

## Reactions of Alkyl-lithium Compounds with Aryl Halides

By Penelope A. Huddle and Guido W. Perold,\* Department of Chemistry, University of the Witwatersrand, Johannesburg 2001, South Africa

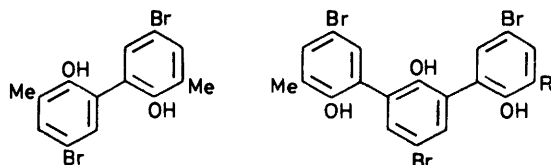
Reaction of methyl-lithium with tribromophenols and with other aryl polyhalides leads directly to bi- and tri-aryl products. *para*-Substituents (Y) of 2,6-dibromo-4-Y-phenols promote arylation of substrates by their own lithiation products as Y becomes more electron-withdrawing. An aryne epoxide is not an intermediate in these reactions. 2,4,6-Tribromo-Z-benzenes react to form coupling products when Z can co-ordinate to an introduced *ortho*-lithium atom or when Z can be directly lithiated. Dimeric aggregation of the organolithium intermediates occurs so as to favour coupling to halogenated substrates. Both polar (ionic) and free-radical pathways are involved.

ORGANOLITHIUM reagents entered into organic synthesis through their halogen-metal interchange reactions with organic halides<sup>1,2</sup> and the mechanisms of these reactions have been discussed.<sup>3-6</sup> Coupling products were later observed.<sup>7</sup> In most cases only specific aspects of these reactions were considered.<sup>8</sup> Full product analyses have now been undertaken to explore syntheses of biphenylol derivatives<sup>9</sup> from halogenated phenols, the reaction of methyl-lithium with 2,4,6-tribromophenol being a typical<sup>10</sup> instance.

The product of metal-halogen interchange, 2,4-dibromophenol, was obtained in low yield (seemingly in accord with the claim<sup>11</sup> that methyl-lithium is a poor lithiating agent), as were the direct methylation products<sup>12</sup> (Table 1); the major products were the biaryl (1) and the triaryls (2) and (3). Methyl-lithium here is therefore not a poor lithiating agent and the course of the reaction is determined by the greater reactivity of the aryl-lithium intermediates. The reactions are therefore probably of a sequential [equations (1) and (2)] rather than a direct [equation (3)] type.<sup>13</sup>



Equation (2) can be expanded for the methylation (4) and arylation (5) reactions, *i.e.* for competition between  $\text{CH}_3^+$  and  $\text{Ar}^+$  [from (5)] for  $\text{Ar}^-$  [from (4)] in accord with their hard-soft characteristics.<sup>14,15</sup>



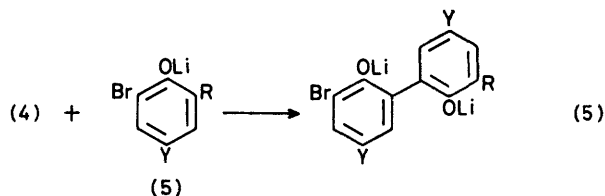
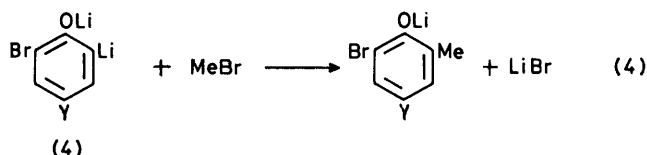
(1)

(2) R = Br

(3) R = Me

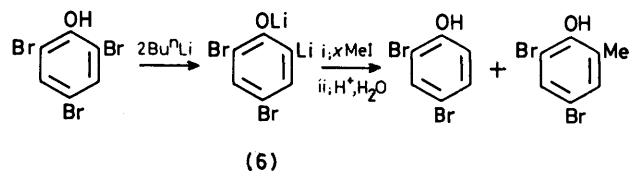
Support for a type (1)—(2) reaction sequence for methylation was provided by treating pre-formed lithium 2,4-dibromo-6-lithiophenolate (6) with increasing proportions of methyl iodide to afford increased yields of methylation product (Table 2).

The enhanced reactivity of the aryl-lithium intermediates relative to methyl-lithium was demonstrated by using the latter to generate an initially equimolar mixture of lithium 2,4-dibromo-6-lithiophenolate,



R = Me, Br, or Li

lithium 2,4,6-tribromophenolate, and methyl bromide [reaction (6)] which finally afforded the unmethylated triaryl (7) (54%), 2,4-dibromo-6-methylphenol (4%), and some biaryl products.



The effect of various substituents (Y) on the reactions of 2,6-dibromo-4-Y-phenols (Table 3) shows that arylation of the substrate by its own lithiation product be-

TABLE 1

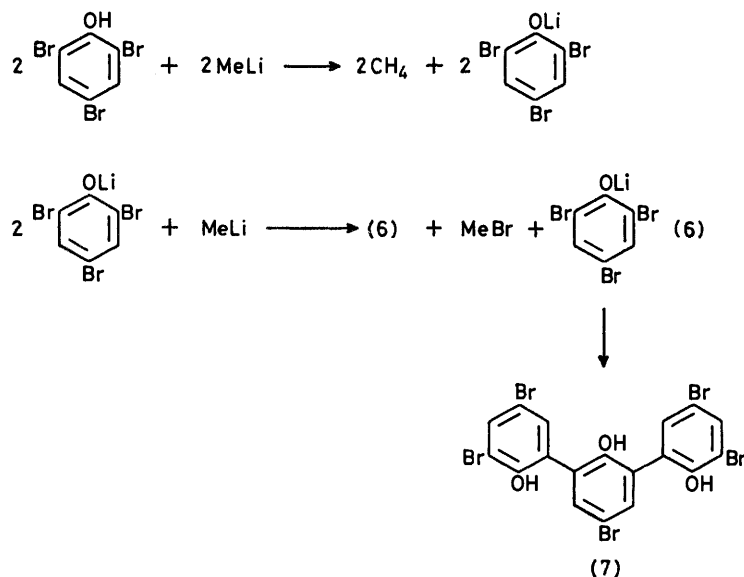
Products from reaction of 2,4,6-tribromophenol with 2 mol equiv. of methyl-lithium

Product	Yield (%) <sup>a</sup>
2,4-Dibromophenol	4.6
2,4-Dibromo-6-methylphenol	5.0
4-Bromo-2,6-dimethylphenol	4.5
(1)	29.0
(2)	29.5
(3)	20.1

<sup>a</sup> Calculated for isolated identified products in terms of substrate consumed.

comes more favoured as Y becomes more electron-withdrawing.<sup>9,16</sup> The particular reactivity of the *ortho*-bromine atoms suggests that an aryne epoxide may be an intermediate<sup>17,18</sup> and this was tested by using 2,4,6-tribromo-3-methylphenol as the substrate. The de-

