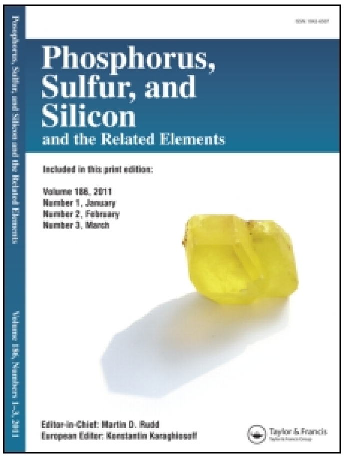

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

OCCURRENCE OF LIGAND COUPLING IN THE REACTIONS OF VARIOUS SULFOXIDES WITH GRIGNARD REAGENTS

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To cite this Article Kawai, Tsutomu , Kodera, Yoichi , Oae, Shigeru , Ishida, Masahiro , Takeda, Takashi , Wakabayashi, Shoji and Furukawa, Naomichi(1987) 'OCCURRENCE OF LIGAND COUPLING IN THE REACTIONS OF VARIOUS SULFOXIDES WITH GRIGNARD REAGENTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 34: 3, 139 — 148

To link to this Article: DOI: 10.1080/03086648708074318

URL: http://dx.doi.org/10.1080/03086648708074318

Phosphorus and Sulfur, 1987, Vol. 34, pp. 139–148
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OCCURRENCE OF LIGAND COUPLING IN THE REACTIONS OF VARIOUS SULFOXIDES WITH GRIGNARD REAGENTS[1,2]

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(*Received March 7, 1987*)

Ligand coupling reactions take place not only between benzyl and 2-pyridyl groups and two 2-pyridyl groups in the treatment of benzyl, alkyl and aryl 2-pyridyl sulfoxides with Grignard reagents, but also between such groups as *p*-benzenesulfonylphenyl, 4-pyridyl, 2-quinolyl and 2-pyrimidyl, and the benzyl group. There are cases in which ligand exchange precedes ligand coupling, especially with 2-heteroaryl groups. In addition, even some alkyl groups were found to couple with the 2-pyridyl group. The ease of coupling seems to be associated with the electronegativity of the coupling carbon atom of the ligand, when one compares the ^{13}C NMR chemical shifts.

Although the reaction of benzylic 2-pyridyl sulfoxides with Grignard reagents always gives 2-benzylpyridine, that of alkyl and phenyl 2-pyridyl sulfoxides with benzyl-magnesium chloride also gives exclusively 2-benzylpyridine. The allyl group likewise readily undergoes coupling with the 2-pyridyl group. When primary alkyl and aryl 2-pyridyl sulfoxides were treated with alkyl or aryl Grignard reagents, the ligand coupling product was 2,2′-bipyridine, which is assumed to be obtained by initial ligand exchange to form 2-pyridyl Grignard reagent that in a subsequent step would attack the original sulfoxide prior to ligand coupling. Secondary and tertiary alkyl 2-pyridyl sulfoxides were also found to react with ethylmagnesium bromide, affording 2-alkylpyridines, the coupling products. A similar reaction, however, was not observed in the treatment of benzyl 2-pyridyl sulfide, sulfone and N-*p*-tosylsulfilimine with phenylmagnesium bromide under the same conditions. Also, in the reaction of benzyl 3-pyridyl sulfoxide with phenylmagnesium bromide, no ligand coupling but only ligand exchange reaction was observed.

Thus, we have attempted to scrutinize the scope of this ligand coupling reaction by extending the reaction to more sulfoxides and examining the occurrence of the ligand coupling reaction by comparison of both IR stretching frequencies and ^{13}C NMR chemical shifts of the coupling ligand carbon atoms.

