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SELECTIVE MONO-ARYLATION AND -ALKYLATION OF BIS(ALKYLTHIO)BENZENES

THE IMPORTANCE OF STERIC EFFECTS IN THE NICKEL-CATALYZED CROSS-COUPLING OF ARYL ALKYL SULPHIDES WITH GRIGNARD REAGENTS

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Abstract—Synthetically useful procedures to effect selective conversion of C–S into C–C bonds have been developed by taking advantage of the sensitivity of reactions of Grignard reagents with aryl alkyl sulphides, catalyzed by low-valent nickel species, to steric effects. It is shown that the course of these reactions is influenced by the steric requirements of both the aryl and the alkyl moieties of the sulphides. Thus, selective mono-arylation and alkylation of easily available bis(alkylthio)benzenes can be effected in medium to high yields. This allows the introduction of two different aryl or alkyl groups into the benzene nucleus by sequential substitution of the two alkylthio functions.

Recently it has been shown that halo,[1] alkoxy[2,3] and alkylthio[4–7] groups on arenes can be substituted easily by aryl or alkyl functions in reactions with Grignard reagents and low-valent Ni species as catalysts. One of the most remarkable and useful reactions may be the selective mono-arylation or -alkylation of bis-substituted aromatic derivatives, permitting the introduction of two different aryl or alkyl groups into the aromatic ring (eqn 1)

$$\mathrm{ArX_2 \rightarrow ArXR \rightarrow ArRR'}. \quad (1)$$

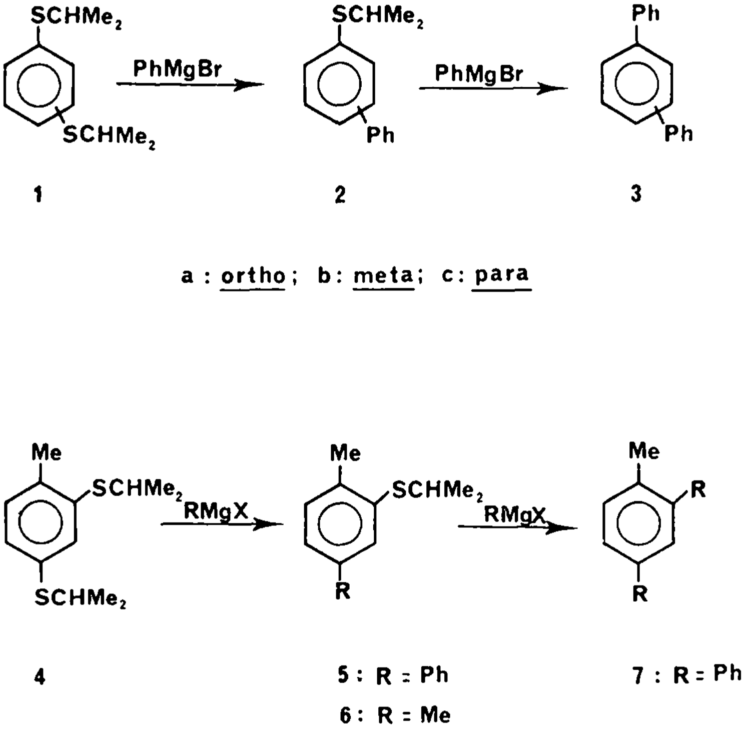
Several attempts to develop a synthetically useful procedure have been made. The reactions of dichlorobenzenes cannot be employed because they gave rise to the formation of bis-substituted products even on use of an equimolecular amount of Grignard reagents.[1] The dimethoxybenzenes also do not seem to be promising in allowing selective mono-substitution.[2] Some interesting results were obtained using Pd catalysts. Thus, halofluorobenzenes react with Grignard reagents to give the products of monosubstitution,[8,9] however the subsequent displacement of F proved to be very difficult.[1] Examples of monosubstitution were obtained by Kumada[10] in the reactions of dibromoarenes with Grignard and organozinc reagents using [1,4-bis(diphenylphosphino)butane]palladium dichloride as catalyst. We have recently reported that selective monosubstitution can be effected also in the presence of Ni catalysts provided the aromatic substrate contains two groups which present different leaving ability;[11] thus, using the chlorophenyl alkyl sulphides it is possible to effect the sequential substitution of the Cl atom and of the alkylthio group with two different Grignard reagents, in the presence of $Ni(PPh_3)_2Cl_2$.

