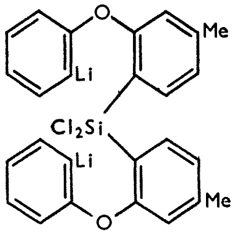
When 2 : 2′-dilithio-4-methyldiphenyl ether (I; R = Me, R′ = H) is used, the same factors enter, but the influence of the methyl group, now *meta* to the silicon, is much weaker. Consequently, the silicon in the dichloro-derivative (as XIII) is less deactivated, and further cyclisation to the monochloro-derivative (as XIV) occurs more readily, and a much higher yield of the silanol results.



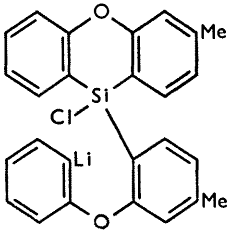
(XIIA)



(XIIC)



(XIII)



(XIV)

In view of the above results, the elucidation of the stereochemistry of the phenoxsilane system by *X*-ray crystal analysis appears to be the most promising.

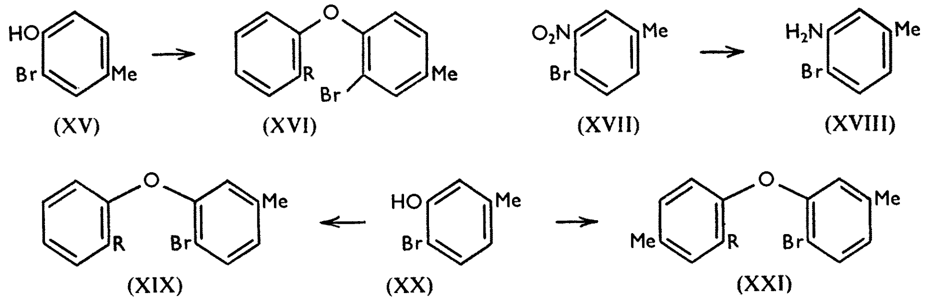
Preparation of Intermediate Compounds.—For the above investigation 2 : 2′-dibromodiphenyl ether and certain methyl derivatives were required for the preparation of their dilithio-derivatives.

2 : 2′-Dibromodiphenyl ether was prepared from 2-amino-2′-bromodiphenyl ether by Mann and Millar's method.[1] 2 : 2′-Dibromo-4-methyldiphenyl ether (XVI; R = Br) was prepared by Campbell's method,[22] 3-bromo-4-hydroxytoluene (XV) [23] being condensed with *o*-chloronitrobenzene to give 2-bromo-4-methyl-2′-nitrodiphenyl ether (XVI; R = NO_2), which was converted into the 2′-amino-derivative (XVI; R = NH_2) and then into the 2′-bromo-derivative (XVI; R = Br).

[22] Campbell, *J.*, 1947, 4.

[23] Zincke and Wiederhold, *Annalen*, 1902, **320**, 199.

For the preparation of 2 : 2′-dibromo-5-methyldiphenyl ether (XIX; R = Br), 4-bromo-3-nitrotoluene (XVII)[24] was reduced with iron filings and aqueous sodium chloride to 3-amino-4-bromotoluene (XVIII), which was then converted into 4-bromo-3-hydroxytoluene (XX).[25] The latter, when condensed with *o*-chloronitrobenzene, gave 2-bromo-5-methyl-2′-nitrodiphenyl ether (XIX; R = NO_2), which by the usual stages afforded the 2 : 2′-dibromo-derivative (XIX; R = Br).


(XV) (XVI) (XVII) (XVIII)

(XIX) (XX) (XXI)

4-Bromo-3-hydroxytoluene (XX), when also condensed with 4-chloro-3-nitrotoluene, afforded 2-bromo-4′ : 5-dimethyl-2′-nitrodiphenyl ether (XXI; R = NO_2), which by similar stages gave 2 : 2′-dibromo-4 : 5′-dimethyldiphenyl ether (XXI; R = Br).