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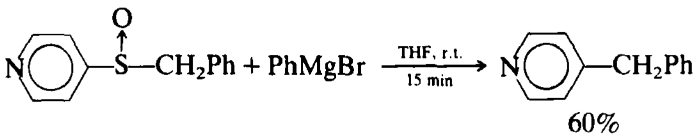
RESULTS AND DISCUSSION

A. *Reactions of Benzyl 2-Pyridyl Sulfide, Sulfoxide, Sulfone and N-p-Tosylsulfilimine with Phenylmagnesium Bromide*

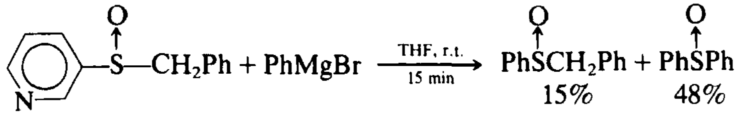
When an equimolar amount of benzyl 2-pyridyl sulfoxide was treated with phenylmagnesium bromide for 15 min at room temperature in THF, 2-benzylpyridine, the ligand coupling product, was obtained nearly quantitatively along with phenyl benzenethiosulfinate. However, under the same conditions, neither the sulfide nor the sulfone underwent any reaction, leading to recovery of the starting materials. The N-*p*-tosylsulfilimine did react a little, but the reaction was different. No ligand coupling product was obtained but a small amount of a Pummerer-type rearrangement product was formed in a mixture of other products; most of the original sulfilimine was recovered. Thus, under these mild conditions, the ligand coupling reaction seems to be rather unique for the sulfoxide. Perhaps, if the reaction mixture is heated to a higher temperature, the sulfilimine would undergo coupling, in view of the facile coupling of two phenyl groups in the reaction of diphenyl N-*p*-tosylsulfilimine with phenylmagnesium bromide.[3]

B. *Reactions of Benzyl 2-, 3- and 4-Pyridyl Sulfoxides with Phenylmagnesium Bromide*

Just as the reaction of benzyl 2-pyridyl sulfoxide with phenylmagnesium bromide gives the coupling product, 2-benzylpyridine, quantitatively, the reaction of benzyl 4-pyridyl sulfoxide with 1 equivalent of phenylmagnesium bromide also gives the coupling product, 4-benzylpyridine, in 60% yield, as shown below.



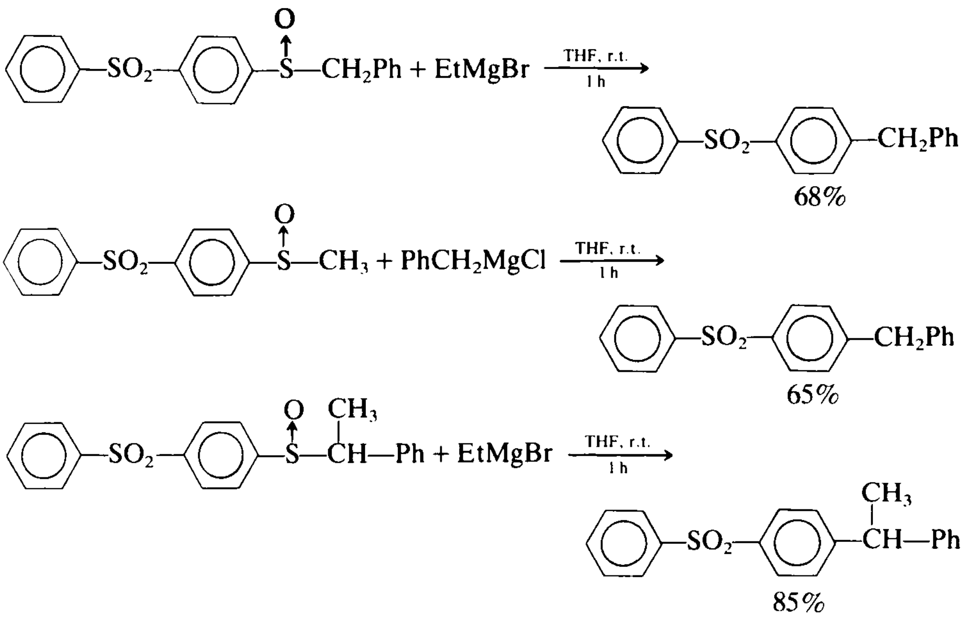
However, when benzyl 3-pyridyl sulfoxide was treated similarly with 1 equivalent of phenylmagnesium bromide, no ligand coupling product, 3-benzylpyridine, but ligand exchange products, phenyl benzyl and diphenyl sulfoxides were obtained as shown below.



