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Cyclisation Reactions of 2-Substituted Biphenyl-2'-yldiazonium Salts Leading to *O*-Alkyldibenzofuranium and *S*-Alkyl-dibenzothiophenium Salts: Modified Meerwein Reagents †

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Abstract: *The preparation of 2-amino-2'-methoxybiphenyl and 2-amino-2'-thiomethoxybiphenyl and analogues and their transformation into diazonium salts and hence into dibenzofuranium and dibenzothiophenium salts is described together with their use as alkylating agents.*

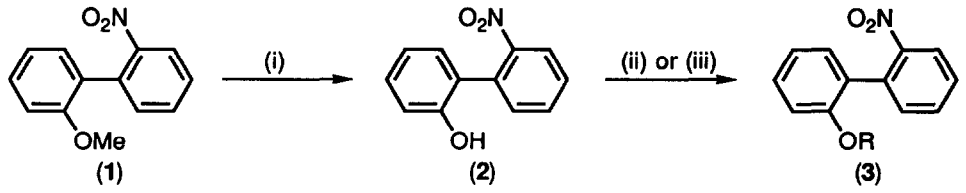
We previously reported in a preliminary communication the use of 2-methoxybiphenyl-2'-yldiazonium fluoroborate as a powerful methylating agent.[1] Related cyclisation reactions include the Mascarelli reaction[2] in which 2-alkylbiphenyl-2'-yldiazonium salts cyclise to afford fluorene derivatives and 2-halobiphenyl-2'-yldiazonium salts give the corresponding halonium salts.[3] We now report full details of the earlier study and in addition some work that was designed to extend the scope of the reaction and the utility of the title reagents. It was also our intention as well to probe the mechanism of the cyclisation and dealkylation steps. It is well established that arenediazonium salts can fragment by heterolytic or homolytic mechanisms,[4] and whereas the generation of the 2-methoxybiphenyl-2'-yl radical does not result in cyclisation the photolysis of of 2-iodo-2'-thiomethoxybiphenyl results in cyclisation together with simultaneous loss of the methyl group.[5]

The investigation required good routes to 2-amino-2'-alkoxybiphenyls and their thio- analogues. We decided that the unsymmetrically substituted biphenyl derivatives could best be prepared by the Ullmann synthesis. It has been shown[6] that unsymmetrical biaryls may be obtained in good yields when one of the aryl halides is activated and the other is not thus activated. Activation is effected by the presence of an electron withdrawing group in an *ortho-* position with respect to the halogen atom in the benzene ring. Aryl bromides are normally the compounds of choice for the activated component though chlorides are sometimes used. The corresponding aryl iodides are inappropriate because they are prone to self condensation which leads to the formation of symmetrical biaryls. However, aryl iodides have found general application as the non-activated component which should lack activating substituents in the *ortho-* position. We therefore carried out mixed Ullmann reactions[7] between *o*-iodoanisole, or its sulphur analogue, and *o*-bromonitrobenzene in the presence of finely divided copper powder. The use of activated copper powder,[8] or the use of either dimethylformamide or nitrobenzene as solvents did not lead to good yields of, for example, 2-methoxy-2'-nitrobiphenyl. We were able to achieve high yields in the reaction by using highly efficient stirring of the heavy sludge formed by the mixture of copper powder and the other components.

†Dedicated to the memory of our friend and colleague Barrie C. Uff; 13 Feb 1937 - 19 Oct 1991

This was achieved by using a copper paddle as stirrer, designed to fit exactly the contours of the large reaction vessel. This simple expedient gave reproducible yields of *ca.* 80% when applied to the preparation of 2-methoxy-2'-nitrobiphenyl. This yield is amongst the highest recorded[9,10] for the synthesis of an unsymmetrical biphenyl. However, the preparation of the sulphur analogue, 2-methylthio-2'-nitrobiphenyl by this method gave a less satisfactory yield (26%).

Higher homologues of the methyl ethers were obtained by the alkylation of 2-hydroxy-2'-nitrobiphenyl which was obtained by two methods. In the first of these we demethylated the ether (**1**). This was achieved efficiently using dibromotriphenylphosphorane, a reagent that had been recommended previously for the preparation of alkyl bromides from ethers.[11]



Scheme 1

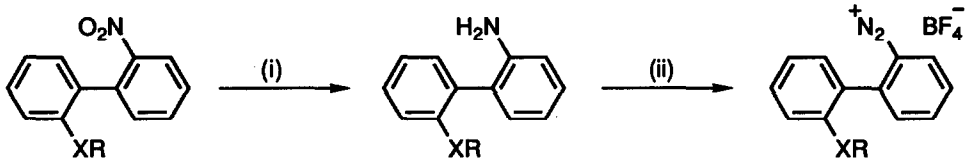
(i), Ph_3PBr_2; (ii) KOH - RX in DMSO; (iii), $RO\text{-}\overset{+}{P}(NMe_2)_3\ PF_6^-$

It should be noted that the use of hydrobromic acid for the demethylation could not be used to prepare analytically pure samples of the homologues of (**1**) because the phenol (**2**) was contaminated by small amounts of 3-bromo-2-hydroxy-2'-nitrobiphenyl, no doubt due to the presence of free bromine in the constant boiling hydrobromic acid. However, in subsequent batch demethylation reactions, hydrobromic acid was used as the contaminating bromo-derivative was debrominated simultaneously with the reduction of the nitro group in the next step of the synthetic sequence. The alternative way of preparing 2-hydroxy-2'-nitrobiphenyl was from 2,2'-dinitrobiphenyl which was reduced to 2-amino-2'-nitrobiphenyl using sodium hydrogensulphide and hence to the required intermediate by diazotisation and hydrolysis. This latter procedure was less satisfactory than the former method.

The re-alkylation of the phenol (**2**) was achieved either by a reaction in which an alkyl halide was added to a solution of the phenol in dimethylsulphoxide containing a suspension of anhydrous potassium hydroxide,[12] or by a reaction of a solution of the phenol in dimethylformamide with solid potassium hydroxide followed by the addition of a tris(dimethylamino)alkoxyphosphonium hexafluorophosphate and heating the mixture under reflux.[13] Both of these procedures led to the formation of ethers (**3**) in good yields. Higher homologues of the thioethers were prepared similarly. The demethylation of 2-methylthio-2'-nitrobiphenyl was followed by re-alkylation. Of the various methods that have been suggested for the demethylation step the most successful was that involving the treatment of the aryl methyl sulphide with chlorine at room temperature which gave selective and essentially quantitative conversion to the trichloromethyl thioether.[14] The slightly impure 2-nitro-2'-trichloromethylthiobiphenyl was characterised by mass spectrometry and then subjected to methanolysis which gave the required thiophenol.