EXPERIMENTAL

The percentage yields obtained in the preparation of the phenoxsilanes are based on the weight of 2 : 2′-dibromodiphenyl ether (or its derivative) employed.

3-*Amino*-4-*bromotoluene* (XVIII).—A suspension of fine iron filings (250 g.) in 5% aqueous sodium chloride (1·25 l.) was boiled under reflux with vigorous stirring for 30 min. 4-Bromo-3-nitrotoluene (XVII) (125 g.) was then slowly added to the mixture, and the boiling continued for a further 3—4 hr. Steam-distillation and ether-extraction then gave the amine (XVIII) in 90% yield. Hodgson and Moore,[25] using tin and hydrochloric acid, obtained the amine in unspecified yield.

2-*Bromo*-5-*methyl*-2′-*nitrodiphenyl ether* (XIX; R = NO_2).—This was prepared essentially by Henley's method,[26] a mixture of 3-hydroxy-4-bromotoluene (XX) (93 g.), powdered potassium hydroxide (28 g., 1 mol.), and water (0·9 g., 0·1 mol.) being heated under an air-condenser in an oil-bath until homogeneous, and *o*-chloronitrobenzene (79 g., 1 mol.) then added during 5 min. The mixture was heated at 195—200° for 75 min., and poured into 7·5% aqueous potassium hydroxide (300 c.c.). The precipitated 2′-*nitro-ether* (XIX; R = NO_2), when collected, dried, and distilled (63% yield), had b. p. 188—191°/0·7 mm., and m. p. 75—76° after crystallisation from ethanol (Found: C, 50·5; H, 3·1. $C_{13}H_{10}O_3NBr$ requires C, 50·7; H, 3·2%).

This nitro-ether was reduced by Campbell's method,[22] a mixture of the ether (XIX; R = NO_2) (106 g.), iron " pin-dust " (125 g.), and 50% aqueous ethanol being stirred and boiled under reflux whilst 48% hydrobromic acid (35 c.c.) was slowly added. After 3 hours' boiling, " Hyflo supercel " was added, and the mixture basified with 40% aqueous potassium hydroxide and filtered whilst hot. The residue, and the filtrate after dilution with water, were extracted with ether. Distillation gave the 2′-*amino-ether* (XIX; R = NH_2) (58%), b. p. 168—170°/0·8 mm., 148·5—149·5°/0·3 mm. (Found: C, 56·1; H, 4·3. $C_{13}H_{12}ONBr$ requires C, 56·1; H, 4·3%). It gave a *benzoyl derivative* (XIX; R = NHBz), m. p. 102—104° (from aqueous ethanol) (Found: C, 62·9; H, 4·3. $C_{20}H_{16}O_2NBr$ requires C, 62·8; H, 4·2%), and an *acetyl derivative*, m. p. 92—93° when similarly recrystallised (Found: C, 55·7; H, 4·2. $C_{15}H_{14}O_2NBr$ requires C, 56·3; H, 4·4%).

The 2′-amino-ether (XIX; R = NH_2) (19 g.) was dissolved in a hot stirred mixture of 48% hydrobromic acid (150 c.c.) and water (150 c.c.), which was quickly cooled to *ca.* 5° by the addition of ice (*ca.* 300 g.). The suspension was diazotised with sodium nitrite (5·2 g., 1·1

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[24] Gibson and Johnson, *J.*, 1929, 1229.

[25] Hodgson and Moore, *J.*, 1926, 2036.

[26] Henley, *J.*, 1930, 1222.