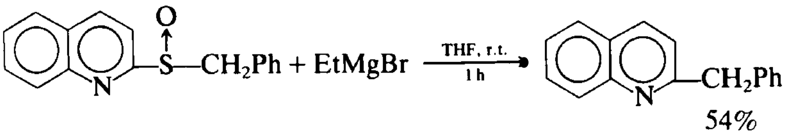
Phenyl benzyl sulfoxide is undoubtedly the primary ligand exchange product, which would receive the nucleophilic attack of phenylmagnesium bromide to afford the secondary ligand exchange product, i.e., diphenyl sulfoxide. This means that the 3-pyridyl group is a better leaving group than the benzyl group which in turn is a better leaving group than phenyl, as in the alkaline hydrolyses of quaternary phosphonium salts, which are believed to involve hypervalent intermediates.[4] The 3-pyridyl group has been shown not to undergo coupling with another 3-pyridyl group in contrast to the reaction of alkyl or 2-pyridyl sulfoxides with Grignard reagents.[5]

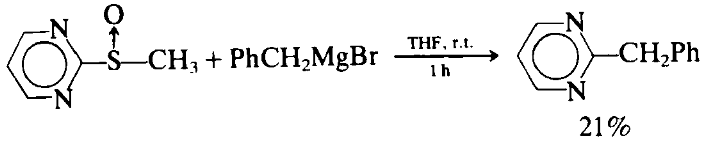
C. Reactions of Various Aryl and Heteroaryl Benzyl Sulfoxides with Grignard Reagents

The reaction of phenyl benzyl sulfoxide with phenylmagnesium bromide gave diphenyl sulfoxide, the ligand exchange product, but no ligand coupling product, diphenylmethane. Reactions of *p*-chlorophenyl, *p*-anisyl benzyl and dibenzyl sulfoxides with ethylmagnesium bromide also did not give any ligand coupling product. The treatment of phenyl methyl sulfoxide with benzylmagnesium chloride also did not give any coupling product. In all these compounds, aryl groups are not as electron withdrawing as 2- or 4-pyridyl groups. In order for aryl and heteroaryl groups to couple with the benzylic group, those groups are considered to be sufficiently electron-withdrawing but not too electron-withdrawing as 2-benzothiazolyl group. Indeed, when an electron-withdrawing group is substituted on the phenyl ring, such as in *p*-benzenesulfonylphenyl benzyl sulfoxide, the aryl group underwent coupling with Grignard reagents, as shown below.



Heteroaryl sulfoxides were also found to react with Grignard reagents affording coupling products with the benzyl group, as shown below. However, the modes of both ligand coupling and ligand exchange seem to vary with different heteroaryl or aryl substituents in the original sulfoxides used for the reaction with Grignard reagents, as will be reported shortly from our laboratories.