Re-alkylation reactions were then performed using the methods outlined above. We also investigated the possibility of alkylating 2-iodobenzenethiol before carrying out the Ullmann reaction and this route was used, for example, for the preparation of 2-*neo*-pentylthio-2'-nitrobiphenyl. The 2-alkoxy-2'-nitrobiphenyl and 2-alkylthio-2'-nitrobiphenyl derivatives were reduced in ethanolic solution to the corresponding amines in high yields using hydrazine hydrate in the presence of a catalytic quantity of palladium on charcoal.[15] This useful, though not widely used, method of reduction also removes halogens (Cl, Br, and I) from aromatic systems[16] and therefore allowed the use of the bromine contaminated phenol for the preparation of the amines. The more recently introduced procedure in which aromatic nitro compounds are reduced by hydrazine hydrate in the

presence of graphite does not result in the removal of halogen.[17] An alternative method involving the use of palladium on carbon which does result in dechlorination uses cyclohexene in transfer hydrogenation.[18]



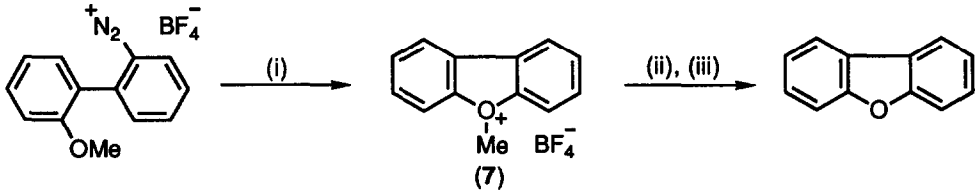
(4) X=O or S (5) X=O or S (6) X=O or S

Scheme 2

(i), N_2H_4, Pd-C; (ii), $NaNO_2$, H_2O, HBF_4

Conversion of the amines into the corresponding diazonium fluoroborates was achieved by diazotisation in aqueous fluoroboric acid while the other diazonium salts were obtained by metathetical reactions from a solution of the diazonium chloride. In the case of 2-methoxybiphenyl-2'-yldiazonium fluoroborate the diazonium salt was found to be very unstable: it could be stored in vacuo over phosphoric anhydride at room temperature for a safe maximum of two to three days. Other counter ions were used in association with this diazonium cation *viz.* hexafluorophosphate, hexafluoroantimonate, hexafluoroarsenate, tetraphenylborate, and 2,4,6-trinitrobenzenesulphonate. The stability of the various diazonium salts was qualitatively estimated by observing the disappearance of the band at *ca.* 2275 cm^{-1} in the infrared spectrum of each salt. However, only the diazonium tetraphenylborate and 2,4,6-trinitrobenzenesulphonate showed any improvement in stability. These two salts could be stored in vacuo over phosphoric anhydride for 10-12 days. When the salts were left for a longer period of time decomposition slowly occurred. The identification of the decomposition product in the case of, for example, 2-methoxybiphenyl-2'-yldiazonium fluoroborate as dibenzofuran suggested that the diazonium salts collapse by an intramolecular cyclisation *via* the oxonium salt (7), the volatile products of the decomposition being presumably nitrogen, boron trifluoride , and methyl fluoride. The stability of 2,4-dimethoxybiphenyl-2'-yldiazonium fluoroborate, which was prepared by an analogous sequence starting with 2,4-dimethoxyiodobenzene and *o*-bromonitrobenzene, was marginally greater than (6, X=O, R = Me).

2-Methylthiobiphenyl-2'-yldiazonium fluoroborate (8), which is bright yellow, is significantly more stable than its oxygen analogue. A sample of the salt (8) was still undecomposed after 50 days when stored *in vacuo* over phosphoric anhydride at -20° C. Nevertheless the salt (8) decomposes to afford a colourless product in *ca.* 12h when stirred at room temperature in dichloromethane. Evaporation of the solvent gave *S*-methyldibenzothiophenium fluoroborate (9) in 86% yield after recrystallisation. A comparison of infrared, ultraviolet, and ^1H nuclear magnetic resonance spectra with those of a sample prepared[19] from dibenzothiophene confirmed the structure of the product. Dibenzothiophene was also isolated from the reaction mixture in 14% yield. Unfortunately other diazonium salts such as the *neo*-pentylthio- analogue decomposed to afford dibenzothiophen directly, presumably because of a low energy pathway involving a relatively stable carbenium ion.

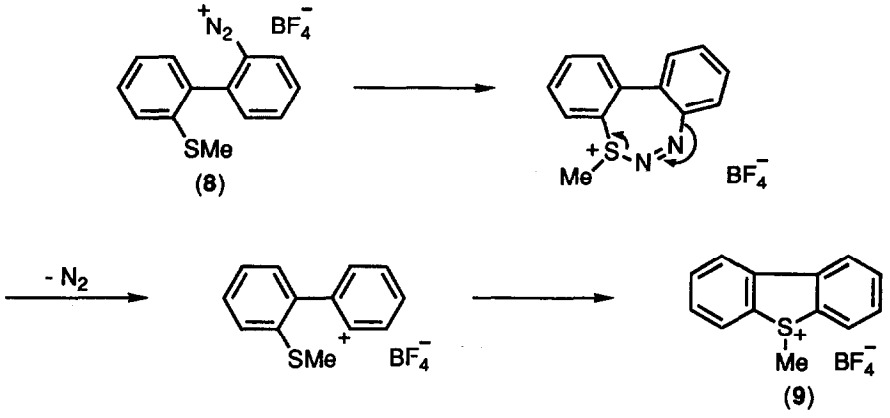


(7)