mols.), filtered, and then vigorously stirred whilst bromine (12·0 g., 1·1 mols.) in 48% hydrobromic acid (40 c.c.) was added dropwise, the temperature being kept below 10°. The precipitated yellow perbromide was collected, washed with ice-water, and added in small portions to acetic acid at 105°. The solution was boiled under reflux for 30 min., then poured into cold water, and the resulting suspension extracted with chloroform. The extract was washed with 20% aqueous potassium hydroxide and with water and dried. Distillation at 0·4 mm. gave fractions (*a*) b. p. 135—144°, (*b*) b. p. 144—170°, (*c*) b. p. 170—180°. Fraction (*a*) was discarded. Fraction (*b*) on redistillation gave 2 : 2′-*dibromo*-5-*methyldiphenyl ether* (XIX; R = Br) (13·3 g., 57%), b. p. 156—158°/0·4 mm. (Found: C, 45·6; H, 2·9. $C_{13}H_{10}OBr_2$ requires C, 45·6; H, 2·9%). Fraction (*c*) solidified, and when recrystallised four times from ethanol afforded 2 : 2′ : *x-tribromo*-5-*methyldiphenyl ether*, m. p. 62—64° (Found: C, 36·9; H, 2·4. $C_{13}H_9OBr_3$ requires C, 37·1; H, 2·1%); this compound was unaffected by hot aqueous-ethanolic sodium hydroxide, and the third bromine atom is almost certainly also in the aromatic nucleus.

The dibromo-ether (XIX; R = Br) was also obtained in 25% yield from the amine by the Sandmeyer method.

2-*Bromo*-4′ : 5-*dimethyl*-2′-*nitrodiphenyl ether* (XXI; R = NO_2).—This was prepared as the 5-methyl compound (XIX; R = NO_2), from 4-bromo-3-hydroxytoluene (93 g.), potassium hydroxide (28 g., 1 mol.), and water (0·9 g., 1 mol.), and then 4-chloro-3-nitrotoluene (87 g., 1 mol.). Distillation gave the 2′-*nitro-ether* (XXI; R = NO_2), b. p. 175—179°/0·5 mm., m. p. 98—100° after crystallisation from ethanol (Found: C, 52·5; H, 3·7. $C_{14}H_{12}O_3NBr$ requires C, 52·2; H, 3·7%).

Reduction of this compound with " pin-dust " and hydrobromic acid gave the 2′-*amino-ether* (XXI; R = NH_2) (71%), b. p. 160—161°/0·7 mm., m. p. 32—35° (Found; C, 57·6; H, 4·5. $C_{14}H_{14}ONBr$ requires C, 57·6; H, 4·8%). The *benzoyl derivative* had m. p. 108—110° (from ethanol) (Found: C, 63·8; H, 4·5. $C_{21}H_{18}O_2NBr$ requires C, 63·7; H, 4·5%).

This amino-ether was converted by the Sandmeyer reaction, followed by distillation, into 2 : 2′-*dibromo*-4 : 5′-*dimethyldiphenyl ether* (XXI; R = Br) (42%), b. p. 165—167°/0·5 mm., m. p. 85—86° (from ethanol) (Found: C, 47·0; H, 3·4. $C_{14}H_{12}OBr_2$ requires C, 47·2; H, 3·4%).

The preparation of the dibromo-ether (XXI; R = Br) by the above perbromide reaction gave considerable nuclear bromination and was abandoned.

A solution of *n*-butyl-lithium in light petroleum (b. p. 40—60°) was prepared by the method of Gilman and his co-workers [27] and standardised before use.

10 : 10-*Disubstituted Phenoxsilanes. General Method.*—The above solution of *n*-butyl-lithium (2·2 mols.) was added to a stirred solution of 2 : 2′-dibromodiphenyl ether (1 mol.) in light petroleum (b. p. 40—60°) or in ether under nitrogen, and the mixture boiled under reflux for 2 hr. The chloro-silane (1·2 mols.) in ether was then added to the hot stirred solution, which was next boiled under reflux for 3 hr. The chilled product was treated with water, and the organic layer separated, dried, and worked up as stated below.

(i) *Dichlorodimethyl-silane.* The organic layer on distillation gave 10 : 10-dimethylphenoxsilane (78%), b. p. 159—161°/9 mm., m. p. 74·5—77° after crystallisation from ethanol (Found: C, 74·2; H, 6·3. Calc. for $C_{14}H_{14}OSi$: C, 74·3; H, 6·2%) (lit.[3] m. p. 78·5—79°).