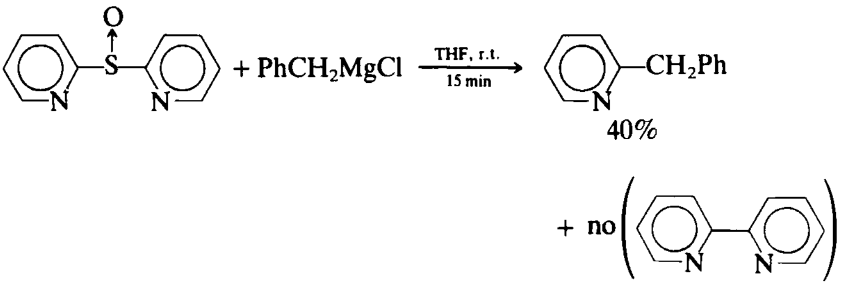


Only the 2-benzothiazolyl group appeared to be too electron-withdrawing to couple with the benzyl group and underwent mainly ligand exchange along with self-coupling as described in our previous paper.[5]

D. *Reaction of Benzyl Pyridyl Sulfoxides with Various Organometallic Species*

Although all the data on ligand couplings of the 2-pyridyl group with aryl, heteroaryl and alkyl groups seem to suggest that the benzylic group is the most favored for coupling, we have carried out the reactions of benzyl 2-pyridyl sulfoxide with various organometallic species, since the attacking nucleophile is considered always to enter from an axial site, whereas the 2-pyridyl group, being an aromatic π-system, tends to assume an equatorial position and hence has a better chance to couple with the entering nucleophile from an axial site without pseudorotation. On the other hand, in order for benzyl and 2-pyridyl groups to couple, the σ-sulfurane, formed by the nucleophilic attack, has to undergo pseudorotation to place the benzyl group at an axial site. However, in all cases the coupling product was 2-benzylpyridine, as shown in Table I.

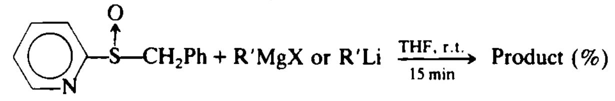
Especially interesting is the reaction with 2-pyridyl lithium, since the 2-pyridyl group can assume, upon nucleophilic attack on a sulfinyl sulfur atom, an axial position for direct ligand coupling to afford 2,2′-bipyridine. However, even in this case 2-benzylpyridine was the only coupling product, though the yield was poor. Another interesting reaction is the following.

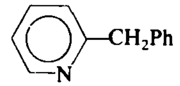
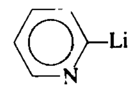
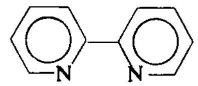


Here again, there was no formation of 2,2′-bipyridine and 2-benzylpyridine was the sole coupling product. These data reveal clearly that benzyl is the most favored for coupling with 2-pyridyl among those employed, even when prior pseudorotation is required. Perhaps, the intermediary σ-sulfurane in which benzyl is attached to the central sulfur atom appears to undergo pseudorotation

TABLE I

Reaction of benzyl 2-pyridyl sulfoxide with various organometallic species



CH_3MgBr	 (83)
C_2H_5MgBr	,, (90)
PhMgBr	,, (98)
n-BuLi	,, (46)
	,, (26) no 

and subsequent coupling more readily than those bearing other groups in the reaction with Grignard reagents. Further studies along this line are now underway in these laboratories.

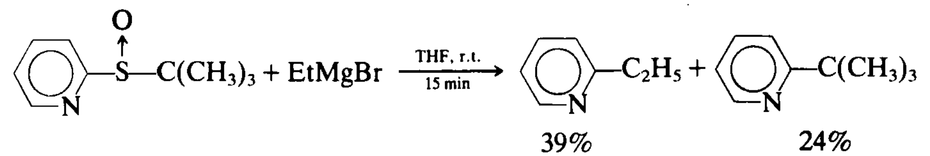
E. Reaction of Primary Alkyl or Aryl 2-Pyridyl Sulfoxides with Grignard Reagents—Ligand Exchange and Subsequent Coupling

The reaction of alkyl and phenyl 2-benzyl sulfoxides with either alkyl or phenylmagnesium bromide always gives 2,2'-bipyridine in appreciable yields as revealed in the data listed in Table II and described in the previous paper.[5]

Only when benzylmagnesium chloride was used did coupling of benzyl and 2-pyridyl groups take place without prior ligand exchange to generate 2-pyridylmagnesium halide.