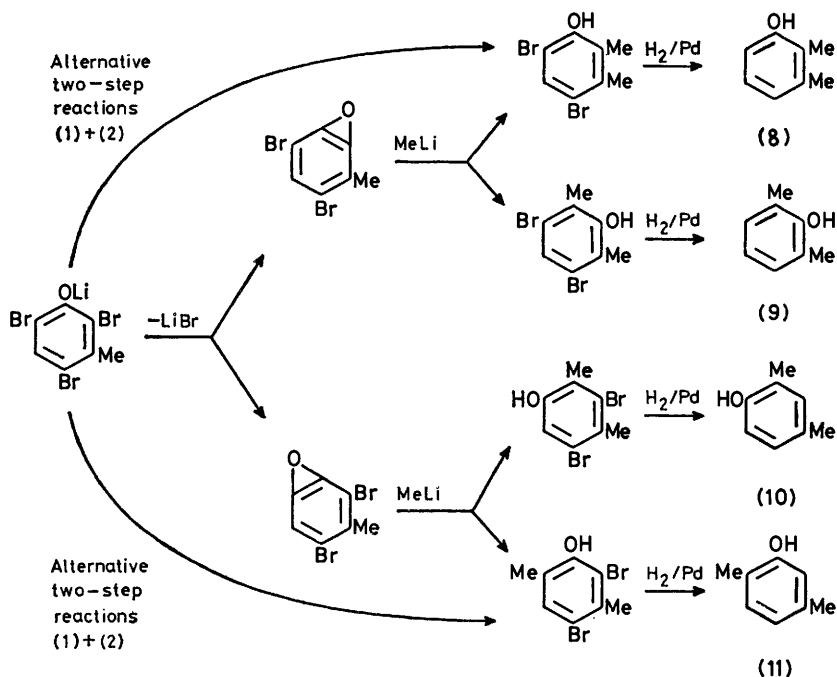
methyl-lithium. The results (Table 4) show that biaryl coupling occurs where Z can co-ordinate to a lithium atom *ortho* to it or, to a lesser extent, where metallation of Z is possible. The hydroxy-group meets both requirements and allows applications in synthesis. Polarisation



halogenated monomethylation products consisted of only the two 'normal' products (8) and (11) in the ratio 6 : 94 respectively, as would be, expected<sup>9</sup> on account of steric hindrance, and an aryne oxide is therefore not a likely intermediate.

The role of the hydroxy-group was therefore assessed by treating a series of 2,4,6-tribromo-Z-benzenes with

effects, and hence the possibility of ionic intermediates, are suggested by the substituent effects observed. This was clearly shown in the reaction of 2,3,5,6-tetrabromo-4-methylphenol (12) with 2-lithioanisole: with this more highly halogenated substrate the reaction was so fast that it was diffusion controlled, with the substrate being so active that both bromine atoms *ortho* to the hydroxy-



group could be replaced by nucleophilic attack within ten seconds of mixing. Metal-halogen exchange occurred concurrently [(13) and (14)] and 2-bromoanisole was

TABLE 2

Methylation of the aryl-lithium (6) with methyl iodide

2,4,6-Tri-bromophenol (mol)	n-Butyl-lithium (mol)	Methyl iodide (mol)	Composition <sup>a</sup> of monoaryl product mixture <sup>b</sup>	
			2,4-Dibromophenol (%)	2,4-Dibromo-6-methylphenol (%)
1	2	1	85	15
1	2	7	47	53
1	2	19	14 <sup>c</sup>	86 <sup>c</sup>

<sup>a</sup> Composition analysis of the monoaryl fractions was by g.l.c. calibrated for the detector response for each compound.

<sup>b</sup> The yields of these two products together were of the order of 30%. <sup>c</sup> Products from this reaction were separated in the usual manner and yielded 2,4-dibromophenol (6%) and 2,4-dibromo-6-methylphenol (22%).

found in all runs. Different conditions of mixing therefore affected the product distribution (Table 5) and with most rapid mixing the two biaryls (13) and (14) were the only products isolated.

molecules co-ordinated to the bridging lithium atoms,<sup>26</sup> then the solvated lithium lithiophenolate (17) could be (18). The phenolic oxygen may however allow an alternative mode of aggregation (19), as in complexes of hexamethyldialuminium with acetone (20), benzonitrile (21), *etc.*,<sup>27</sup> and through co-ordination of the 'free' OLi group of (19) stabilise the Li...Li bridge as do solvent molecules in ether solutions.<sup>26</sup> The tetrahedral oxygen atom of (19) would then hold an *ortho* bromine atom close to a lithium bridge atom and so facilitate elimination of lithium bromide with formation of the biphenyl bond in (23).

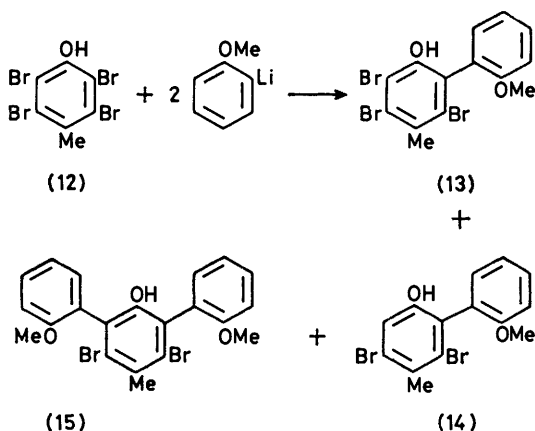
The unsymmetrical bridging in structure (22) would be more susceptible to polar effects as the mesomeric effect of the oxygen atom on ring B will be weaker than for the monomer (17) or the symmetrical dimer (18). This was shown by coupling different aryl systems X<sub>n</sub>Ar<sub>A</sub>OLi and Ar<sub>B</sub>Br to afford the unsymmetrical biphenylol X<sub>n</sub>(OH)Ar<sub>A</sub>Ar<sub>B</sub> *via* a dimeric intermediate X<sub>n</sub>Ar<sub>A</sub>O:::(Li)<sub>2</sub>:::Ar<sub>B</sub>, and by comparing the outcome with the case where formation of such an intermediate

TABLE 3

Average yields (%) <sup>a</sup> of products from reaction of 2,6-dibromo-4-Y-phenol with 3 mol equiv. of methyl-lithium

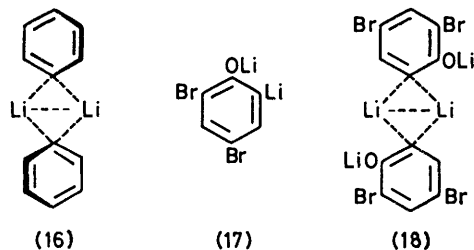
Y							Triaryl compounds <sup>b</sup> and small amounts of more complex products	Methylation <sup>c</sup> (%)	Arylation <sup>d</sup> (%)
	R = Br	R = Me	R = Br	R = Me	R = Br	R = Me			
Me		15	12	9	(13) <sup>e</sup>	42	9	95	30
H		7	9	5		44	35	90	45
Br	1	10		7		30	42	80	50
Cl		12		5		27	45	78	55
F				f		34	60	70	60

<sup>a</sup> All runs were duplicated. Values found were within  $\pm 2\%$  and are for isolated and characterised products. <sup>b</sup> The triaryl compounds are the *p*-Y-analogues of structures (2) and (3) and typically constituted the remainder of the reaction mixture (ref. 10). <sup>c</sup> Calculated in terms of the *ortho*-bromine atoms replaced by methyl groups. <sup>d</sup> Calculated as the sum of half the yield of biaryl products and two-thirds of the yield of triaryl products. <sup>e</sup> Characterised only by its t.l.c. behaviour. <sup>f</sup> Some 3% of a defluorinated product C<sub>6</sub>H<sub>4</sub>BrO was isolated (ref. 10).