(ii) *Dichlorodiphenyl-silane.* (*a*) Use of a solution of 2 : 2′-dibromodiphenyl ether in the petroleum, and evaporation of the organic layer, gave a pale brown solid which on crystallisation from ethanol gave the 10 : 10-diphenylphenoxsilane (III; R = R′ = H) (59%), m. p. 175—177°, unchanged by recrystallisation from the petroleum or by sublimation at 200°/0·5 mm. (Found; C, 82·0; H, 4·9%; *M*, in boiling acetone, 360. Calc. for $C_{24}H_{18}OSi$; C, 82·2; H, 5·2%; *M*, 350) (lit.,[3] m. p. 178—179°).

(*b*) 2 : 2′-Dibromo-4-methyldiphenyl ether gave 2-*methyl*-10 : 10-*diphenylphenoxsilane* (III; R = Me, R′ = H), m. p. 153—155°, after crystallisation from the petroleum and sublimation at 160°/0·001 mm. (Found: C, 82·2; H, 5·6. $C_{25}H_{20}OSi$ requires C, 82·4; H, 5·5%) (yield of pure material, 55% of additional recovered material, 6%).

(*c*) An ethereal solution of 2 : 2′-dibromo-5-methyldiphenyl ether similarly gave 3-*methyl*-10 : 10-*diphenylphenoxsilane* (III; R = H, R′ = Me), m. p. 161—162°, after crystallisation and sublimation as before (Found: C, 82·2; H, 5·9. $C_{25}H_{20}OSi$ requires C, 82·4; H, 5·5%) (yield of pure material, 43%).

(*d*) 2 : 2′-Dibromo-4 : 5′-dimethyldiphenyl ether (XXI; R = Br) gave, on evaporation of the organic layer, a pale brown sticky residue, which after recrystallisation from the petroleum gave

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[27] Gilman, Langham, and Moore, *J. Amer. Chem. Soc.*, 1940, **62**, 2327.

2 : 7-*dimethyl*-10 : 10-*diphenylphenoxsilane* (V) (46%), m. p. 155—161°, increased to 166—168° by recrystallisation from acetic acid, and then not affected by subsequent recrystallisation from the petroleum or by sublimation at 170°/0·001 mm. (Found: C, 82·4; H, 5·8. $C_{26}H_{22}OSi$ requires C, 82·6; H, 5·8%).

Derivatives of 2-*Methyl*-10 : 10-*diphenylphenoxsilane* (III; R = Me, R′ = H).—*N*-Bromosuccinimide (1·0 g., 1 mol.) was added to a solution of the silane (2·1 g.) in carbon tetrachloride (50 c.c.), which was boiled under reflux for 2 hr. Deposited succinimide (0·55 g.) was collected from the cold solution, which was then evaporated to dryness. The residue, when recrystallised from light petroleum (b. p. 60—80°) gave the 2-*bromomethyl-silane* (III; R = CH_2Br, R′ = H) (93%), m. p. 131·5—132° (decomp.) (from ethyl acetate) (Found: C, 67·5; H, 4·7. $C_{25}H_{19}OBrSi$ requires C, 67·7; H, 4·3%).

The use of *N*-bromosuccinimide (2·2 mols.) with a trace of benzoyl peroxide afforded, on evaporation of the solution, the 2-dibromomethyl-silane (III; R = $CHBr_2$, R′ = H) as a pale brown gum. Its solution in boiling 2-ethoxyethanol was therefore treated with aqueous silver nitrate (3·2 mols.) and, after boiling for a further 30 min., the solution was cooled and filtered into water, depositing the gummy 2-aldehydo-silane (III; R = CHO, R′ = H). This aldehyde did not crystallise, but in ethanolic solution gave an immediate copious red precipitate of the 2 : 4-*dinitrophenylhydrazone* [III; R = $CH{:}N{\cdot}NH{\cdot}C_6H_3(NO_2)_2$, R′ = H], m. p. 286—288° (decomp.) (from much acetic acid) (Found: C, 66·1; H, 4·8; N, 10·5. $C_{31}H_{22}O_5N_4Si$ requires C, 66·6; H, 4·0; N, 10·0%), very slightly soluble in the usual solvents.