F. Reactions of Secondary, Tertiary Alkyl and Allyl 2-Pyridyl Sulfoxides with Grignard Reagents

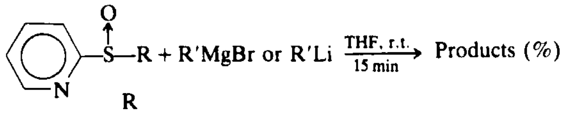
When sec. and tert. alkyl 2-pyridyl sulfoxides were treated with ethylmagnesium bromide, no ligand exchange preceded and coupling of alkyl and 2-pyridyl group took place. One representative example is shown below.

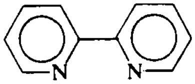
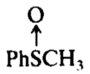
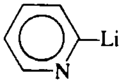
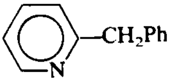
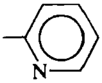
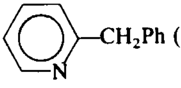


Apparently electron-donating alkyl groups, which would form relatively stable carbonium ions, seem to be favored for coupling. Even then, the incoming group tends to couple preferentially over the original alkyl group bound to the sulfinyl

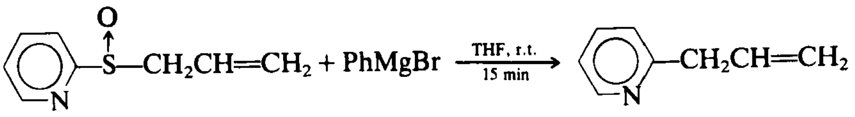
TABLE II

Reaction of primary alkyl and phenyl 2-pyridyl sulfoxides with grignard reagents



$-CH_3$	0.5 CH_3MgBr			(73)
,,	0.5 C_2H_5MgBr		,,	(63)
,,	0.5 PhMgBr		,,  $Ph\overset{\overset{O}{\uparrow}}{S}CH_3$	(79) (36)
,,		(Temp. −18°C)	,,	(59)
$-Ph$	0.5 C_2H_5MgCl		,,	(71)
$-C_2H_5$	0.5 C_2H_5MgBr		,,	(55)
$-CH_3$	$PhCH_2MgCl$		,,  (79)	(0)
	$PhCH_2MgCl$		,,  (40)	(0)

sulfur atom. Allyl seems to couple favorably with 2-pyridyl as shown in the following example.



61%

Like benzyl, allyl seems to couple preferentially with the 2-pyridyl group.

G. Scope of the Ligand Coupling in the Reactions of Sulfoxides with Grignard Reagents

As shown in the various examples cited in this and previous papers of this series,[1,2,3] the ligand coupling reaction observed in the treatments of sulfoxides with Grignard reagents seems to take place generally between the highly electron-withdrawing carbon-centered π-aryl ligands and also between highly electron-withdrawing π-aryl ligands and those carbon groups that are capable of forming relatively stable carbonium ions, such as benzyl, allyl and tertiary alkyl groups. However, owing to the limited number of ligand coupling reactions, it is not easy to predict even qualitatively which combination of sulfoxides and Grignard reagents would give coupling products. Nevertheless, the occurrence of the coupling seems to be associated with the electronic state of the coupling carbon atom of the coupling ligands. The electronic state of the carbon ligand and that of sulfinyl sulfur are considered to be diagnosed roughly on the basis of ^{13}C NMR chemical shifts and IR stretching frequencies of sulfinyl linkages. Thus, both ^{13}C NMR spectra and IR stretching frequencies have been measured and the data are summarized in Table III, together with the feasibility of ligand coupling.