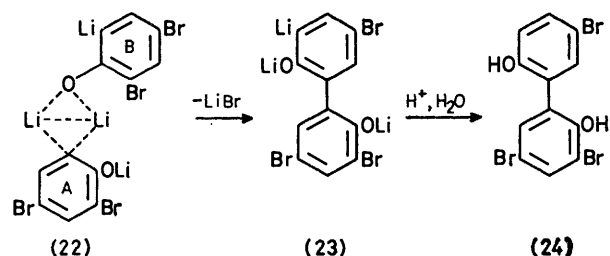
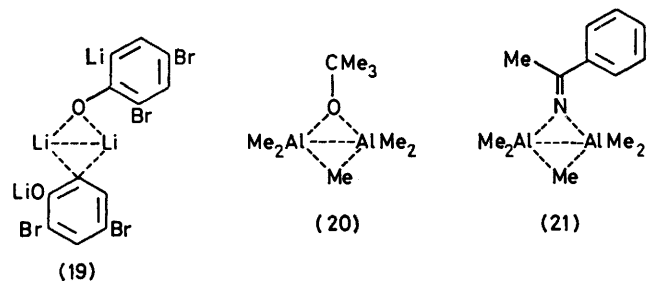
The states of aggregation of the aryl-lithium intermediates represent a further determining factor.<sup>19-25</sup> If phenyl-lithium in ether solution is (16),<sup>22</sup> with ether

was not favoured. Thus 2,4,6-tribromo-3-methylphenol (25), in which the alkyl group retards<sup>28</sup> direct lithium-halogen interchange, with two equivalents of 2-lithio-3-methoxytoluene (26) gave<sup>9</sup> product (27) in



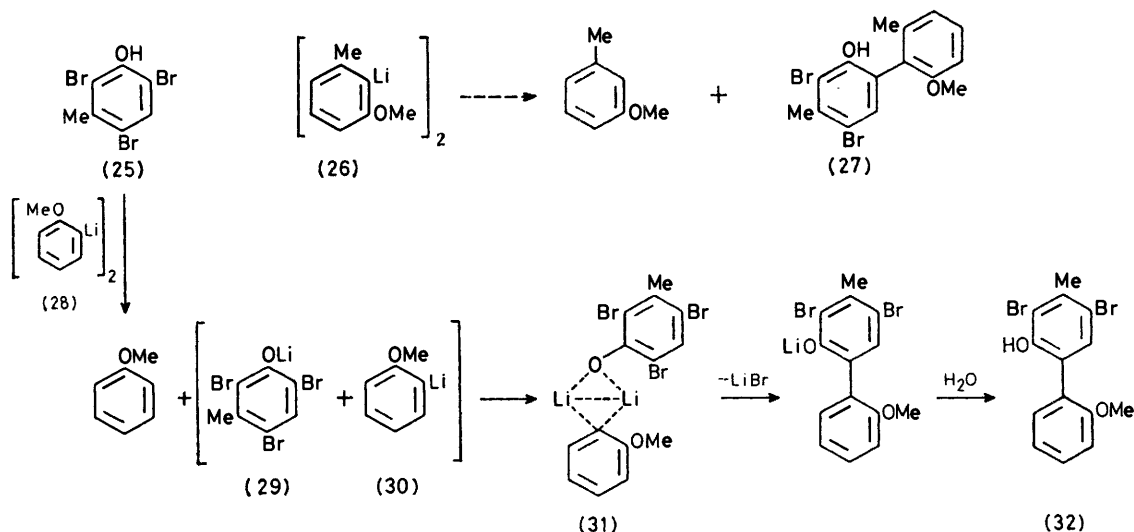
33% yield; with two equivalents of the sterically less hindered 2-lithioanisole (28) the yield of product (32) now rose to 48%. However, when *pre-formed* lithium 2,4,6-tribromo-3-methylphenolate (29) (see Experimental

section) was treated with *one* equivalent of (28) no biaryl (32) was obtained at all. Thus in the former cases the rapid and irreversible formation of the lithium



phenolate (29) is accompanied by formation of the unsymmetrical type dimer (31), as the primary lithiating agent (28) is itself a dimer of type (16). The dimeric aggregate (28) reacts with substrate (25) to give the *O*-lithiate (29) in contact with a molecule of 2-lithioanisole (30) and hence promotes formation of dimer (31) in an inter-cluster process. In the latter case the initial irreversible *O*-lithiation occurs separately and the prepared lithium phenolate (29) can react with the dimeric aggregate (28) only if the latter first dissociates.

The need for 2 mol of lithiating reagent in dimeric form



in these reactions recalls the success of lithium cuprates in coupling reactions where also 'the unusual reactivity and usefulness of the lithium cuprate reagent was probably as a result of its dimeric structure.'<sup>29</sup> Intervention

of dimeric aggregates of the aryl-lithium intermediates also accords with the phenomenon of *ca.* 130% coupling in these reactions (Table 3). Each coupling event uses one molecule of organolithium reagent and regeneration *via* a free-radical mechanism must occur, as in photo-induced coupling reactions<sup>30</sup> where loss of an electron from an aryl-lithium dimer leads to transient formation of  $\text{Li}^0$ . The latter would react with the organo-halides present to regenerate organolithium entities.

Free-radical intervention was here demonstrated by

TABLE 4

Products yield (%) from the reaction of 2,4,6-tribromo-*Z*-benzenes with 1 mol equiv. of methyl-lithium

<i>Z</i>	Other monoaryl products		Triaryl compounds and more complex products		
	R = H	R = Me	R = Br	R = Me	
OLi	9	8	9	30	25
OMe	8	4	21	10	37
3 × Me <sup>a</sup>		48	(11) <sup>b</sup>		21
Me		24	(5) <sup>d</sup>		21
H		52	(5) <sup>d</sup>		

<sup>a</sup> For the case of 2,4,6-tribromo-1,3,5-trimethylbenzene.

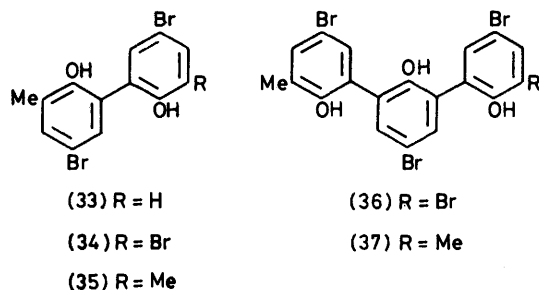
<sup>b</sup> The biaryl product here was 3,3'-dibromo-2,2',4,4',6,6'-hexamethylbiphenyl, *i.e.* it was not methylated during the reaction.

<sup>c</sup> 30% of 2,6-dibromo-1,4-dimethylbenzene. <sup>d</sup> 5% of an inseparable mixture of four products. <sup>e</sup> 24% of a mixture of bromobenzene (8%) and an inseparable mixture (16%) of 2,4-dibromobenzene and 3-bromo-1-methylbenzene.