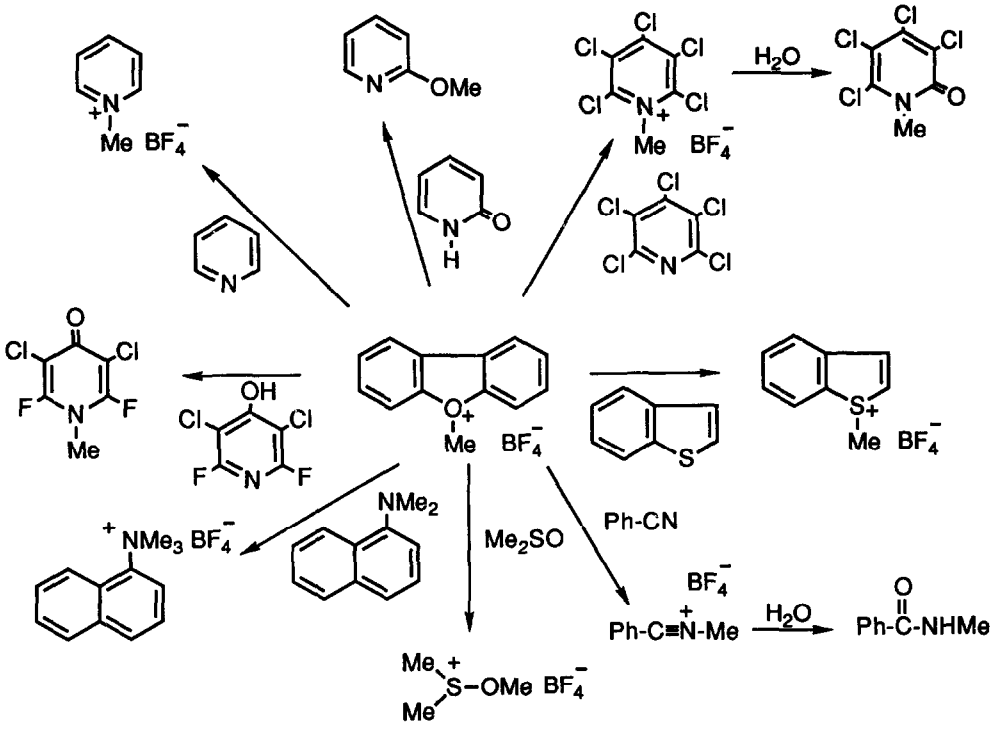
Scheme 3

(i), $-N_2$; (ii), $-BF_3$; (iii), -MeF

A number of mechanistic interpretations of the formation of dibenzofuran and *S*-methyldibenzothiophenium fluoroborate should be considered. It is not unreasonable to assume that a similar mechanism operates in both cases. An S_N2 displacement of nitrogen from the diazonium salts by the alkoxy or thioalkoxy groups can be excluded on arguments based on geometry. The photolysis of 2-thiomethoxy-2'-iodobiphenyl in benzene solution, which is interpreted as proceeding *via* the 2-thiomethoxy-2'-biphenylyl radical, affords dibenzothiophene and toluene.[5] We may therefore exclude a radical mechanism. We are left with the problem of explaining the increased instability of the diazonium fluoroborates which results from the proximity of the methoxy- and thiomethoxy- functions. This suggests that anchimeric assistance may play an important part involving a seven-membered ring. It is noteworthy that both *syn*- and *anti*- diazoethers have been reported on many occasions[4] and that the *anti*- diastereoisomer is the more stable form.

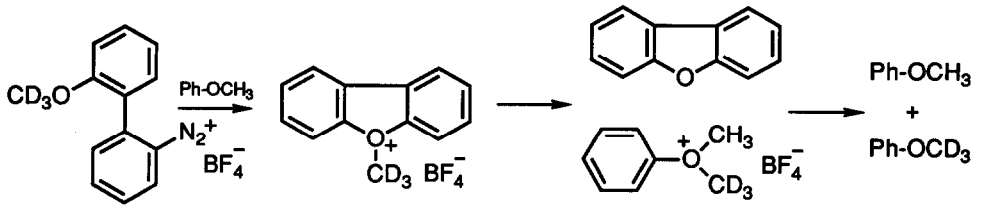


When the diazonium salt (**6**, X=O, R = Me) was heated in anhydrous benzene an off-white solid was obtained, which was presumed to be the oxonium salt (**7**). The ability of this material to act as a methylating agent was established by performing a series of reactions with various lone pair and π- bases. Thus the addition of an excess of pyridine in anhydrous benzene resulted in the formation of *N*-methylpyridinium fluoroborate in 28% yield which was characterised[20] as its double picrate salt. It is noteworthy that 2-methoxybiphenyl-2'-yldiazonium 2,4,6-trinitrobenzenesulphonate is a more stable diazonium salt. but when it was heated under reflux in dry benzene a grey solid was obtained in *ca.* 90% yield which lacked the diazonium ion stretching frequency at 2270 cm^{-1}. The grey solid gave, after reaction with pyridine, *N*-methylpyridinium 2,4,6-trinitrobenzenesulphonate in 44% yield. Higher yields of methylated products were obtained when reactions were performed *in situ*. For example, when 2-methoxybiphenyl-2'-yldiazonium fluoroborate was heated in dichloromethane in the presence of pyridine, *N*-methylpyridinium fluoroborate was obtained in essentially quantitative yield. Although pyridine is readily alkylated by conventional reagents the introduction of halogens to the ring gives rise to a strong deactivating inductive effect which makes alkylation very difficult. For example, the reaction of pentachloropyridine with triethyloxonium fluoroborate has been reported[21] to give *N*-ethylpentachloropyridinium fluoroborate in a yield of only 12%. On the other hand the decomposition of a slight excess of the diazonium salt (**6**, X=O, R = Me) in the presence of pentachloropyridine afforded a 41% yield of *N*-methylpentachloropyridinium fluoroborate. Excellent yields of methylated derivatives of highly halogenated pyridine derivatives have been obtained by using methyl fluorosulphate as reagent and solvent.[21,22] In our experiments we made no attempt to maximise the yields by using a large excess of the diazonium salt (**6**, X=O, R = Me). The following ***Chart*** highlights the uses of *O*-methyldibenzofuranium fluoroborate in some reactions with π- and lone pair bases.



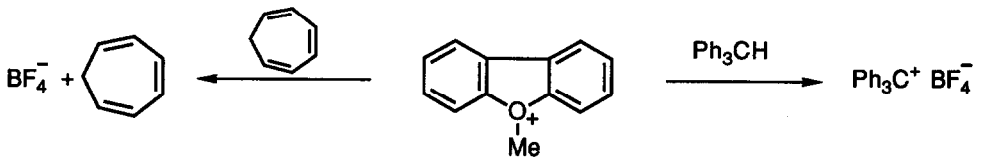
The *N*-methylpentachloropyridinium salt gives a good yield of 3,4,5,6-tetrachloro-1-methyl-2-pyridone on hydrolysis. The methylation of 3,5-dichloro-2,6-difluoro-4-hydroxypyridine gave, after neutralisation, 3,5-dichloro-2,6-difluoro-1-methyl-4-pyridone in 60% yield.The alkylation of 2-pyridone, as expected gave 2-methoxypyridine. Whereas soft alkylating agents like methyl iodide react at nitrogen, harder reagents (which have better leaving groups) alkylate the oxygen of 2-pyridone.