Inspection of the spectroscopic data in Table III seems to suggest that there are certain good combinations of the sulfoxides and the Grignard reagents or organolithium reagents for coupling to proceed. When the ^{13}C NMR chemical shift of C^1 carbon atom attached directly to the sulfinyl function appears at higher than *ca.* 150 ppm while that of the C^2 atom ranges between *ca.* 50 ppm and *ca.* 65 ppm, coupling of both C^1 and C^2 ligands appears to take place, upon nucleophilic attack of a proper Grignard reagent. Ligand coupling seems to be favored when the IR stretching frequency of sulfinyl is higher than *ca.* 1040 cm^{-1}.

Among those groups that have not been examined, 2-thienyl and 2-furyl have their ^{13}C NMR chemical shifts at C^1 carbon atoms higher than 150 ppm, whereas that of vinyl carbon is quite close to 150 ppm. Indeed, our preliminary work indicates that the 2-thienyl group undergoes coupling with benzyl groups, though to a small extent, upon nucleophilic attack of a Grignard reagent on 2-thienyl benzyl sulfoxide, as will be reported shortly elsewhere. Among C^2 ligands, not only benzyl and allyl but also 2-pyridylmethyl should undergo coupling with 2-pyridyl and similar groups since its ^{13}C NMR chemical shift is close to 60 ppm. Many more groups will be found to fit to this requirement in more extensive surveys planned in future.

EXPERIMENTAL

General. All the melting points were uncorrected and were taken on a Yanaco micro melting-point apparatus. The IR spectra were obtained on a JASCO A-3 spectrometer and the NMR spectra were obtained on a HITACHI R-600 FT-NMR spectrometer or a JEOL LNM-MH-100 spectrometer in $CDCl_3$ or CCl_4 using TMS as an internal standard. All the reactions were monitored by chromatography, namely, TLC (Merck, Kieselgel 60-GF_{254}, aluminum oxide 60 GF_{254}), GLPC, (HITACHI 163, using a 5% silicon Ge SE-30 on 60–80 mesh or 2% silicon OV-1 chromosorb W on 80–100 mesh in column). Silica gel used for column chromatography was Merck kieselgel 60. Alumina used for column chromatography was Wako activated aluminum oxide about 200 mesh. Mass spectra were taken with a HITACHI RMU-6MG mass spectrometer. Elemental analyses were carried out at the Chemical Analysis Center in this University.

Materials. All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co., or Aldrich Chemical Co. The reagents using as reaction solvents were further purified by general methods. Starting sulfoxides were prepared from the corresponding sulfides with hydrogen peroxide or *m*-chloroperbenzoic acid, according to the general method.[6]

Benzyl p-benzenesulfonylphenyl sulfide: mp 150.0–151.0°C; IR (KBr) 1150, 1315 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 4.15$ (s, 2 H), 7.13–8.16 (m, 14 H); MS m/z 340 (M^+, 23.9%), 197 (0.4), 91 (100); *Sulfoxide*: yield 60%; mp 181.0–182.0°C; IR (KBr) 1030, 1150, 1315 cm^{-1}; ^1H NMR ($CDCl_3$)

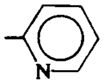
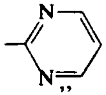
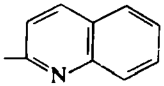
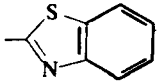
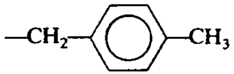
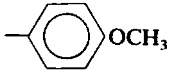
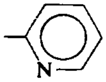
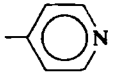
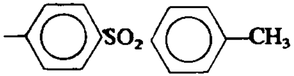
TABLE III

^{13}C NMR Chemical Shifts and IR Stretching Frequencies of Sulfoxides

$\mathrm{C^1{-}\overset{\overset{O}{\uparrow}}{S}{-}C^2\ \ (=R{-}\overset{\overset{O}{\uparrow}}{S}{-}R')}$

^{13}C NMR (ppm) solvent: CDCl$_3$

IR (cm^{-1}) liquid cell (CHCl$_3$)