We now report the obtainment of the same goal by the use of benzene derivatives substituted by two leaving groups whose displacement by Grignard reagents depends on steric, rather than electronic effects. Thus selective monosubstitution can be executed easily starting from appropriate bis(alkylthio) benzenes using Grignard reagents and $Ni(PPh_3)_2Cl_2$ as catalyst. The resultant products then can react with a different Grignard reagent to give a bis-arylated or -alkylated benzene as indicated in eqn (1). The synthetic utility of this method is enhanced greatly by the easy availability of the starting substances, bis(alkylthio)benzenes being obtained conveniently by the efficient interaction of dichlorobenzenes and alkanethiolates in HMPA (eqn 2)[12]

$$\mathrm{C_6H_4Cl_2 \xrightarrow{RSNa} C_6H_4ClSR \xrightarrow{R'SNa} C_6H_4(SR)SR'}. \quad (2)$$

RESULTS AND DISCUSSION

The reactions of *o*-, *m*- and *p*-bis(i-propylthio)benzenes (**1**) with an excess of PhMgBr, in benzene at 50°, in the presence of $Ni(PPh_3)_2Cl_2$, afforded in about 4 hr, *o*-, *m*- and *p*-terphenyls (**3**) in 67, 77 and 74% yield respectively (Scheme 1). Under the influence of [1,2-bis(diphenylphosphino)ethane]nickel dichloride, $Ni(dppe)Cl_2$, as catalyst, the *p*-bis(i-propylthio)benzene (**1c**) was converted into *p*-terphenyl (**3c**) (4 hr) in better yields (84%). These reactions however were not selective. Even at the early reaction stages (or by the use of an unsufficient quantity of PhMgBr) the terphenyls (**3**) were already present in considerable amount together with the products of monosubstitution (**2**). Thus the two consecutive reactions occur with comparable rates with all the three isomers, a behaviour similar to that encountered in the case of the dichlorobenzenes.[1] However, the same reaction on the 2,4-bis(i-propylthio)toluene (**4**) occurs more easily at the C–S bond at position 4 than



1 2 3

a : ortho; b: meta; c: para

4

5 : R = Ph
6 : R = Me

7 : R = Ph

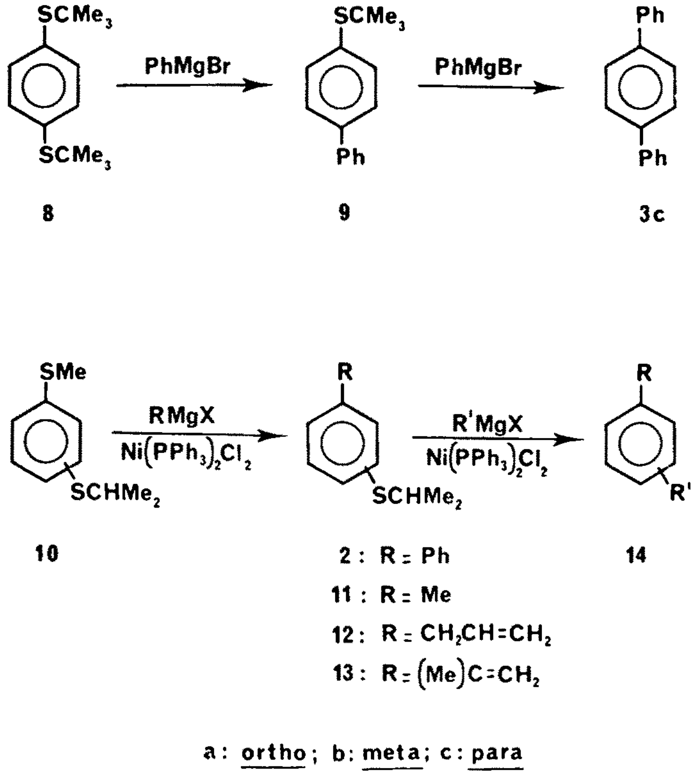
Scheme 1.

position 2 (Scheme 1). Thus, the use of an equimolecular amount of PhMgBr (2.5 hr) or MeMgI (1 hr) led to the products of monosubstitution (**5** and **6**) in 55 and 45% yields respectively. This represents a clear example of the sensitivity of these reactions to steric effects, the desired reaction occurring selectively at the less sterically hindered C–S bond. A similar effect was observed in the case of alkenes. Thus, for instance, the interaction of diethyl methylketenethioacetal, $MeCH{=}C(SEt)_2$, with PhMgBr gives 1-phenyl-1-ethylthiopropene, wherein the phenyl group had substituted the ethylthio group *cis* to the olefinic hydrogen.[13] This kind of selectivity seems to be peculiar of the alkyl sulphides. In fact, when the same reaction with PhMgBr and $Ni(PPh_3)_2Cl_2$ was applied to the 2,4-dichlorotoluene the reaction was not selective and a mixture of 3-chloro,4-methylbiphenyl and 2-methyl,5-chlorobiphenyl was obtained together with some starting compound and some 2,4-diphenyltoluene (**7**). The sensitivity to steric effects of the reactions of aryl alkylsulphides is also indicated by the fact that from the reaction of **4** with an excess of PhMgBr, in the presence of $Ni(PPh_3)_2Cl_2$, a complete transformation of **5** into **7** could not be obtained even with prolonged reaction times (36 hr). Compound **7** could be prepared in 94% yields using excess PhMgBr and $Ni(dppe)Cl_2$ as catalyst (15 hr).