The power of the salt (7) as an alkylating agent is not surprising. The lower basicity of dibenzofuran as compared with, for example dimethyl ether, suggested to us that dibenzofuran would be a better leaving group than dimethyl ether an hence that the oxonium salt (7) would be a more powerful methylating agent than trimethyloxonium fluoroborate. It is noteworthy, in this connection, that attempts to prepare the diphenylmethyloxonium ion by the treatment of diphenyl ether with the antimony pentafluoride methyl fluoride complex in SO_2ClF at -120° C resulted only in methylation of the aromatic rings.[23] The methylation of anisole and the rearrangement of the dimethylphenyloxonium hexafluoroantimonate and related oxonium species which afford ring methylated products by an intermolecular mechanism has also been reported.[23,24] Further evidence concerning the relative reactivity of oxonium salts was obtained by preparing 2-[$^2H_3$]methoxybiphenyl-2'-yldiazonium fluoroborate which was allowed to decompose in dichloromethane in the presence of anisole. The resultant dibenzofuran was separated from recovered anisole after an aqueous work-up and was shown by various spectroscopic methods to consist of a mixture of anisole and [$^2H_3$]methoxybenzene [***Scheme 4***]. A further advantage of the oxonium salt (7) over trimethyloxonium fluoroborate is that (7) is more soluble in common organic solvents than the simpler Meerwein reagent. This property is exemplified by the esterification of mesitoic acid which was carried out using equimolar amounts of 2-methoxybiphenyl-2'-yldiazonium fluoroborate, mesitoic acid, and di-*iso*propylethylamine in dichloromethane at room temperature. The low yield obtained is probably due to a reaction between the Hünig base and the oxonium salt (7).



Scheme 4

The ability of *O*-methyldibenzofuranium fluoroborate to alkylate σ-donor bases was also studied. The isolation of triphenylcarbenium fluoroborate (21% yield) and tropylium fluoroborate (54% yield), after allowing the diazonium salt (**6**, X=O, R = Me) to decompose in the presence of triphenylmethane and *cyclo*heptatriene respectively, exemplifies this property.



Scheme 5

Attempts to extend this work to the potentially powerful acylating *O*-acyldibenzofuranium reagents were unsuccessful. The reduction of 2-acetoxy- and 2-benzoyloxy-2'-nitrobiphenyl resulted in the formation of the 2-acylamino-2'-hydroxybiphenyl derivatives in excellent yields when we used a variety of reducing systems, including hydrogen in the presence of palladium on carbon.

The only oxonium salt which we are aware of except those involving primary alkyl groups is the *O*-isopropyloxyranylium ion.[24] We were able to investigate the potential of a number of other 2-*O*-alkylbiphenyl-2'-yldiazonium and 2-*S*-alkylbiphenyl-2'-yldiazonium salts. However, only in the case of primary alkoxybiphenyl derivatives were we able to carry out alkylation reactions satisfactorily. 2-*iso*-Propyloxybiphenyl-2'-yldiazonium fluoroborate, for example, decomposed rapidly to afford dibenzofuran and, presumably, propene.

Experimental

2-Methoxy-2'-nitrobiphenyl

Copper powder (100g) was added in portions over a period of about 1h to a well-stirred mixture of *o*-iodoanisole (82.6g, 0.35mol) and *o*-bromonitrobenzene (83g, 0.413mol) which was maintained at 200° C under an atmosphere of nitrogen. The copper paddle stirrer was designed to sweep the whole of the lower surface of the reaction vessel. After a further 2.5h the copper powder had lost its shiny appearance and the mixture had become viscous. After allowing the reaction mixture to cool it was exhaustively extracted with ether. Removal of the solvent gave an orange oil which was placed on a column of alumina and eluted with ether-light petroleum (5:95) to afford 2-methoxy-2'-nitrobiphenyl (58-64g, 70-77%), m.p. 81-2° C (from methanol), lit.[7] m.p. 83° C. δ_H ($CDCl_3$) 3.66 (O*Me*) and 7.3-8.0 (Ar*H*) ppm.

Demethylation of 2-methoxy-2'-nitrobiphenyl

(a). Bromine (4.3g) was added slowly to a stirred solution of triphenylphosphine (8.6g) in benzonitrile (100ml) under nitrogen. A colourless precipitate of dibromotriphenylphosphorane was obtained and the mixture was heated to 110° C before 2-methoxy-2'-nitrobiphenyl (5.0g) was added in one portion. The mixture was stirred and heated at 125° C for a further 12h. An aqueous solution of acetone (100 ml, 50%) was added to the cold mixture and the resulting two phase system was stirred at *ca.* 60° C for 4h before the mixture was made

alkaline with aqueous sodium hydroxide. The aqueous layer was separated and acidified and extracted with ether. The solution was dried ($MgSO_4$) and the solvent removed to afford 2-hydroxy-2'-nitrobiphenyl (2.55g, 55%), m.p. 139-140° C (from benzene), lit.[25] m.p. 140° C. ν_{max} 3430 cm^{-1}.

(b) Hydrobromic acid (25ml, 48%) was added slowly to a solution of 2-methoxy-2'-nitrobiphenyl (20g, 0.09 mol) in acetic anhydride (25ml) at 0° C. The solution was heated under reflux for 48h and gave a dark brown solution which was diluted with water (250ml). The reaction mixture was extracted with ether and the ether layer extracted with aqueous sodium hydroxide. Acidification of the aqueous layer, extraction with ether, and removal of the solvent after drying ($MgSO_4$), gave a brown oil which slowly solidified. The solid (16.3g, 91%) m.p. 132-138° C was shown by mass spectrometry and ^1H nmr spectroscopy to contain 3-bromo-2-hydroxy-2'-nitrobiphenyl in addition to 2-hydroxy-2'-nitrobiphenyl.

Alkylation of 2-hydroxy-2'-nitrobiphenyl

(a) Dimethylsulfoxide (100ml) was added to powdered potassium hydroxide (2.24g, 0.04mol) and 2-hydroxy-2'-nitrobiphenyl (2.15g, 0.01mol) was added and the mixture was stirred for 30min. Ethyl iodide (3.12g, 0.02mol) was added and the mixture was stirred for a further 2h before water (100ml) was added. The mixture was extracted with ether and the ether layers washed with a saturated solution of sodium chloride, dried over $MgSO_4$, and the solvent removed to afford a colourless oil which was placed on a column of alumina. Elution with ether-light petroleum (1:9) and gave 2-ethoxy-2'-nitrobiphenyl (2.26g, 97%), m.p. 84-5° C (from light petroleum), lit.[26] m.p. 82-3° C: δ_H ($CDCl_3$) 1.2 ($CH_2.\boldsymbol{CH_3}$, *t J* = 7.5 Hz), 3.92 ($\boldsymbol{CH_2}.CH_3$, *q J* = 7.5 Hz), and 6.75-8.0 (Ar***H***, ***m*** 8H) ppm.

(b) Similarly, *2-nitro-2'-n-propoxybiphenyl* was prepared in 94% yield, m.p. 71-2° C (from light petroleum) (Found: C, 70.2; H, 5.9, N, 5.3%; M^+ 257: $C_{15}H_{15}NO_3$ requires C, 70.05, H, 5.85, N 5.45% M^+ 257): δ_H ($CDCl_3$) 0.8 ($CH_2\boldsymbol{CH_3}$, *t J* = 8Hz), 1.63 ($CH_2.\boldsymbol{CH_2}.CH_3$, *s J* = 8Hz), 3.85 ($\boldsymbol{CH_2}.CH_2.CH_3$, *t J* = 8Hz), and 6.8-8.0 (Ar***H***, ***m*** 8H) ppm.