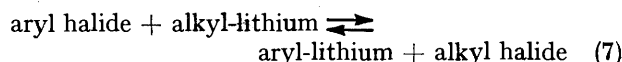
the effect of molecular oxygen, which reacts with alkyl radicals 600 times faster than with phenyl radicals,<sup>31</sup> and which (Table 6 and Experimental section) reduced the extent of methylation but not of arylation. Re-

generation of methyl-lithium was demonstrated, after the main reaction had proceeded for 30 min, by adding some galvinoxyl (38) which was converted into the addition product (39).

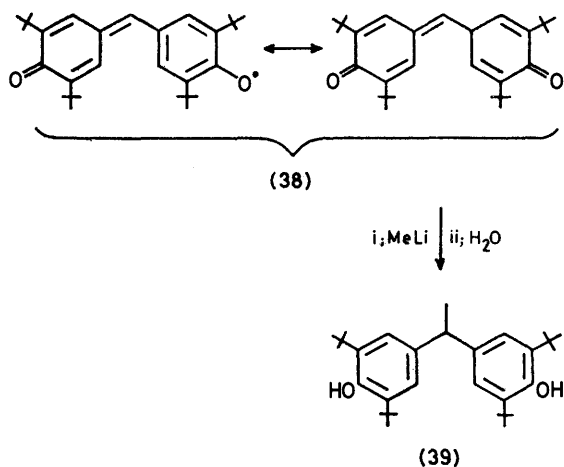
The intervention of free-radical processes under these conditions was also illustrated by reaction of lithium 2-lithiophenolate with a large excess of methyl iodide,



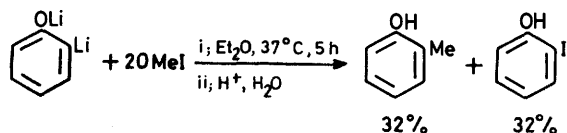
when both 2-methylphenol and 2-iodophenol were obtained in equal yield. The equilibrium for the interchange reaction (7) lies so far over to the right<sup>32</sup> that it is



irreversible;<sup>33</sup> it is also not a free-radical process.<sup>34</sup> The aryl radicals for this halogen abstraction reaction<sup>31,35</sup> could therefore again arise from electron loss from an aryl-lithium dimer as before.



Halogenated phenols can therefore react with organolithium reagents by way of ionic (polar) and free-radical processes side by side, and polar steering through intro-



duction of halogen substituents on substrates can serve for directed synthesis of bi- and tri-aryl systems.

#### EXPERIMENTAL

Instruments and usages have been indicated elsewhere<sup>36</sup> and detailed descriptions of the experiments are available.<sup>10</sup>

**General Procedure.**—The standardised<sup>37</sup> organolithium reagent (in ether) was stirred under high purity nitrogen and

the aryl halide (in ether) added dropwise. After heating as required the solution was cooled, quenched with 2M-hydrochloric acid, washed with brine, evaporated, and products separated by chromatography on silica gel. Elemental analyses and spectral data for compounds marked with an

TABLE 5

Variation of products and substrate (12) under various mixing conditions

Conditions	Unchanged substrate (%)	Relative % composition of products		
		(13)	(14)	(15)
Substrate added in portions	30	36	25	39
Substrate added gradually over 8 min	36	37	22	41
Substrate added instantaneously	9	65	35	

asterisk are available as Supplementary Publication No. SUP 22863 (12 pp.) (see Notice to Authors No. 7 in *J. C. S. Perkin I*, 1979, Index issue).

**Reaction of Methyl-lithium (2 mol) and 2,4,6-Tribromophenol (Table 1).**—2,4,6-Tribromophenol (0.99 g, 3 mmol) in ether (10 ml) was added to methyl-lithium (6 mmol) in ether (7 ml) at 25 °C. The mixture was stirred at 37 °C for 22 h and worked up to afford products (0.59 g, solid), separated by chromatography to yield 2,4-dibromophenol\* (distilled *in vacuo*, 35 mg), m.p. 38 °C (from benzene) (lit., 40 °C); 2,4-dibromo-6-methylphenol\* (40 mg), m.p. 56 °C (lit., 58 °C); 4-bromo-2,6-dimethylphenol\* (distilled, 72

TABLE 6

Product distribution (%) under various atmospheres for the reaction of 2,4,6-tribromophenol with 2 mol equiv. of methyl-lithium

Products	Atmosphere and solutions		
	(degassed)	(low oxygen)	(21% oxygen)
2,4-Dibromophenol		7	
4-Bromo-2-methylphenol		1	
4,6-Dibromo-2-methylphenol	5	2	
4-Bromo-2,6-dimethylphenol	8	4	
(33)			17
(34)			
(35)	10	9	30
(36)	35	30	30
(37)	6	11	3
(37)	22	15	18
Total recovery (%)	86	79	68
Methylation (%)	78	60	50
Arylation (%)	41	36	39

mg), m.p. 79 °C (from light petroleum) (lit., 79.5 °C); 5,5'-dibromo-2,2'-dihydroxy-3,3'-dimethylbiphenyl (1) (162 mg, distilled *in vacuo*, m.p. 176 °C (from benzene-ethanol) (Found: C, 45.8; H, 3.0. C<sub>14</sub>H<sub>12</sub>Br<sub>2</sub>O<sub>2</sub> requires C, 45.4; H, 3.2%),  $\nu_{\text{max}}$  3 350 br (OH), 2 900w (CH<sub>3</sub>), 1 560m and 1 465m (arom. ring), 1 200s (C-O), and 840 (single H on ring),  $\delta_{\text{max}}$  374/372(25%)/370 (M<sup>+</sup>) and 212(100),  $\delta$  (CCl<sub>4</sub>) 7.26 (2 H, d, J 2 Hz, H-6 and -6'), 7.09 (2 H, d, J 2 Hz, H-4 and -4'), 5.08 (2 H, s, OH, disappears in D<sub>2</sub>O), and 2.26 (6 H, s, 2 × CH<sub>3</sub>); 5,5',5''-tribromo-2,2',2''-trihydroxy-3,3''-dimethyl-m-terphenyl (3) (160 mg), m.p. 275 °C (from benzene-hexane) (Found: C, 43.3; H, 3.3. C<sub>20</sub>H<sub>15</sub>Br<sub>3</sub>O<sub>3</sub> requires C, 44.0; H, 2.8%),  $\nu_{\text{max}}$  3 400br (OH), 2 910w (CH<sub>3</sub>), 1 465s (arom. ring), 1 200m (C-O), and 855s (single H on arom. ring), *m/e* 546/544/542-(100%)/540 (M<sup>+</sup>),  $\delta$ [(CD<sub>3</sub>)<sub>2</sub>CO] 7.15—7.0 (6 H, m, ArH), 5—4br (3 H, s, OH, disappears in D<sub>2</sub>O), and 2.19 (6 H, s, 2 × CH<sub>3</sub>); and 3,5,5',5''-tetrabromo-2,2',2''-trihydroxy-3''-