The results obtained from these preliminary experiments induced us to look also for selectivity due to the steric demand of the thioalkyl groups. When a reaction with an excess of PhMgBr was carried out on *p*-bis(t-butylthio)benzene (**8**), in the presence of $Ni(PPh_3)_2Cl_2$ (90 hr), transformation into *p*-terphenyl (**3c**) remained uncomplete, the compound of monosubstitution (**9**) being present in considerable amounts (Scheme 2). A clean reaction could be obtained in this case also (89% of *p*-terphenyl) using $Ni(dppe)Cl_2$. The results obtained from **8** in the presence of $Ni(PPh_3)_2Cl_2$ is of considerable relevance, since it indicates that the steric requirements of the alkyl groups are also important in determining the rate of the aryl-S bond fission. This effect can be fruitfully employed to develop synthetically useful selective monosubstitutions. In fact, if the aromatic substrate contains two alkylthio groups which have different steric requirements, the reaction should occur more easily at the less sterically hindered aryl-S bond. This has been successfully verified in the case of the (methylthio)phenyl i-propyl sulphides.

The reactions of *m*- and *p*-(methylthio)phenyl i-propyl sulphides (**10**) with 1.3 equiv. of several Grignard reagents gave selectively the products of mono-substitution. In every case the reaction took place at the less sterically hindered Ar–SMe bond to give (i-propylthio)benzene derivatives **2** and **11–13** (Scheme 2). Only minute amounts of the $C_6H_4(R)SMe$ compounds could be detected by GLC. The results of these experiments are summarized in Table 1. As expected even better results were obtained (run 6) with *p*-(methylthio)phenyl t-butyl sulphide (**15**). Since the reactions were allowed to proceed until all the starting product was consumed, some bissubstituted product (**14**: $R = R'$) was obtained also. The latter, however, could be separated easily from **2** and **11–13** by column chromatography. The reactions could be stopped before **14** started to form and the compounds of monosubstitution could be separated from **10** by column chromatography.

Although the mechanism of the Ni-catalyzed reactions of aryl alkyl sulphides with Grignard reagents has not been clarified yet, the coupling may occur through a reaction sequence similar to that of aromatic halides[1,14] which has been suggested to apply also to alkenyl sulphides.[15] The proposed catalytic cycle consists of oxidative addition of an aromatic or vinylic halide or sulphide

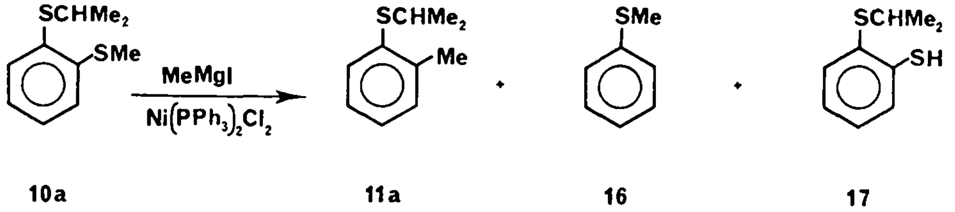


Scheme 2.

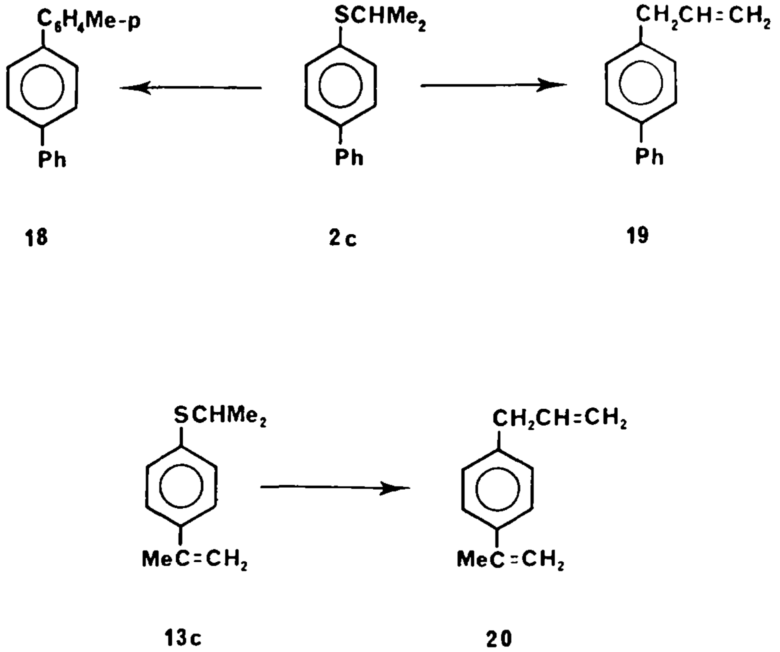
Table 1. The reactions of bis(alkylthio)benzenes (0.01 mols) with 1.3 eqv. of Grignard Reagents in the presence of 0.1 eqv. of $Ni(PPh_3)_2Cl_2$ (A) or $Ni(dppe)Cl_2$ (B) in benzene at 50°