spiro*Bis*-10-*phenoxsilane* (IV).—A solution of *n*-butyl-lithium (3·2 g., 2·2 mols.) in light petroleum (b. p. 40—45°) (50 c.c.) was added rapidly under nitrogen to a stirred solution of 2 : 2′-dibromodiphenyl ether (7·7 g.) in the petroleum (100 c.c.), which was boiled under reflux for 1 hr. The heating was stopped and a solution of silicon tetrachloride (4·3 g., 1·1 mols.) in ether (265 c.c.) rapidly added to the stirred mixture, which, after the vigorous reaction had ceased, was boiled for 3 hr. The solvent was removed, and the residue extracted under nitrogen with pure dioxan (Soxhlet). The extract, when concentrated and cooled, deposited crystals (2·5 g.), and no further crystalline material was obtained from the mother-liquors. The crystals, when sublimed at 280°/0·4 mm., gave the crude silane (IV) (61%), m. p. 255—271°, increased to 280—282° by recrystallisation from carbon tetrachloride or acetone (Found: C, 78·7; H, 4·5%; *M*, in freezing ethylene dibromide, 360. Calc. for $C_{24}H_{16}O_2Si$; C, 79·1; H, 4·4%; *M*, 364).

In a similar experiment, the 2 : 2′-dibromodiphenyl ether was used in ethereal solution, silicon tetrachloride (0·7 mol.) was added, and the final reaction mixture was cooled and hydrolysed with water. The white precipitate was collected, dried, and extracted with chloroform, which on concentration afforded the silane (IV), m. p. 280—282°, in 30% yield (Found: C, 78·8; H, 4·3%), a further 17% being recovered from the total organic liquors.

The Silanol (?VII; R = Me, R′ = H).—2 : 2′-Dibromo-4-methyldiphenyl ether (XVI; R = Br) (57 g.) in ether (300 c.c.) was lithiated under nitrogen with *n*-butyl-lithium (2·2 mols.) in light petroleum (b. p. 40—60°) (176 c.c.), treated with silicon tetrachloride (15·5 g., 0·55 mol.) in ether (100 c.c.), and boiled under reflux for 4 hr. The cold stirred solution was hydrolysed with water (50 c.c.), and the organic layer dried and distilled. The viscous residue, when crystallised from light petroleum (b. p. 60—80°), gave the *silanol* (5·7 g., 17%, including a second crop from the mother liquors), which when again recrystallised and then sublimed at 260°/0·1 mm. had m. p. 177—182° (Found: C, 75·9; H, 5·6%. $C_{26}H_{22}O_3Si$ requires C, 76·1; H, 5·4%; *M*, 410), and when then recrystallised from acetic acid and resublimed had m. p. 198—200° (Found: C, 75·9; H, 5·3%; *M*, in freezing ethylene dibromide, 380, in boiling acetone, 420).

The silanol (1·2 g.), when treated in carbon tetrachloride solution (50 c.c.) with *N*-bromosuccinimide (1·2 g., 2·2 mols.) and benzoyl peroxide (*ca.* 50 mg.) with subsequent boiling for 2 hr., deposited succinimide (0·65 g., *ca.* 100%). The filtrate on evaporation left a yellow glass, which when crystallised from acetic acid and ethyl acetate gave the white *di*-(2-*bromomethyl*)-*silanol* (?VII; R = CH_2Br, R′ = H) (0·6 g., 43%), m. p. 168—171° (decomp.) (Found: C, 55·1; H, 3·6. $C_{26}H_{20}O_3Br_2Si$ requires C, 55·0; H, 3·5%). A solution of this compound (3·8 g.) in chloroform (30 c.c.) was treated with a saturated chloroform solution of hexamethylenetetramine (2·1 g., 2·1 mols.) and boiled under reflux for 2 hr., cooled, and filtered. The collected hexaminium salt (4·9 g., 85%) had m. p. 175—180° (decomp.). A mixture of this salt (0·5 g.) and 50% aqueous acetic acid (7 c.c.) was heated under reflux at 145° for 70 min., diluted with concentrated hydrochloric acid (5 c.c.), and boiled for 5 min. The cold suspension, when collected and recrystallised from acetic acid gave the *di-*(2-*aldehydo*)-*silanol* (?VII; R = CHO, R′ = H) (0·1 g., 40%), m. p. 230—231° (Found: C, 71·3; H, 4·1. $C_{26}H_{18}O_5Si$ requires C, 71·3; H, 4·1%). The infrared spectra of these two derivatives gave no indication of a hydroxyl group.