methyl-*m*-terphenyl (2) (122 mg), m.p. > 340 °C,  $\delta[(\text{CD}_3)_2\text{-CO}]$  7.47 (1 H, d,  $J$  2.5 Hz, H-4''), 7.20 (3 H, br, H-6, -4', and -6'), 7.10—7.0 (2 H, s + d,  $J$  2.5 Hz, H-4 and -6''), 5.60 (3 H, s,  $3 \times \text{OH}$ , disappears in  $\text{D}_2\text{O}$ ), and 2.20 (3 H, s,  $\text{CH}_3$ ). As the last product (2) was very insoluble and hence not readily analysable, it was dehalogenated in ethanol under hydrogen over Pd— $\text{CaCO}_3$  to afford 2,2',2''-trihydroxy-3''-methyl-*m*-terphenol, m.p. 136—137 °C (from ethanol) (Found: C, 74.1; H, 5.7.  $\text{C}_{19}\text{H}_{16}\text{O}_3$  requires C, 74.6; H, 5.5%),  $\bar{\nu}_{\text{max}}$  3 400br,  $\nu$  (OH), 2 900w ( $\text{CH}_3$ ), 1 560w, 1 450m, and 1 429s (arom. ring), 1 200 (C—O), and 835m, 818m, 796m, 764m, and 744s, (ArH),  $m/e$  292(100%,  $M^+$ ),  $\delta[(\text{CD}_3)_2\text{CO}]$  7.47 (1 H, d,  $J$  2 Hz), 7.20br (3 H), 7.10 (2 H, s + d), 5.62 (3 H, s,  $3 \times \text{OH}$ , disappears in  $\text{D}_2\text{O}$ ), and 2.20 (3 H, s,  $\text{CH}_3$ ).

*Methylation of Lithium 4,6-Dibromo-2-lithiophenolate with Methyl Iodide (Table 2).*—2,4,6-Tribromophenol (993 mg, 3 mmol) in chilled ether (3 ml) was treated dropwise with *n*-butyl-lithium (6 mmol) in ether, and the mixture was stirred at room temperature for 1 h. Methyl iodide (3, 21, or 57 mmol as required) in ether was added and the mixture refluxed for 5 h and then worked up. The product mixture was in each case analysed by g.l.c. after calibrating the detector (FID) response for the two compounds concerned. In the third case the products (545 mg) were separated in the usual manner to afford, after purification, 2,4-dibromophenol (45 mg, 6%) and 2,4-dibromo-6-methylphenol (174 mg, 22%), identified by direct comparison with authentic compounds.

*Reaction of 2,4,6-Tribromophenol (2 mol) with Methyl-lithium (3 mol).*—Methyl-lithium (7.5 mmol) in ether was added over 3 min to 2,4,6-tribromophenol (1.65 g, 5 mmol, in ether (10 ml) at 0 °C, and the mixture was refluxed for 5 h, quenched, and worked up. The products contained 2,4-dibromo-6-methylphenol (50 mg, 4%), 5,5'-dibromo-2,2'-dihydroxy-3,3'-dimethylbiphenyl (50 mg, 6%), and 3,5,5'-tribromo-2,2'-dihydroxy-3-methylbiphenyl (85 mg, 8%), all characterised by direct comparison with authentic compounds (above), and 3,3'',5,5',5''-pentabromo-2,2',2''-trihydroxy-*m*-terphenyl\* (602 mg, 54%), m.p. 207—208 °C (from benzene—acetone).

*Methyl-lithium (3 mol) and 2,6-Dibromo-4-Y-phenol (Table 3).*—The phenol (3, 4, or 5 mmol) in ether (10 ml) was added to chilled solution of methyl-lithium (9, 12, or 15 mmol) in ether (18 ml), the mixture stirred at 37 °C for 24 h and worked up. All runs were duplicated but only one run is here described to identify products for each case.

For Y = Me. 2,6-Dibromo-4-methylphenol (1.33 g) afforded products (0.72 g) containing 2,4-dimethylphenol (88 mg, liquid, distilled *in vacuo* from biaryl product as below); 2-bromo-4,6-dimethylphenol\* (117 mg, liquid, distilled at 80 °C and 0.5 Torr); 2,4,6-trimethylphenol\* (58 mg, sublimed *in vacuo*), m.p. and mixed m.p. 71—72 °C (lit., 72 °C); and 2,2'-dihydroxy-3,3',5,5'-tetramethylbiphenyl\* (254 mg after removing 2,4-dimethylphenol *in vacuo*), m.p. 137—138 °C (from ethanol) (lit., 137.5—138.5 °C).

For Y = H. 2,6-Dibromophenol (1.26 g) gave products (0.63 g) containing 2-methylphenol (40 mg, liquid, distilled from biaryl product); 6-bromo-2-methylphenol\* (80 mg), b.p. 50—55 °C at 1 Torr (lit., 71—73 °C at 7 Torr); 2,6-dimethylphenol (32 mg), m.p. and mixed m.p. 48 °C (from ethanol) (lit., 49 °C); and 2,2'-dihydroxy-3,3'-dimethylbiphenyl\* (230 mg, sublimed), m.p. 112 °C (lit., 113 °C).

For Y = Br. 2,4,6-Tribromophenol (1.00 g) gave products (0.90 g) containing 2,4-dibromophenol (7 mg), 4-

bromo-2,6-dimethylphenol (42 mg), 5,5'-dibromo-2,2'-dihydroxy-3,3'-dimethylbiphenyl (1) (100 mg), 3,5,5',5''-tetrabromo-2,2',2''-trihydroxy-3''-methyl-*m*-terphenyl (2) (162 mg), and 5,5',5''-tribromo-2,2',2''-trihydroxy-3,3''-dimethyl-*m*-terphenyl (3), m.p. 275 °C, all identical to the products obtained above (mixed m.p., i.r., and g.l.c.); 4-bromo-2-methylphenol\* (56 mg), m.p. 63 °C (from light petroleum) (lit., 64 °C); and 3,5,5'-tribromo-2,2'-dihydroxy-3'-methylbiphenyl (130 mg), m.p. 193—194 °C (from hexane—benzene) (Found: C, 35.5; H, 2.0.  $\text{C}_{13}\text{H}_9\text{Br}_3\text{O}_2$  requires C, 35.55; H, 2.1%),  $\bar{\nu}_{\text{max}}$  3 400br (OH), 2 900w ( $\text{CH}_3$ ), 1 545 and 1 450 (arom. ring), 1 200 (C—O), and 850 (single H on ring),  $m/e$  440/438/436(78%)/434 ( $M^+$ ) and 278/276(100%),  $\delta[(\text{CD}_3)_2\text{SO}]$  7.65 (1 H, d,  $J$  2 Hz, H-4), 7.21 (1 H, d,  $J$  2 Hz, H-6), 7.20 (1 H, d,  $J$  2 Hz, H-6'), 7.02 (1 H, d,  $J$  2 Hz, H-4'), 3.5 (2 H, s, OH), and 2.17 (6 H, s,  $2 \times \text{CH}_3$ ).