(c) Similarly, *2-nitro-2'-iso-propoxybiphenyl* was prepared in 95% yield, m.p. 91-2° C (from light petroleum) (Found: C, 70.2; H, 5.9, N, 5.5%; M^+ 257: $C_{15}H_{15}NO_3$ requires C, 70.05, H, 5.85, N 5.45% M^+ 257): δ_H ($CDCl_3$) 1.18 (CH ($\boldsymbol{CH_3}$)$_2$, *d J* = 6.5Hz), 4.45 ($\boldsymbol{CH}$ (CH_3)$_2$, *s J* = 6.5Hz), and 6.8-8.0 (Ar***H***, ***m*** 8H) ppm.

(d) Similarly, *2-n-butoxy-2'-nitrobiphenyl* was prepared in 79% yield, m.p. 72-3° C (from light petroleum) (Found: C, 70.4; H, 6.1, N, 5.2%; M^+ 271: $C_{16}H_{17}NO_3$ requires C, 70.85, H, 6.3, N 5.15% M^+ 271): δ_H ($CDCl_3$) 0.88 (.$CH_2.\boldsymbol{CH_3}$, *t J* = 7Hz), 1.0-1.8 ($CH_2.\boldsymbol{CH_2}.\boldsymbol{CH_2}.CH_3$, ***m*** 4H), 3.88 (O.$\boldsymbol{CH_2}.CH_2$.,*t J* = 7Hz), and 6.8-8.0 (Ar***H***, ***m*** 8H) ppm.

(e) Similarly, *2-n-allyloxy-2'-nitrobiphenyl* was prepared in 93% yield, m.p. 43-4° C (from light petroleum) (Found: C, 70.6; H, 5.1, N, 5.25%; M^+ 255: $C_{15}H_{13}NO_3$ requires C, 70.6, H, 5.1, N 5.5% M^+ 255): δ_H ($CDCl_3$) 4.3-4.5 (CH=$\boldsymbol{CH_2}$, ***m***), 5.05-5.35 ($\boldsymbol{CH_2}$.CH=CH_2, ***m***), 5.65-4.2 ($CH_2.\boldsymbol{CH}$=CH_2.,***m***), and 6.8-8.0 (Ar***H***, ***m*** 8H) ppm.

(f) Similarly, *2-n-benzyloxy-2'-nitrobiphenyl* was prepared in 67% yield, m.p. 84-5° C (from light petroleum) (Found: C, 74.6; H, 4.8, N, 5.0%; M^+ 305: $C_{19}H_{15}NO_3$ requires C, 74.75, H, 4.95, N 4.6% M^+ 305): δ_H ($CDCl_3$) 4.98 ($\boldsymbol{CH_2}$, *s*) and 6.8-8.0 (Ar***H***, ***m*** 13H) ppm.

(g) Similarly, *2-[$^2H_3$]methoxy-2'-nitrobiphenyl* was prepared in 96% yield, m.p. 83-4° C (from methanol) M^+ 232: δ_H ($CDCl_3$) 6.75-8.05 (Ar***H***, 8H) ppm.

Reduction of 2-methoxy-2'nitrobiphenyl

(a) Hydrazine hydrate (31ml, 64%) was added slowly to 2-methoxy-2'-nitrobiphenyl (22.9g, 0.1mol) and palladium on carbon (300mg, 5%)in ethanol (250ml) at 50° C. After the addition was completed (30min) a further amount of catalyst (100mg) was added and the mixture was heated under reflux for 6h. Removal of the catalyst and solvent gave a colourless oil which crystallised and after recrystallisation gave 2-amino-2'-

methoxybiphenyl (16.1g, 80%) m.p. 78-9° C (from methanol) lit.[7] m.p. 80° C; M^+, 199 ν_{max} 3420 and 3290 cm^{-1} δ_H ($CDCl_3$) 3.58 (**br** 2H, D_2O exchange), 3.75 (O***Me***) and 6.6-7.45 (Ar***H***, ***m***, 8H) ppm.

(b) Similarly, *2-amino-2'-*[$^2H_3$]methoxybiphenyl was prepared in 78% yield, m.p. 71-2° C (from methanol); M^+ 202, ν_{max} 3450, 3380, 2220, and 2080 cm^{-1} δ_H ($CDCl_3$) 3.45 (**br** 2H, D_2O exchange) and 6.6-7.5 (Ar***H***, ***m***, 8H) ppm.

(c) Similarly, *2-amino-2'-ethoxybiphenyl* was prepared in 80% yield, m.p. 75-6° C (from light petroleum) (Found: C, 79.3; H, 7.1; N, 6.4% M^+213: $C_{14}H_{15}NO$ requires C, 78.9, H, 7.1, N 6.6% M^+213):, ν_{max} 3480 and 3390 cm^{-1} δ_H ($CDCl_3$) 1.25 (***CH***$_3$.CH_2, *t J* = 8Hz), 3.6 (**br** 2H, D_2O exchange), 4.0 (O***CH***$_2$$CH_3$, *q J* = 8Hz) and 6.6-7.45 (Ar***H***, ***m*** 8H) ppm.

(d) Similarly, *2-amino-2'-n-propoxybiphenyl* was prepared in 55% yield, an oil (Found: C, 79.8; H, 7.2; N, 5.6% M^+, 227: $C_{15}H_{17}NO$ requires C, 79.3, H, 7.5, N 6.1% M^+227): ν_{max} 3480 and 3390 cm^{-1} δ_H ($CDCl_3$) 0.85 (***CH***$_3$.CH_2., *t J* = 7Hz), 1.65 (CH_2.***CH***$_2$.CH_3, *s J* = 7Hz), 3.6 (**br** 2H, D_2O exchange), 3.88 (O***CH***$_2$$CH_2$., *t J* = 7Hz) and 6.6-7.45 (Ar***H***, ***m*** 8H) ppm.

(e) Similarly, *2-amino-2'-isopropoxybiphenyl* was prepared in 87% yield, m.p. 51-2° C (from light petroleum) (Found: C, 79.7; H, 7.0; N, 6.0% M^+, 227: $C_{15}H_{17}NO$ requires C, 79.3, H, 7.5, N 6.1% M^+227): ν_{max} 3470 and 3390 cm^{-1} δ_H ($CDCl_3$) 1.12 (CH (***CH***$_3$)$_2$, *d J* = 9Hz), 4.28 (***CH*** (CH_3)$_2$, *s J* = 9Hz), 3.68 (**br** 2H, D_2O exchange), and 6.6-7.4 (Ar***H***, ***m*** 8H) ppm.