The Silanol (?VII; R = H, R′ = Me).—This compound was prepared as the previous silanol, and evaporation of the organic layer gave a viscous residue which when twice recrystallised from acetic acid and sublimed at 210°/0·001 mm. gave the crude white silanol (4%), m. p. 200—210°. Repeated alternate crystallisation from acetic acid and sublimation ultimately gave the pure *silanol*, m. p. 215—217° (Found: C, 75·9; H, 5·2%; *M*, in freezing benzene, 390. $C_{26}H_{22}O_3Si$ requires C, 76·1; H, 5·4%; *M*, 410).

Dipole moments.

10 : 10-*Diphenylphenoxsilane* (III; R = R′ = H)

w	ϵ	v	n
0·010378	2·2804	1·1414	0·00142
0·008806	2·2790	—	—
0·008462	2·2787	1·1420	0·00112
0·006455	2·2776	1·1427	0·00083
0·003712	2·2753	1·1435	0·00043
0·002332	2·2747	1·1440	0·00024
0·002225	2·2745	—	—

$\epsilon = 2{\cdot}2728 + 0{\cdot}714w$; $v = 1{\cdot}1447 - 0{\cdot}321w$;
$\Delta n_D = -\,0{\cdot}00011 + 0{\cdot}147w$; $\mu = 0{\cdot}97 \pm 0{\cdot}03$ D;
${}_EP = 114{\cdot}10$ c.c. ${}_TP = 133{\cdot}2$ c.c.

2 : 7-*Dimethyl*-10 : 10-*diphenylphenoxsilane* (V)

w	ϵ	v	n
0·008638	2·2785		
0·007044	2·2772		
0·006213	2·2768		
0·005552	2·2764		
0·004349	2·2755		
0·003026	2·2744		
0·002125	2·2741		
0·008708	—	1·1420	0·00113
0·007470	—	1·1424	0·00095
0·005965	—	1·1429	0·00073
0·004590	—	1·1433	0·00058
0·001723	—	1·1440	0·00020

$\epsilon = 2{\cdot}2727 + 0{\cdot}670w$; $v = 1{\cdot}1445 + 0{\cdot}284w$;
$\Delta n_D = -\,0{\cdot}00003 + 0{\cdot}132w$; $\mu = 1{\cdot}01 \pm 0{\cdot}03$ D;
${}_EP = 124{\cdot}08$ c.c.; ${}_TP = 144{\cdot}87$ c.c.

Dipole Moments.—The determinations (see Table) were carried out in benzene at 25°. The symbol w represents weight fraction of solute in benzene, ε the dielectric constant of solution, v the specific volume of solution, and Δn_D the refractive-index difference between solution and benzene for Na_D light.

The equations show the rectilinear relation between ε, v, and Δn_D, respectively, and w.

The Halverstadt–Kumler treatment [28] was used to determine the dipole moments, μ, and the electronic polarisations at infinite dilution ${}_EP$. The differences are $\Delta\mu = 0{\cdot}09 \pm 0{\cdot}06$ D; $\Delta_EP = 9{\cdot}98$ c.c. The difference between the electronic polarisations agrees as well as can be expected with the value for two CH_2 groups given in Landolt and Börnstein's Tables, *viz.*, 9·23 c.c. No allowance has been made for ${}_AP$ other than that implicit in using $[R]_D$ as the distortion polarisation.

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[28] Halverstadt and Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.