For Y = Cl. 2,6-Dibromo-4-chlorophenol (1.146 g) yielded 4-chloro-2-methylphenol (67 mg, distilled from biaryl product below), m.p. and mixed m.p. 50 °C (lit., 51 °C); 4-chloro-2,6-dimethylphenol\* (32 mg, sublimed), m.p. 83—84 °C (lit., 83 °C); 5,5'-dichloro-2,2'-dihydroxy-3,3'-dimethylbiphenyl (153 mg after distilling off volatile component, see above), m.p. 154 °C (from benzene—hexane) (Found: C, 59.5; H, 4.2.  $\text{C}_{14}\text{H}_{12}\text{Cl}_2\text{O}_2$  requires C, 59.4; H, 4.2%),  $\bar{\nu}_{\text{max}}$  3 300br (OH), 1 468m (arom. ring), and 858s (single H on ring),  $m/e$  286(9%)/284(45)/282(57) ( $M^+$ ) and 212(100),  $\delta[(\text{CD}_3)_2\text{CO}]$  7.3—7.0 (m, overlaid ArH and ArOH signals) and 2.30 (s,  $\text{CH}_3$ ); 3-bromo-5,5'-dichloro-2,2'-dihydroxy-3'-methylbiphenyl (66 mg) was impure and was characterised only by the ion for  $\text{C}_{13}\text{H}_9\text{BrCl}_2\text{O}_2$ .

For Y = F. 2,6-Dibromo-4-fluorophenol (810 mg) gave products (386 mg) from which only one major product was obtained, *viz.* 5,5'-difluoro-2,2'-dihydroxy-3,3'-dimethylbiphenyl (130 mg, sublimed), m.p. 130 °C (from light petroleum—acetone—benzene),  $\bar{\nu}_{\text{max}}$  3 100br (OH), 2 990w and 2 935w ( $\text{CH}_3$ ), 1 590m and 1 470s (arom. ring), 1 225m (C—O), and 860 (s, single H on ring),  $m/e$  250(100%,  $M^+$ ),  $\delta[\text{CDCl}_3 + (\text{CD}_3)_2\text{CO}]$  6.95 (2 H, dd,  $J_{\text{H-H}}$  8,  $J_{\text{H-F}}$  3 Hz, H-4 and -4'), 6.80 (2 H, dd,  $J_{\text{H-H}}$  8.5,  $J_{\text{H-F}}$  3 Hz, H-6 and -6'), 6.3—6.0br (2 H, s, OH, disappears in  $\text{D}_2\text{O}$ ), and 2.31 (6 H, s,  $2 \times \text{CH}_3$ ).

*Test for Aryne Epoxide Intermediate.*—2,4,6-Tribromo-*m*-cresol (1.035 g, 3.0 mmol) in ether (5 ml) was added slowly to methyl-lithium (6.0 mmol) in chilled ether (3.6 ml), and the solution was refluxed for 2 h, quenched, and worked up. The product (757 mg), apparently (g.l.c.) a dibrominated xylenol, was dehalogenated by shaking under hydrogen with palladium—calcium carbonate (2%; 2.5 g) in ethanol (40 ml). The calcium carbonate was dissolved by carefully adding hydrochloric acid, the solution was filtered (Celite), and the halogen-free product was recovered (410 mg) and distilled to free it of higher molecular products; it consisted of essentially only one xylenol (g.l.c.). A distinction between 2,4- and 2,5-dimethylphenols was here required and could not be achieved by g.l.c. of these compounds themselves or of their silylation,<sup>40</sup> acetylation, nitration,<sup>41</sup> or benzylation products. Clear distinction was however achieved by re-halogenation under controlled conditions when mono-halogenated products were obtained from 2,4- and 2,6-dimethylphenols, and di-halogenated products from the 2,3- and 2,5-isomers. A sample (12 mg) of each of the pure 2,3-, 2,4-, 2,5-, and 2,6-dimethylphenols in carbon tetrachloride (3 ml) was titrated with 0.5M-bromine in carbon tetrachloride to a faint permanent red end-point and the solutions were shaken for 10 min and dried *in vacuo*.

Chlorination was carried out similarly using a saturated solution of chlorine gas in carbon tetrachloride for 20 min. On a  $0.006 \times 1.5$  m column of SE-52 (5%) with 0.4 bar nitrogen carrier gas, the halogenated products behaved as shown in Table 7. The dehalogenated reaction product on

TABLE 7

Retention times (min) of halogenation products of xylenols

Dimethyl substituents	2,3-	2,4-	2,5-	2,6-
Chlorinated products, column temp. 150 °C	12.0	4.8	11.0	8.8
Brominated products, column temp. 160 °C	10.5	3.0	9.3	5.0

re-halogenation with bromine and with chlorine as above showed only two (halogenated) components with each reagent, corresponding to 2,3- and 2,5-dimethylphenol in the ratio (peak areas) of 6 : 94. The sensitivity of the measurement would have allowed the detection of the 2,4- and 2,6-dimethylphenols at a level of 0.001% of the reaction products.

**Methyl-lithium (1 mol) and 2,4,6-Tribromo-Z-benzenes (Table 4).**—The aryl halide (3 mmol) in ether (20 ml) was added to a chilled solution of methyl-lithium (3 mmol in all cases except for 2,4,6-tribromophenol, when 6 mmol were used so as to form the lithium phenolate initially) in ether (2.5 ml). The mixture was then stirred in a bath at 25 °C for 5 h, quenched with hydrochloric acid, and worked up.

**For Z = OLi.** 2,4,6-Tribromophenol (993 mg) yielded products (643 mg) which afforded 2,4-dibromophenol (64 mg), 2,4-dibromo-6-methylphenol (59 mg), 5,5'-dibromo-2,2'-dihydroxy-3,3'-dimethylbiphenyl (1) (168 mg), and 3,5,5'-tribromo-2,2'-dihydroxy-3'-methylbiphenyl (56 mg).

**For Z = OCH<sub>3</sub>.** 2,4,6-Tribromoanisole (1.031 g) yielded products (667 mg) which afforded 2,4-dibromoanisole\* (60 mg, distilled at 40 °C at 0.1 Torr); 2,4-dibromo-6-methylanisole\* (34 mg, distilled at 80 °C at 1 Torr); 3,5,5'-tribromo-2,2'-dimethoxy-3'-methylbiphenyl (148 mg), m.p. 73–74 °C (from benzene-hexane) (Found: C, 39.3; H, 2.8. C<sub>15</sub>H<sub>13</sub>Br<sub>3</sub>O<sub>2</sub> requires C, 38.8; H, 2.8%),  $\bar{\nu}_{\max}$  2 925 (CH<sub>3</sub>), 1 540w, 1 487m, 1 457s, and 1 410m (arom. ring), 1 235s (C–O), and 856m (single H on ring), *m/e* 468/466/464(75%)/462 and 453/451/449(100)/447 (*M* – CH<sub>3</sub>),  $\delta(\text{CCl}_4)$  7.20 (4 H, s, ArH), 3.41 (6 H, s, 2 × OCH<sub>3</sub>), and 2.29 (3 H, s, ArCH<sub>3</sub>); 5,5'-dibromo-2,2'-dimethoxy-3,3'-dimethylbiphenyl (61 mg), m.p. 131 °C (from light petroleum) (Found: C, 47.8; H, 4.0. C<sub>16</sub>H<sub>16</sub>Br<sub>2</sub>O<sub>2</sub> requires C, 48.0; H, 4.0%),  $\bar{\nu}_{\max}$  2 948m, 2 920m, and 2 825w (CH<sub>3</sub>), 1 568w, 1 463s, and 1 420m (arom. ring), 1 400s (C–O), and 862s (single H on ring), *m/e* 402/400(100%)/398 (*M*<sup>+</sup>),  $\delta(\text{CCl}_4)$  7.14 (4 H, s, ArH), 3.39 (6 H, s, 2 × OCH<sub>3</sub>), and 2.25 (3 H, s, ArCH<sub>3</sub>).