Run	Starting Products	R in RMgX	Catalyst	Reaction Time (hr)	Reaction Products[a]	Yields (%)[b]
1	*o*-$C_6H_4(SMe)SCHMe_2$	Ph	A	7	*o*-$PhC_6H_4SCHMe_2$	35[c]
2	*o*-$C_6H_4(SMe)SCHMe_2$	Ph	B	2	d	
3	*m*-$C_6H_4(SMe)SCHMe_2$	Ph	A	0.5	*m*-$PhC_6H_4SCHMe_2$	56[e]
4	*p*-$C_6H_4(SMe)SCHMe_2$	Ph	A	6	*p*-$PhC_6H_4SCHMe_2$	55[e]
5	*p*-$C_6H_4(SMe)SCHMe_2$	Ph	B	7	f	
6	*p*-$C_6H_4(SMe)SCMe_3$	Ph	A	0.5	*p*-$PhC_6H_4SCMe_3$	76[e]
7	*m*-$C_6H_4(SMe)SCHMe_2$	Me	A	1.5	*m*-$MeC_6H_4SCHMe_2$	48
8	*p*-$C_6H_4(SMe)SCHMe_2$	Me	A	1	*p*-$MeC_6H_4SCHMe_2$	87
9	*o*-$C_6H_4(SMe)SCHMe_2$	$-CH_2CH=CH_2$	A	24	*o*-$C_6H_4(CH_2CH=CH_2)_2$	38[g]
10	*m*-$C_6H_4(SMe)SCHMe_2$	$-CH_2CH=CH_2$	A	19	*m*-$CH_2=CHCH_2C_6H_4SCHMe_2$	37[g]
11	*p*-$C_6H_4(SMe)SCHMe_2$	$-CH_2CH=CH_2$	A	8	*p*-$CH_2=CHCH_2C_6H_4SCHMe_2$	65[g]
12	*m*-$C_6H_4(SMe)SCHMe_2$	$-(Me)C=CH_2$	A	45	*m*-$CH_2=C(Me)C_6H_4SCHMe_2$	48[g]
13	*p*-$C_6H_4(SMe)SCHMe_2$	$-(Me)C=CH_2$	A	24	*p*-$CH_2=C(Me)C_6H_4SCHMe_2$	47[g]

[a] Biphenyl was also present in all the reactions run with PhMgBr. [b] Yields based on isolated products after column chromatography. [c] A 35% yield of *o*-terphenyl was obtained also. [d] The glc analysis of the reaction mixture showed the presence of starting material, 2-(methylthio)- and 2-(*i*-propylthio)biphenyl and *o*-terphenyl in the ratio of 28:18:30:24. [e] A 10-15% yield of terphenyl also was obtained. [f] The glc analysis of the reaction mixture showed the presence of 4-(methylthio)- and 4-(*i*-propylthio)biphenyl and *p*-terphenyl in the ratio of 12:70:18. [g] Some $C_6H_5SCHMe_2$, derived from the reduction of the SMe group, also was isolated.



Scheme 3.



Scheme 4.

to a low valent Ni species and reductive elimination of the coupling product from a diorganometal complex. The results reported above thus indicate that the oxidative addition of the aryl alkyl sulphide to the low valent Ni species is very sensitive to steric effects and occurs preferentially at the less sterically hindered aryl-S bond.

The results collected in the table indicate that with $CH_2{=}CHCH_2MgBr$ and $CH_2{=}C(Me)MgBr$ a secondary process also takes place to some extent and the cross-coupling compounds are accompanied by the reduction products of the alkylthio function. This reaction also was completely selective and occurred at the Ar–SMe bond to give $C_6H_5SCHMe_2$ (runs 10–13).