(f) Similarly, *2-amino-2'-n-butoxybiphenyl* was prepared in 90% yield, an oil (Found: C, 80.0; H, 8.0; N, 5.5% M^+, 241: $C_{16}H_{19}NO$ requires C, 79.65, H, 7.95, N 5.8% M^+241): ν_{max} 3490 and 3400 cm^{-1} δ_H ($CDCl_3$) 0.85 (.CH_2.***CH***$_3$, *t J* = 6Hz), 1.1-1.75 (CH_2.***CH***$_2$.***CH***$_2$.CH_3, ***m*** 4H), 3.65 (**br** 2H, D_2O exchange), 3.9 (O.***CH***$_2$.CH_2.,*t J* = 6Hz), and 6.6-7.45 (Ar***H***, ***m*** 8H) ppm.

(g) Similarly, *2-amino-2'-benzyloxybiphenyl* was prepared in 95% yield, m.p. 96-7° C (from light petroleum) (Found: M^+, 241: $C_{19}H_{17}NO$ requires M^+241): ν_{max} 3470 and 3380 cm^{-1} δ_H ($CDCl_3$) 4.45 (**br** 2H, D_2O exchange), 4.95 (***CH***$_2$, *s*), and 6.55-7.65 (Ar***H***, ***m*** 8H) ppm.

Preparation of 2-methoxybiphenyl-2'-yldiazonium fluoroborate

2-Amino-2'-methoxybiphenyl (7.8g, 0.04mol) was dissolved in THF (30ml) and fluoroboric acid (75ml, 40% aqueous solution) and water (20ml) was added. The solution was cooled to 0° C and a solution of sodium nitrite (2.8g) in water (30ml) was added dropwise to the stirred solution keeping the temperature at 0° C. After 30min the yellow diazonium salt was filtered off, washed with cold fluoroboric acid and cold THF, and dried overnight in vacuo over phosphoric anhydride to give 2-methoxybiphenyl-2'-yldiazonium fluoroborate (11.6g, 98%), ν_{max} 2270 cm^{-1}. 2,4-Dimethoxybiphenyl-2'-yldiazonium fluoroborate was prepared in 97% yield from 2-amino-2',4'-dimethoxybiphenyl.[27]

Preparation of 2-methoxybiphenyl-2'-yldiazonium hexafluorophosphate

2-Amino-2'-methoxybiphenyl (1.99g, 0.01mol) in hydrochloric acid (6ml, 12M) was diazotised at 0° C by the slow addition of sodium nitrite (0.7g) in water (4ml). After 15 min ammonium hexafluorophosphate (1.6g) in water (3ml) was added rapidly. Ether (10ml) was added and after 30 min the yellow diazonium salt was filtered off., washed with cold methanol and cold ether and dried overnight in vacuo over phosphoric anhydride to give 2-methoxybiphenyl-2'-yldiazonium hexafluorophosphate (2.7g, 75%), ν_{max} 2270 cm^{-1}.

Similar procedures allowed the preparation of other 2-methoxybiphenyl-2'-yldiazonium salts including the hexafluoroantimonate (80% yield), hexafluoroarsenate (90% yield), tetraphenylborate (90%yield), and trinitrobenzenesulfonate (68% yield). In addition the analogous diazonium fluoroborate salts were prepared from the amines listed above.

Formation of *O*-methyldibenzofuranium salts and reactions with pyridine

2-Methoxybiphenyl-2'-yldiazonium fluoroborate (1.0g, 3.3 mmol) was heated in anhydrous benzene at *ca.* 50° C for 1h and then under reflux for 1h. The solid rapidly changed colour from yellow to off-white. Pyridine (0.78g, 10 mmol) was added and after 6h the solvent was removed to leave an oil which was extracted with ether to leave *N*-methylpyridinium fluoroborate as a colourless oil (0.17g, 28%). The oil was dissolved

in water (5ml) and after the addition of a saturated aqueous solution of sodium picrate gave *N*-methyl-pyridinium picrate-sodium picrate (0.37g, 70%), m.p. 217-8° C; lit.[20] m.p. 216-9° C. Ir spectrum identical to that of an authentic sample.

2-Methoxybiphenyl-2'-yldiazonium 2,4,6-trinitrobenzenesulphonate (0.6g) was heated under reflux in dry benzene (25ml) for 1h. The grey solid (0.51g, 90%), m.p. >300° C d, (ir band at 2270 cm^{-1} absent) was added to a solution of pyridine (0.92g) in dichloromethane (30ml). Standard work-up gave *N*-methyl-pyridinium picrate-sodium picrate (0.19g, 44%), m.p. 217-8° C; ir spectrum identical to that of an authentic sample.

In Situ Reactions

The decomposition of 2-methoxybiphenyl-2'-yldiazonium fluoroborate (1g, 3.3mmol) in dichloromethane (25ml) in the presence of dimethylsulfoxide (1.3g, 16.6mmol) gave after removal of the solvent and extraction with ether *O*-methyldimethylsulfoxonium fluoroborate (0.48g, 79%) m.p. 107-9° C (from dichloromethane-ether), lit.[28] m.p. 106-8° C; δ_H ($CDCl_3$) 3.28 (*s*, 6H) and 4.0 (*s*, 3H) ppm. The ether extract was washed with water and dried (Mg SO_4) and the solvent removed to afford dibenzofuran (0.49g, 87%) m.p. 87-8° C (from light petroleum), lit.[29] m.p. 86-7° C.

The decomposition of 2-methoxybiphenyl-2'-yldiazonium fluoroborate (1g, 3.3mmol) in dichloromethane (25ml) in the presence of pyridine (0.8g, 10mmol) gave *N*-methylpyridinium fluoroborate (0.61g, 99%) as a colourless oil (insoluble in ether) (lit.[30] m.p. 10-11.5° C). The addition of an excess of an aqueous solution of sodium picrate to an aqueous solution of the oil gave *N*-methyl-pyridinium picrate-sodium picrate (1.5g, 75%), m.p. 217-8° C; lit.[20] m.p. 216-9° C.

The decomposition of 2,4-dimethoxybiphenyl-2'-yldiazonium fluoroborate (0.6g, 1.8mmol) in dichloromethane (20ml) in the presence of pyridine (0.53g, 6.7mmol) gave, after extraction with ether, *N*-methylpyridinium fluoroborate (0.61g, 99%) as a colourless oil (lit.[30] m.p. 10-11.5° C). The addition of an excess of an aqueous solution of sodium picrate to an aqueous solution of the oil gave *N*-methyl-pyridinium picrate-sodium picrate (0.25g, 48%), m.p. 217-8° C; lit.[20] m.p. 216-9° C. The ether extract was washed with aqueous hydrochloric acid, and dried (Mg SO_4) and the solvent removed to afford 3-methoxydibenzofuran (0.31g, 87%) m.p. 94-6° C (from light petroleum), lit.[27] m.p. 95-95.5° C. δ_H ($CDCl_3$) 7.9-6.75 (***m*** 7H) and 3.8 (*s*, 3H) ppm.