**For Z = 3 × Me.** 2,4,6-Tribromo-1,3,5-trimethylbenzene (1.017 g) gave products (738 mg) which afforded 4,6-dibromo-1,2,3,5-tetramethylbenzene\* (322 mg), m.p. (sealed tube) 198 °C (from benzene), (lit., 198 °C) and 3,3'-dibromo-2,2',4,4',6,6'-hexamethylbiphenyl\* (65 mg), m.p. 112 °C (from benzene) (lit., 112–113 °C).

**For Z = Me.** 2,4,6-Tribromotoluene (988 mg) gave products (565 mg) containing two main components which were separated with difficulty on repeated chromatography, *viz.* 2,6-dibromo-1,4-dimethylbenzene\* (239 mg) m.p. 35.5 °C (from ethanol) (lit., 36 °C), and 3,5-dibromo-1,2-dimethylbenzene (187 mg), m.p. 63 °C (from ethanol) (Found: C, 36.2; H, 3.4. C<sub>8</sub>H<sub>8</sub>Br<sub>2</sub> requires C, 36.3; H, 3.0%),  $\bar{\nu}_{\max}$  2 950w, 2 920m and 2 860w (CH<sub>3</sub>), 1 580m, 1 500m, and

1 458s (arom. ring), and 850s (single H on ring), *m/e* 266/264(100%)/262 (*M*<sup>+</sup>),  $\delta(\text{CCl}_4)$  7.49 (1 H, d, *J* 2 Hz, H-4), 7.15 (1 H, d, *J* 2 Hz, H-6), and 2.30 (6 H, s, 2 × ArCH<sub>3</sub>).

**For Z = H.** 1,3,5-Tribromobenzene (1.575 g) gave products (1.078 g) which yielded only one pure major component, *viz.* 3,5-dibromomethylbenzene\* (615 mg, distilled), m.p. 39 °C (lit., 39 °C); bromobenzene and a mixture of 2,4-dibromobenzene and 3-bromomethylbenzene were characterised by their mass spectra only.

**Reaction of 2-Lithioanisole (2 mol) with 2,3,5,6-Tetrabromo-4-methylphenol.**—n-Butyl-lithium (3 mmol) in ether was added to 2-bromoanisole (561 mg, 3 mmol) in chilled ether (10 ml) and then stirred at room temperature for 1 h. 2,3,5,6-Tetrabromo-4-methylphenol<sup>42</sup> (636 mg, 1.5 mmol) was partly dissolved in ether (10 ml), and the solution was injected into the chilled 2-lithioanisole solution while stirring. The remainder of the substrate was then dissolved in more ether (10 ml) and similarly added 2 min later. The reaction mixture was refluxed for 24 h, quenched, and worked up as before. The products (800 mg) yielded unchanged substrate (95 mg, 0.22 mmol), m.p. and mixed m.p. 198–199 °C; 3,4,6-tribromo-2-hydroxy-2'-methoxy-5-methylbiphenyl (17) (122 mg; 21% on substrate consumed), m.p. 98–99 °C (from benzene-ether) (Found: C, 37.7; H, 2.6. C<sub>14</sub>H<sub>11</sub>Br<sub>3</sub>O<sub>2</sub> requires C, 37.4; H, 2.5%),  $\bar{\nu}_{\max}$  3 440br (OH), 2 920w and 2 820w (CH<sub>3</sub>), 1 590m, 1 560m, 1 490s, 1 455s, 1 455s, and 1 410s (arom. ring), 1 240s (C–O), and 745s (4 adjacent H on ring), *m/e* 454/452/450(100%)/448 (*M*<sup>+</sup>), 373/371(50)/369 (*M* – Br) and 358/356(100%)/354 (*M* – Br – CH<sub>3</sub>),  $\delta[(\text{CD}_3)_2\text{CO}]$  7.50br (s, OH), 7.31 (d, *J* 3 Hz), 7.27 (dd, *J* 6 and 3 Hz), 7.03 (t, *J* 3 Hz) and 6.98 (d, *J* 6 Hz) (integral over 7.5–6.9 equals 5 H), 3.68 (3 H, s, OCH<sub>3</sub>), and 2.62 (3 H, s, ArCH<sub>3</sub>); 4,6-dibromo-2-hydroxy-2'-methoxy-5-methylbiphenyl (18) (51 mg, 11%), m.p. 160.5–161 °C (from ether-chloroform and from acetone-water) (Found: C, 45.2; H, 3.2. C<sub>14</sub>H<sub>12</sub>Br<sub>2</sub>O<sub>2</sub> requires C, 45.2; H, 3.2%),  $\bar{\nu}_{\max}$  3 400br m and 3 360br m (OH), 2 920w and 2 880w (CH<sub>3</sub>), 1 580m, 1 565m, 1 480m, 1 450m, 1 430s and 1 420s (arom. ring), 1 220s (C–O), 870m (single H on ring), and 730s (4 adjacent H on ring), *m/e* 374/372(100%)/370 (*M*<sup>+</sup>) and 358/356(50)/354,  $\delta[(\text{CD}_3)_2\text{CO}]$  7.5–6.9 (6 H, m, OH + 5 × ArH), 3.80 (3 H, s, OCH<sub>3</sub>), and 2.34 (3 H, s, ArCH<sub>3</sub>); 4',6'-dibromo-2'-hydroxy-2,2'-dimethoxy-5'-methyl-*m*-terphenyl (19) (100 mg, 16%) as a glass (distilled at 230 °C and 0.3 Torr). On repeating the experiment on 4 mmol of 2-bromoanisole and 2 mmol of 2,3,5,6-tetrabromo-4-methylphenol, but using, again, two 10 ml portions ether for the addition, the proportion of unchanged substrate was higher, as expected (37%), and the yields of the three products (on substrate consumed) were 11% for (17), 11% for (18), and 38% for (19) (in terms of materials recovered).