Also reported in the table are the results obtained with the *o*-(methylthio)-phenyl i-propyl sulphide (**10a**). In this case selective monosubstitution could not be obtained. With PhMgBr a considerable amount of *o*-terphenyl (**3a**) was obtained (run 1). With $CH_2{=}CHCH_2MgBr$, even at the early stages of the reaction, the product of monosubstitution (**12a**) could not be detected by GLC and the only product obtained was the *o*-bis(allyl)benzene. A complicated picture emerges from these experiments and a straightforward interpretation cannot be given at present; it seems that the presence of the two SR groups in the *ortho* position produces a decrease of the difference in rates of the two consecutive reactions. On the other hand the reaction of **10a** with MeMgI gave some unexpected results (Scheme 3). The monosubstitution product (**11a**) was obtained in very low yields (16%) together with thioanisole (**16**) and with *o*-(mercapto)phenyl i-propyl sulphide (**17**). This latter compound, which was fully characterized as the already described *o*-(ethylthio)phenyl i-propyl sulphide, is interesting because it represents the first example in which the reaction of a Grignard reagent with an aryl alkyl sulphide leads to the fission of the alkyl-S bond.

An interesting point which emerges from the results presented above is that the structure of the ligands in the Ni catalyst greatly influences the selectivity of the reactions of Grignard reagents with aryl alkyl sulphides. Thus, $Ni(dppe)Cl_2$ is more efficient than $Ni(PPh_3)_2Cl_2$, as indicated by the reactions of PhMgBr with *p*-$C_6H_4(SCHMe_2)_2$, *p*-$C_6H_4(SCMe_3)_2$ and with **4**. However, with $Ni(dppe)Cl_2$ the reaction rates at the Ar–SMe and Ar–$SCHMe_2$ bonds become comparable with a consequent loss of selectivity (runs 2 and 5). This different behaviour of the two catalysts also may be attributed to steric effects of the ligands.

Finally, some examples of sequential substitutions to obtain compounds of type **14** were carried out also. From the reaction of 4-(i-propylthio)biphenyl (**2c**) with *p*-MeC_6H_4MgBr and $CH_2{=}CHCH_2MgBr$, in the presence of $Ni(PPh_3)_2Cl_2$, compounds **18** and **19** were obtained in 65 and 42% yields respectively. Similarily, *p*-(1-methylethenyl)phenyl i-propyl sulphide (**13c**) reacted with $CH_2{=}CHCH_2MgBr$ to afford **20** in 48% yields.

The results described in this paper demonstrate that the cross-coupling reactions of Grignard reagents and aryl alkyl sulphides are very sensitive to steric effects. The course of the reaction is influenced strongly by the steric requirements of both the aryl and the alkyl moieties of the sulphides. These effects have been utilized to develop selective conversions of C–S into C–C bonds. This allows the introduction of two different aryl or alkyl groups into the benzene nucleus by sequential substitution of two alkylthio functions. In view of the starting materials being easily available, this procedure can find useful applications in organic syntheses.

EXPERIMENTAL

Products were identified by comparison of their physical and spectral properties with those reported in the literature and by ^1H-NMR spectra. NMR spectra were recorded, in $CDCl_3$ solns, on a 90 MHz Varian EM 390 instrument.[16] GLC analyses were carried out on a Hewlett–Packard 5830A chromatograph with a 20 in. 10% UCW 982 column. Elemental analyses were carried out on a C. Erba Elemental Analyzer Mod. 1106. Sulphones were obtained by oxidation with H_2O_2 in AcOH. Grignard reagents were prepared in a standard manner. Nickel diphenylphosphine dichloride[17] and [1,2-bis(diphenylphosphino)ethane]nickel dichloride[18] were prepared as described in the literature.

Starting products. Compounds **1a–c**[12a] and **10a–c**[12d] were prepared as described.

p-*Bis*(*t-butylthio*)*benzene* (**8**). This compound was obtained in 65% yield from *p*-dichlorobenzene and excess (4 mol) of Me_3CSNa in HMPA at 100° according to the procedure described for the synthesis of other bis(alkylthio)benzenes.[12] M.p. and mixed m.p. 110–2° (lit.[19] 112–3°).