The decomposition of 2-methoxybiphenyl-2'-yldiazonium fluoroborate (4.5g, 15mmol) in dichloromethane (60ml) in the presence of α-pyridone (2.25g, 23mmol) after removal of the solvent gave a colourless oil. Extraction with ether and basification of the insoluble portion gave 2-methoxypyridine (1.24g, 81%), b.p. 138-141° C (lit.[31] b.p. 142-3° C). M^+, 109, δ_H ($CDCl_3$) 8.2-6.75 (***m*** 4H) and 3.92 (*s*, 3H) ppm.

The decomposition of 2-ethoxybiphenyl-2'-yldiazonium fluoroborate (1.2g) in dichloromethane (25ml) in the presence pyridine (0.92g) gave after removal of the solvent *N*-ethylpyridinium fluoroborate (0.81g, 98%) as a tan solid (insoluble in ether) m.p. 58-9° C (lit.[32] m.p. 58-59.5° C). δ_H (D_2O) 9-7.9 (***m*** 5H), 4.75 (*q*, 2H, J = 7Hz),and 1.7 (*t*, 3H, J = 7Hz) ppm.

The decomposition of 2-methoxybiphenyl-2'-yldiazonium fluoroborate (2.3g, 7.7mmol) in dichloromethane (40ml) in the presence of pentachloropyridine (0.64g, 2.6mmol) gave *N*-methylpenta-chloropyridinium fluoroborate (0.37g, 41%) as white needles m.p. 269-271° C (from dichloromethane), δ_H (DMSO d_6) 3.68 ppm. A sample of *N*-methylpentachloropyridinium fluoroborate (0.11g)was added to water (25ml) at 60° C and stirred for 1h to give *N*-methyltetrachloro-2-pyridone (0.44g, 55%) m.p. 150-1° C (lit.[33] m.p. 148.5-149.5° C); δ_H ($CDCl_3$) 3.78 ppm.

The decomposition of 2-methoxybiphenyl-2'-yldiazonium fluoroborate (1g, 3.3mmol) in dichloromethane (25ml) in the presence of 3,5-dichloro-2,6-difluoro-4-hydroxypyridine (1.31g, 6.6mmol) gave a colourless oil which after basification afforded ***N-methyl-3,5-dichloro-2,6-difluoro-4-pyridone*** (0.29g, 43%) m.p. 173-5° C (from tetrachloromethane) ν_{max} 1670 cm^{-1}, λ_{max} 261 ($\log_{10}\varepsilon$ 4.13) nm; (Found: M^+, 212.9549

$C_6H_3Cl_2F_2NO$ requires M^+ 212.9559).

The decomposition of 2-methoxybiphenyl-2'-yldiazonium fluoroborate (3g, 10mmol) in dichloromethane (40ml) in the presence of benzo[b]thiophen (2.8g, 20mmol) gave 1-methylbenzo[b]thiophenium fluoroborate (1.81g, 77%) m.p. 70-3° C (from dichloromethane-ether) (lit.[19] m.p. 72-3° C; δ_H ($CDCl_3$) 8.0-7.08 (***m*** 6H) and 3.3 (***s***, 3H) ppm.

The decomposition of 2-methoxybiphenyl-2'-yldiazonium fluoroborate (1.5g, 5mmol) in dichloromethane (20ml) in the presence of benzonitrile (2.5g, 25mmol) gave *N*-methylbenzonitrilium fluoroborate (0.95g, 87%) m.p. 108-118° C (a brown hygroscopic solid) which was dissolved in water (30ml) and kept at 60° C for 2h. The aqueous solution was extracted with ether, dried ($MgSO_4$) and the solvent removed to afford *N*-methylbenzamide (0.36g, 57%) m.p. 81-2° C (from ethanol), (lit.[34] m.p. 82° C); δ_H ($CDCl_3$) 7.95-7.20 (***m*** 5H), 7.1 (***br***, ***s***, 1H, D_2O exchange) and 2.92 (***d***, 3H, J = 6Hz) ppm.

The decomposition of 2-methoxybiphenyl-2'-yldiazonium fluoroborate (1g, 3.3mmol) in dichloromethane (25ml) in the presence of *N,N*-dimethyl-1-naphthylamine (1.2g, 6.5mmol) gave ***N,N,N-trimethyl-1-naphthylammonium fluoroborate***, a dark oil, (0.93g, 52%) δ_H ($CDCl_3$) 8.3-7.4 (***m*** 7H), and 3.28 (***s***, 9H) ppm; (Found: M^+, $C_{13}H_{13}BF_4N$ requires M^+ 212.9559).

The decomposition of 2-methoxybiphenyl-2'-yldiazonium fluoroborate (4g, 13mmol) in dichloromethane (60ml) in the presence of cycloheptatriene (0.92g, 10mmol) gave tropylium fluoroborate (1.3g, 54%) m.p. 200-260° C (lit.[35] m.p. 210-270° C).

The decomposition of 2-methoxybiphenyl-2'-yldiazonium fluoroborate (4g, 13mmol) in dichloromethane (60ml) in the presence of triphenylmethane (2.1g, 9mmol) gave triphenylcarbenium fluoroborate (0.94g, 21%) m.p. 190-235° C d (lit.[36] m.p. *ca.* 200° C).

The decomposition of 2-methoxybiphenyl-2'-yldiazonium fluoroborate (0.94g, 3.15mmol) in dichloromethane (40ml) in the presence of mesitoic acid (0.47g, 2.85mmol) and diisopropylamine (0.5ml, 2.85mmol) gave, after chromatography on silica gel eluting with light petroleum, dibenzofuran (130mg, 24%) m.p. 87-8° C (from light petroleum), lit.[29] m.p. 86-7° C; and then eluting with light petroleum-ether methyl mesitoate (100mg, 25%), b.p. 93° C ν_{max} 1730 cm^{-1}.

Anisole (0.2g, 2.08mmol) was condensed under high vacuum into a reaction vessel containing 2-[$^2H_3$]methoxybiphenyl-2'-yldiazonium fluoroborate (0.627g, 2.08mmol) and dichloromethane (30ml) cooled with liquid nitrogen. The mixture was allowed to warm to -70° C and stirred at that temperature for 1h before being allowed to come to room temperature. After being stirred for 14h the mixture was worked up and gave, after chromatography on a column of silica gel, dibenzofuran (0.3g, 84%) m.p. 84-86° C (from light petroleum) (lit.[29] m.p. 86-7° C) and anisole (0.04g, 20%), ν_{max} 2070 cm^{-1} M^+ 111 and 108.