The effect of mixing conditions was studied for three cases (Table 5). In every case g.l.c. of the products after work-up showed, besides anisole and 2-bromoanisole, unchanged starting material (16) and only the three products (17), (18), and (19) with retention times of 8.7 [for (16)], 11.1 [for (17)], 12.7 [for (18)], and 16.0 min [for (19)] on a  $0.004 \times 1.0$  m column of SE-52 (10% loading) run at 12% min<sup>-1</sup> from 150 to 300 °C at 1.2 bar nitrogen inlet pressure. The mixing conditions were (a) 'in portions': the substrate (2 mmol) was added in portions to prepared 2-lithioanisole (4 mmol) in the manner described above, (b) 'gradually over 8 min': the substrate (0.5 mmol), all dissolved in ether (8 ml), was added to 2-lithioanisole (1 mmol) dropwise over 8 min, and (c) 'instantaneously': a two-bulb two-septum flask was pro-

vided with 2-bromoanisole (2 mmol) in one and with 2,3,5,6-tetrabromo-4-methylphenol (1 mmol) in the other bulb. The former reagent was lithiated in ether with *n*-butyl-lithium (2 mmol) as before, the substrate was all separately dissolved in ether (15 ml), and the solutions contained in the two separate bulbs were mixed as quickly as possible; at 10 s, at 1 min, and at 100 min after mixing, aliquot samples were withdrawn, quenched by injection into 2*M*-hydrochloric acid as before, and analysed by g.l.c. (as above): all three aliquot samples gave identical g.l.c. traces, so that no further reaction had occurred after the first sampling at 10 s after mixing.

*Reaction of 2-Lithioanisole (2 mol) with 2,4,6-Tribromo-3-methylphenol.*—*n*-Butyl-lithium (2 mmol in ether) was added to 2-bromoanisole (374 mg, 2 mmol) in chilled ether (5 ml). The mixture was stirred at room temperature for 1 h and chilled again before adding 2,4,6-tribromo-3-methylphenol (345 mg, 1 mmol) in ether (5 ml). The mixture was refluxed for 18 h before quenching. The products (400 mg) contained (g.l.c.) as the major product 3,5-dibromo-2-hydroxy-2'-methoxy-4-methylbiphenyl (15) (155 mg, 42%), m.p. 147.5–148 °C (from chloroform-ether) (Found: C, 45.4; H, 3.0.  $C_{14}H_{12}Br_2O_2$  requires C, 45.4; H, 3.2%),  $\nu_{max}$  3 365br (OH), 2 915w and 2 830w (CH<sub>3</sub>), 1 592w, 1 575w, 1 490m, and 1 455m (arom. ring), 880 (m, single H on ring), and 746 (s, 4 adjacent H on ring), *m/e* 374/372(100%)/370 (*M*<sup>+</sup>),  $\delta$ (CDCl<sub>3</sub>) 7.50 (1 H, s, H-6), 7.45–7.05 (4 H, m, H-3', -4', -5', and -6'), 6.43 (1 H, s, OH, disappears in D<sub>2</sub>O), 3.90 (3 H, s, OCH<sub>3</sub>), and 2.63 (3 H, s, ArCH<sub>3</sub>). On repeating the reaction on one-fourth scale the yield of isolated main product (15) rose to 48%.

*Reaction of 2-Lithioanisole with Pre-formed Lithium 2,4,6-Tribromo-3-methylphenolate (13).*—In one bulb of the two-bulb flask 2-bromoanisole (1 mmol) was lithiated with *n*-butyl-lithium (1 mmol) in ether for 1 h as above. The other bulb contained 2,4,6-tribromo-3-methylphenol (1 mmol) which was treated by separate injection with *n*-butyl-lithium (1 mmol) for 5 min at room temperature and the apparatus then tilted to mix the reactants which were then refluxed overnight before working up as above. G.l.c. analysis of the product (100  $\mu$ g sample) showed no observable peak at or near that for product (15) of the preceding experiment under conditions where 2% of (15) would be clearly observable.

*Reaction of Methyl-lithium (2 mol) with 2,4,6-Tribromophenol under Controlled Concentrations of Oxygen (Table 6).*—(a) Methyl-lithium (10 mmol) in ether (12 ml; distilled over sodium wire and benzophenone on to 3A molecular sieve before use) in the upper bulb of the two-bulb flask and 2,4,6-tribromophenol (1.655 g, 5 mmol) in ether (10 ml) as above in the lower bulb were rigorously degassed by repeated cycles of freezing in liquid nitrogen, pumping out, and liquefaction. After admitting high purity nitrogen and mixing the separately degassed solutions the mixture was refluxed for 5 h, quenched, and worked up as before to yield products (1.336 g) which were separated to afford 4,6-dibromo-2-methylphenol (65 mg), 4-bromo-2,6-dimethylphenol (80 mg), and compounds (22) (108 mg), (23) (320 mg), (24) (65 mg), and (25) (200 mg). (b) This reaction was carried out as under (c) below but under an atmosphere of high-purity nitrogen. (c) 2,4,6-Tribromophenol (1.655 g, 5 mmol) in a two-necked flask under a balloon flushed with medical air (21% v/v oxygen) was dissolved in ether (10 ml), chilled, and treated with methyl-lithium (10 mmol) in ether, and the mixture was refluxed for 5 h, quenched, and worked up to yield pro-

ducts (1.14 g) separated to afford only compounds (21) (150 mg), (23) (277 mg), (24) (30 mg), and (25) (160 mg), all characterised as before.

*Reaction of 2,4,6-Tribromophenol with Methyl-lithium and with Galvinoxyl.*—Methyl-lithium (10 mmol) in ether was added over 3 min to 2,4,6-tribromophenol (1.655 g, 5 mmol) in chilled ether (18 ml) and stirred for 30 min. Galvinoxyl (150 mg, 0.356 mmol) in dry benzene (10 ml) was added, the deep purple colour changing to pale yellow after 5 min. After 30 min at 25 °C the reaction was quenched with water only, aluminium oxide (17.5 g) was added, and the mixture was refluxed for 30 min before filtering and drying. Chromatography followed by distillation yielded from the first eluate (145 mg) the addition product, 1,1-bis-(4-hydroxy-3,5-di-*t*-butylphenyl)ethane (39) (110 mg, 71%), m.p. 156 °C (from light petroleum) (Found: C, 82.4; H, 10.4.  $C_{30}H_{46}O_2$  requires C, 82.1; H, 10.6%),  $\nu_{max}$  3 600s and 3 400br (OH), 2 940s and 2 845m (CH<sub>3</sub>), 1 445m and 1 425s (arom. ring), 1 220s (C-O), and 865m (single H on ring, *m/e* 439 (54%, *M* + 1), 438(92, *M*<sup>+</sup>), 424(84), and 423(*M* - CH<sub>3</sub>, 100%),  $\delta$ (CDCl<sub>3</sub>) 7.04 (4 H, s, ArH), 5.00 (2 H, s, OH), 3.95 (1 H, q, *J* 8 Hz, -CHCH<sub>3</sub>), 2.62 (3 H, d, *J* 8 Hz, -CHCH<sub>3</sub>), and 1.41 (36 H, s, 4 × Bu<sup>t</sup>). Other products of this reaction were (by t.l.c.) the usual products described earlier.

*Reaction of Lithium 2-Lithiophenolate with Methyl Iodide.*—*n*-Butyl-lithium (5.7 mmol) in ether was added to 2-bromophenol (493 mg, 2.85 mmol) in chilled ether (8 ml), and the solution was stirred at 25 °C for 1 h before methyl iodide (8.1 g, 57 mmol) in ether (10 ml) was added over 1 min. The solution was refluxed for 5 h, quenched, and worked up and the products (450 mg) were chromatographed to yield 2-iodophenol\* (200 mg, 32%, distilled), m.p. 38–39 °C (lit., 43 °C), 2-methylphenol (98 mg, 32%), and phenol (23 mg, 9% recovery).

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