p-(*Methylthio*)*phenyl t-butyl sulphide* (**15**). The reaction of *p*-dichlorobenzene with 1.5 mol of Me_3CSNa in HMPA at 120° for 6 hr afforded, after the usual work-up[12] and column chromatography on silica gel, the p-*chlorophenyl t-butyl sulphide*, oil (55%), δ 7.35, 7.15 (AA'BB', 4 H), 1.25 (s, 9 H). This compound (0.6 g) was allowed to react, for 5 hr at 100°, with MeSNa (0.7 g) in HMPA. The cooled mixture was treated with MeI and then worked-up as usual to give the desired **15**, oil (94%), δ 7.4, 7.1 (AA'BB', 4 H), 2.4 (s, 3 H), 1.25 (s, 9 H). (Found: C, 62.25; H, 7.81; S, 30.24. $C_{11}H_{16}S_2$ requires: C, 62.20; H, 7.61; S, 30.19%.) Bissulphone, m.p. 207–9° from EtOH, δ (in CD_3COCD_3) 8.25, 8.15 (AA'BB', 4 H), 3.2 (s, 3 H), 1.35 (s, 9 H). (Found: C, 47.63; H, 5.81; S, 23.34. $C_{11}H_{16}O_4S_2$ requires: C, 47.80; H, 5.85; S, 23.20%.)

2,4-*Bis*(*i-propylthio*)*toluene* (**4**). This compound was obtained in 69.5% yield from 2,4-dichlorotoluene and Me_2CHSNa in HMPA at 100° for 20 hr δ 7.45 (d, J = 2 Hz, 1 H), 7.1 (dd, J = 2 and 8 Hz, 1H), 7.0 (d, J = 8 Hz, 1 H), 3.35 (spt, 1 H), 3.25 (spt, 1 H), 2.35 (s, 3 H), 1.25 (d, 6 H), 1.2 (d, 6 H). (Found: C, 65.07; H, 8.18; S, 26.42. $C_{13}H_{20}S_2$ requires: C, 64.93; H, 8.40; S, 26.67%.) Bissulphone, m.p. 133–5° from EtOH, δ 9.4 (d, J = 2 Hz, 1 H), 7.9 (dd, J = 2 and 8 Hz, 1 H), 7.5 (d, J = 8 Hz, 1 H), 3.3 (spt, 1 H), 3.2 (spt, 1 H), 2.8 (s, 3 H), 1.3 (d, 6 H), 1.2 (d, 6 H). (Found: C, 51.35; H, 6.55; S, 21.23. $C_{13}H_{20}O_4S_2$ requires: C, 51.28; H, 6.63; S, 21.06%.)

Cross-coupling reactions of Grignard reagents with bis(*alkylthio*)*benzenes.* To a stirred mixture of the bis(alkylthio)benzene (0.01 mols) and the catalyst (0.1 equiv.) in benzene (50 ml) an ethereal soln of the Grignard reagent (1.3 or 3 equiv.) was added. The mixture was stirred, under N_2, at 50°, for the time indicated under the Results section. The progress of the reaction was monitored by TLC and GLC. Quenching with a saturated soln of NH_4Cl was effected, when all the starting material had been consumed. After the usual work-up the residue from the organic soln was chromatographed through a silica gel column using a mixture of light petroleum–ethyl ether (95:5) as eluant. Reaction times and yields of products are given in the Table and under the Results section.

The physical and NMR data of the products are given below. *p*-Terphenyl (**3c**) and thioanisole (**16**) were commercial products.

2-(*i-Propylthio*)*biphenyl* (**2a**), oil, δ 7.5–7.1 (m, 9 H), 3.15 (spt, 1 H), 1.15 (d, 6 H), identical with an authentic sample prepared from 2-bromobiphenyl and Me_2CHSNa in HMPA.[12] Sulphone, m.p. 68–9°, δ 8.1 (dd, J = 2 and 8 Hz, 1 H), 7.6–7.2 (m, 8 H), 2.6 (spt, 1 H), 1.1 (d, 6 H). (Found: C, 69.32; H, 6.11; S, 12.45. $C_{15}H_{16}O_2S$ requires: C, 69.19; H, 6.21; S, 12.31%.)

3-(*i-Propylthio*)*biphenyl* (**2b**), oil. δ 7.55–7.0 (m, 9 H), 3.3 (spt, 1 H), 1.25 (d, 6 H), identical with an authentic sample prepared from 3-bromobiphenyl and Me_2CHSNa in HMPA.[12] Sulphone, viscous oil, δ 8.1 (t, J = 2 Hz, 1 H), 7.9–7.3 (m, 8 H), 3.25 (spt, 1 H), 1.35 (d, 6 H). (Found: C, 69.10; H, 6.34; S, 12.23. $C_{15}H_{16}O_2S$ requires: C, 69.19; H, 6.21; S, 12.31%.)