Preparation of 2-methylthiobiphenyl-2'-yldiazonium fluoroborate and *S*-methyldibenzothiophenium fluoroborate

o-Iodothioanisole[37] (30g, 0.12mol) and *o*-bromonitrobenzene (28.3g, 0.14mol) were heated with copper powder (30g, 0.48gatom) and afforded **2-methylthio-2'-nitrobiphenyl** (7.7g, 26%), orange crystals, m.p. 51-2° C (from methanol); δ_H ($CDCl_3$) 8.1-6.9 (***m*** 8H), and 2.30 (***s***, 3H) ppm; (Found: M^+, 245.0500 $C_{13}H_{11}NO_2S$ requires: M^+ 245.0510

2'-Methylthio-2-nitrobiphenyl (5.6g, 23mmol) in ethanol (100ml) containing Pd/C (0.4g, 5%) was treated with aqueous hydrazine (20ml, 64%) and heated for 6h and gave **2-amino-2'-methylthiobiphenyl** (4.9g, 100%), m.p. 87-8° C (from methanol); δ_H ($CDCl_3$) 7.35-6.6 (***m*** 8H), 3.45 (***br s*** 2H D_2O exchange), and 2.35 (***s***, 3H) ppm; (Found: M^+, 215.0760 $C_{13}H_{13}NS$ requires: M^+ 215.0769

2-Amino-2'-methylthiobiphenyl (0.92g, 4.3 mmol) in a mixture of THF (10ml) and aqueous fluoroboric acid (45ml, 40%) was diazotised at 0° C with sodium nitrite (0.33g, 4.8mmol) in water (10ml) and gave 2-methylthiobiphenyl-2'-yldiazonium fluoroborate (**8**) (1.11g, 82%), bright orange crystals, m.p. 65-70° C, d,

ν_{max} 2275 cm^{-1}. The diazonium salt (8) (0.9g, 2.9mmol) was stirred in dichloromethane (25ml) at room temperature until the colour was discharged (*ca.* 12h); an excess of dry ether was added and the mixture was set aside at -20° C and gave *S*-methyldibenzo[b,d]thiophenium fluoroborate (0.71g, 86%), m.p. 148-150° C (from dichloromethane-ether) lit.[19] m.p. 149-151° C; δ_H (CD_3CN) 8.35-7.64 (*m* 8H), and 3.35 (*s*, 3H) ppm; δ_C (CD_2CCl_2) 139.3, 134.5 131.8, 130.7, 128.5, 124.4, and 35.4 ppm. Evaporation of the solvent from the filtrate gave dibenzothiophen (70mg, 14%), m.p. 97-100° C (from ethanol) lit.[38] m.p. 99° C.

Preparation of 2-neopentylthiobiphenyl-2'-yldiazonium fluoroborate and its decomposition to dibenzothiophen

o-Aminobenzenethiol (6.25g, 50mmol) was added to a stirred mixture of powdered potassium hydroxide (3.1g, 55mmol) in dry DMF (100ml). After 30min neopentyloxy tris(dimethylamino)phosphonium hexafluorophosphate[39] (19.8g, 50 mmol) was added and the mixture was heated under reflux for 22h. Water (200ml) was added and the mixture was extracted with ether, washed with a saturated solution of sodium chloride, dried (Mg SO_4) and the solvent removed to afford ***o*-aminophenyl neopentylsulphide**, (4.2g, 43%), b.p. 140-2° C at 5mm; ν_{max} 3450, 3350 cm^{-1}; δ_H ($CDCl_3$) 7.50-6.40 (*m* 4H), 4.17 (*s br* 2H D_2O exchange), 2.70 (*s* 2H), and 1.00 (*s* 9H) ppm; (Found: M^+ 195.1075, $C_{11}H_{17}NS$ requires M^+ 195.1082). Diazotisation of o-aminophenyl neopentylsulphide (1.8g, 9.2mmol) and addition to potassium iodide (1.66g, 10mmol) gave, after chromatography on silica gel, ***o*-iodophenyl neopentylsulphide**, (2.32g, 82%); δ_H ($CDCl_3$) 7.85-6.60 (*m* 4H), 2.83 (*s* 2H), and 1.07 (*s* 9H) ppm; (Found: M^+ 305.9928, $C_{11}H_{15}IS$ requires M^+ 305.9941). A reaction of *o*-iodo-phenyl neopentylsulphide (2.32g, 7.6mmol) with o-bromonitrobenzene (1.62g, 8mmol) and copper powder (1.92g) followed by work up and chromatography on silica gel gave **2-neopentylthio-2'-nitrobiphenyl** (1.02g, 45%)ν_{max} 3065, 2965, 2875, 1530, 1355 cm^{-1}; δ_H ($CDCl_3$) 8.15-7.85 (*m* 1H), 7.67-7.00 (*m* 8H), 2.68 (*s* 2H), and 0.90 (*s* 9H) ppm; (Found: M^+ 301.1125, $C_{17}H_{19}NO_2S$ requires M^+ 301.1136).

Reduction of 2-neopentylthio-2'-nitrobiphenyl (0.69g, 2.3mmol) with hydrazine hydrate and palladium on carbon gave **2-amino-2'-neopentylthiobiphenyl** (0.4g, 64%), m.p. 64-7° C (from methanol); ν_{max} 3460, 3370 cm^{-1}; δ_H ($CDCl_3$) 7.40-6.55 (*m* 8H), 3.37 (*s br* 2H D_2O exchange), 2.70 (*s* 2H), and 0.94 (*s* 9H) ppm; (Found: M^+ 271.1384, $C_{17}H_{21}NS$ requires M^+ 271.1395). Diazotisation of 2-amino-2'-neopentylthiobiphenyl (0.43mg, 0.16mmol) in aqueous fluoroboric acid gave 2'-neopentyl-thiobiphenyl-2-yldiazonium fluoroborate (30mg, 51%) a yellow solid (ν_{max} 2285 cm^{-1}) which was suspended in dry benzene at 50-55° C. Nitrogen was evolved and evaporation of the solvent from the colourless solution gave dibenzothiophen (14mg, 95%), m.p. 97-100° C (from ethanol) lit.[38] m.p. 99° C.

The demethylation of 2-methylthio-2'-nitrobiphenyl

Chlorine was bubbled into a solution of 2-methylthio-2'nitrobiphenyl (1.42g, 5mmol) in carbon tetrachloride (50ml) at room temperature during 17h and gave 2-nitro-2'-trichloromethylthiobiphenyl (1.70g, 97%) a colourless oil ν_{max} 1530, 13500 cm^{-1}; δ_H ($CDCl_3$) 8.60-6.90 (*m* 8H) ppm which was heated in methanol in the presence of amberlyst 15 and the solvent gradually removed by distillation through a Vigreux column until the still head temperature reached 64° C. Removal of the residual solventgave **2-mercapto-2'-nitrobiphenyl**, (1.1g, 95%) (Found: M^+ 231.0345, $C_{12}H_9NO_2S$ requires M^+ 231.0354) which was re-methylated in DMSO using potassium hydroxide and then methyl iodide.

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