4-(*i-Propylthio*)*biphenyl* (**2c**), m.p. 50-1°, δ 7.5–7.15 (m, 9 H), 3.3 (spt, 1 H), 1.25 (d, 6 H), identical with an authentic sample prepared from 4-bromobiphenyl and Me_2CHSNa in HMPA.[12] Sulphone, m.p. 145–6° from EtOH, δ 7.85, 7.6 (AA'BB' 4 H), 7.5–7.25 (m, 5 H), 3.25 (spt, 1 H), 1.3 (d, 6H). (Found: C, 69.25; H, 6.12; S, 12.20. $C_{15}H_{16}O_2S$ requires: C, 69.19; H, 6.21; S, 12.31%.)

o-*Terphenyl* (**3a**), m.p. and mixed m.p. 55–6° (lit.[20] 58–9°). δ 7.3 (m, 4 H), 7.05 (m, 10 H).

m-Terphenyl (**3b**), m.p. and mixed m.p. 86–7° (lit.[21] 86°). δ 7.7 (t, J = 2 Hz, 1 H), 7.65–7.0 (m, 13 H).

3-*i-Propylthio-4-methylbiphenyl* (**5**), oil, δ 7.6–7.2 (m, 8 H), 3.4 (spt, 1 H), 2.45 (s, 3 H), 1.3 (d, 6 H). (Found: C, 79.05; H, 7.43; S, 13.46. $C_{16}H_{18}S$ requires: C, 79.27; H, 7.50; S, 13.23%.) Sulphone, m.p. 113–5°, δ 8.15 (d, J = 2 Hz, 1 H), 7.65 (dd, J = 2 and 8 Hz, 1 H), 7.55–7.25 (m, 6 H), 3.3 (spt, 1 H), 2.7 (s, 3 H), 1.3 (d, 6 H). (Found: C, 69.70; H, 6.82; S, 11.55. $C_{16}H_{18}O_2S$ requires: C, 70.03; H, 6.65; S, 11.68%.)

2,5-*Dimethylphenyl i-propyl sulphide* (**6**), oil, δ 7.1 (d, J = 2 Hz, 1 H), 6.95 (d, J = 8 Hz, 1 H), 6.8 (dd, J = 2 and 8 Hz, 1 H), 3.3 (spt, 1 H), 2.35 (s, 3 H), 2.25 (s, 3 H), 1.25 (d, 6 H). (Found: C, 73.41; H, 8.66; S, 17.53. $C_{11}H_{16}S$ requires: C, 73.26; H, 8.96; S, 17.78%.) Sulphone, m.p. 33–5°, δ 7.65 (d, J = 2 Hz, 1H), 7.2 (dd, J = 2 and 8 Hz, 1 H), 7.1 (d, J = 8 Hz, 1 H), 3.2 (spt, 1 H), 2.6 (s, 3 H), 2.35 (s, 3 H), 1.3 (d, 6 H). (Found: C, 62.00; H, 7.75; S, 14.95. $C_{11}H_{16}O_2S$ requires: C, 62.22; H, 7.61; S, 15.10%.)

2,4-*Diphenyltoluene* (**7**), oil, δ 7.75–7.0 (m, 13 H), 2.25 (s, 1 H).[22]

4-(*t-Butylthio*)*biphenyl* (**9**), m.p. 106–8°, δ 7.55–7.3 (m, 9 H), 1.35 (s, 9 H), identical with an authentic sample prepared from 4-Bromobiphenyl and Me_3CSNa in HMPA.[12] (Found: C, 79.16; H, 7.71; S, 13.48. $C_{16}H_{18}S$ requires: C, 79.27; H, 7.50; S, 13.23%.)

o-Tolyl i-propyl sulphide (**11a**), oil, δ 7.25–7.2 (m, 1 H), 7.1–6.95 (m, 3 H), 3.3 (spt, 1 H), 2.4 (s, 3 H), 1.3 (d, 6 H). Sulphone; oil, δ 7.85 (dd, J = 2 and 8 Hz, 1 H), 7.5–7.1 (m, 3 H), 3.25 (spt, 1 H), 2.7 (s, 3 H), 1.3 (d, 6 H).[23]

m-Tolyl i-propyl sulphide (**11b**), oil, δ 7.2–6.9 (*m*, 3 H), 3.3 (spt, 1 H), 2.6 (s, 3 H), 1.3 (d, 6 H).[23]

p-Tolyl i-propyl sulphide (**11c**), oil, δ 7.3, 7.0 (AA'BB', 4 H), 3.25 (spt, 1 H), 2.3 (s, 3 H), 1.25 (d, 6 H).[23] Sulphone, m.p. 81–3°, δ 7.7, 7.3 (AA'BB', 4 H), 3.15 (spt, 1 H), 2.4 (s, 3 H), 1.3 (d, 6 H).

m-(*Allyl*)*phenyl i-propyl sulphide* (**12b**), oil, δ 7.15–6.9 (m, 4 H), 5.9 (ddt, J = 9.6, 17.4 and 6.6 Hz, respectively, 1 H), 5.15–4.9 (m, 2 H), 3.3 (d, J = 6.6 Hz, 2 H), 3.3 (spt, 1 H), 1.3 (d, 6 H). (Found: C, 75.02; H, 8.29; S, 16.49. $C_{12}H_{16}S$ requires: C, 74.93; H, 8.40; S, 16.67%.)

p-(*Allyl*)*phenyl i-propyl sulphide* (**12c**), oil, δ 7.3, 7.0 (AA'BB', 4H), 5.95 (ddt, J = 9.6, 17.4 and 6.6 Hz, respectively, 1 H), 5.15–4.9 (m, 2 H), 3.35 (d, J = 6.6 Hz, 2 H), 3.3 (spt, 1 H), 1.3 (d, 6 H). (Found: C, 74.91; H, 8.35; S, 16.84. $C_{12}H_{16}S$ requires: C, 74.93; H, 8.40; S, 16.67%.)

o-Bis(*allyl*)*benzene* (**14**: $R = R' = CH_2CH{=}CH_2$), oil (lit.[24] b.p. 94°/12 mm), δ 7.1 (s, 2 H), 5.85 (ddt, J = 10, 17 and 6 Hz, respectively, 1 H), 5.0 (dq, J = 10 and 1.5 Hz, respectively, 1 H), 4.95 (dq, J = 17 and 1.5 Hz, respectively, 1 H), 3.35 (dt, J = 6 and 1.5 Hz, respectively, 2 H).

m-(1-*Methylethenyl*)*phenyl i-propyl sulphide* (**13b**), oil, δ 7.45 (t, J = 2 Hz, 1 H), 7.4–7.15 (m, 3 H), 5.45 (dq, J = 1.5 and 1.0 Hz, respectively, 1 H), 5.05 (quintet, J = 1.5 Hz, 1 H), 3.35 (spt, 1 H), 2.15 (dd, J = 1.0 and 1.5 Hz, 3 H), 1.3 (d, 6 H). (Found: C, 74.70; H, 8.65; S, 16.95. $C_{12}H_{16}S$ requires: C, 74.93; H, 8.40; S, 16.67%.)

p-(1-*Methylethenyl*)*phenyl i-propyl sulphide* (**13c**), oil, δ 7.3 (s, 4 H), 5.3 (dq, J = 1.5 and 1.0 Hz, respectively, 1 H), 5.0 (quintet, J = 1.5 Hz, 1 H), 3.35 (spt, 1 H), 2.1 (dd, J = 1.0 and 1.5 Hz, respectively, 3 H), 1.3 (d, 6 H). (Found: C, 75.05; H, 8.37; S, 16.34. $C_{12}H_{16}S$ requires: C, 74.93; H, 8.40; S, 16.67%.)

o-(Mercapto)phenyl i-propyl sulphide (**17**), oil, δ 8.5–6.9 (m, 4 H), 4.5 (s, 1 H), 3.35 (spt, 1 H), 1.3 (d, 6 H). This compound was treated with EtI to give the *o*-(ethylthio)phenyl i-propyl sulphide, oil, δ 7.4–6.9 (m, 4 H), 3.45 (spt, 1 H), 2.9 (q, 2 H), 1.3 (t, 3H), 1.25 (d, 6 H).[12d] Dissulphone, m.p. and mixed m.p. 113–5°.

4-*(p-Tolyl)biphenyl* (**18**), m.p. and mixed m.p. 208–10° (lit.[25] 207–8°), δ 7.6–7.1 (m, 13 H), 2.4 (s, 3 H).

4-*Allylbiphenyl* (**19**), oil, δ 7.6–7.1 (m, 9 H), 5.9 (ddt, J = 9.6, 17.4 and 6.6 Hz, respectively, 1 H), 5.2–4.95 (m, 2 H), 3.3 (d, J = 6.6 Hz, 2 H).[26]

p-(1-*Methylethenyl)allylbenzene* (**20**), oil, δ 7.35, 7.05 (AA'BB', 4 H), 5.95 (ddt, J = 9.6, 16.2 and 6.6 Hz, respectively, 1 H), 5.35 (dq, J = i.5 and 1.0 Hz, respectively, 1 H), 5.2–4.9 (m, 3 H), 3.35 (d, J = 6.6 Hz, 2 H), 2.15 (dd, J = 1.0 and 1.5 Hz, respectively, 3 H). (Found: C, 90.85; H, 8.68. $C_{12}H_{14}$ requires: C, 91.06; H, 8.94%.)

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