R	R′	C¹	C²	ν(SO)	R	R′	C¹	C²	ν(SO)	
	—CH$_3$	165.9	41.3	1049		—CH$_2$Ph	172.6	60.1	1040	
,,	—C$_2$H$_5$	163.7	47.1	1046	,,	—CH$_3$	173.6	39.9	1071	
,,	—CH(CH$_3$)$_2$	163.4	52.5	1051		,,	164.0	60.6	1025	proceed ↑
,,	—C(CH$_3$)$_3$	162.6	57.0	1043						
,,	—CH$_2$CH=CH$_2$	163.6	57.6	1043		,,	176.9	62.8	1058	
,,	—CH$_2$Ph	163.6	59.8	1049						Ligand Coupling
,,		163.7	59.6	1046	—Ph	—CH$_2$Ph	142.8	63.6	1039	Reaction
,,	—CH(CH$_3$)Ph	163.5	62.7	1053		,,	133.6	63.8	1030	↓ no proceed
,,	—Ph	165.7	144.0	1044		,,	141.3	63.5	1042	
,,		163.8	163.8	1048	—Ph	—CH$_3$	146.3	44.0	1038	
,,	—CH$_2$Ph	164.0	60.6	1046	—CH$_2$Ph	—CH$_2$Ph	57.3	57.3	1038	
	,,	153.1	62.8	1051	—CH$_2$Ph	—CH$_3$	60.2	37.3	1041	
	—CH$_3$	151.9	43.9	1051	—CH$_3$	—CH$_3$	40.9	40.9	1052	
,,	—CH$_2$Ph	148.9	63.3	1030	(Ph$_3$S$^+$Br$^-$		123.8)			
,,	—CH(CH$_3$)Ph	148.4	67.7	1035						

$\delta = 4.04$ (s, 2 H), 6.76–8.22 (m, 14 H); MS m/z 356 (M^+, 35.8%), 340 (11.3), 250 (100), 92 (12.1); ^{13}C NMR ($CDCl_3$) $\delta = 148.9$ (s), 144.3 (s), 140.9 (s), 133.6 (d), 130.2 (d), 129.4 (d), 128.5 (d), 128.2 (s), 127.9 (d), 127.7 (d), 125.3 (d), 63.3 (t).

Methyl p-benzenesulfonylphenyl sulfide: mp 93.5–94.7°C; IR (KBr) 1150, 1315 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 2.46$ (s, 3 H), 7.10 –8.10 (m, 9 H); *Sulfoxide*: yield 66%, mp 138.1–139.2°C; IR (KBr) 1040, 1150, 1315 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 3.05$ (s, 3 H), 7.24–8.31 (m, 9 H); ^{13}C NMR ($CDCl_3$) $\delta = 146.6$ (s), 144.7 (s), 140.0 (s), 133.5 (d), 129.5 (d), 128.5 (d), 128.3 (d), 127.8 (d), 44.1 (q).

1-Phenylethyl p-benzenesulfonylphenyl sulfide: mp 95.0 –95.5°C; IR (KBr) 1158, 1317 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 1.55$ (d, 3 H, $J = 7$ Hz), 4.42 (q, 1 H, $J = 7$ Hz), 7.11–7.92 (m, 14 H). *Sulfoxide*: yield 52%; mp 115.0–116.0°C; IR (KBr) 1035, 1055, 1320 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 1.65$ (d, 3 H, $J = 8$ Hz), 4.20 (q, 1 H, $J = 8$ Hz), 7.07 –8.02 (m, 14 H); ^{13}C NMR ($CDCl_3$) $\delta = 148.4$ (s), 144.1 (s), 141.0 (s), 134.7 (s), 133.5 (d), 129.4 (d), 128.6 (d), 128.5 (d), 127.7 (d), 127.6 (d), 125.8 (d), 67.7 (d), 14.3 (q); MS m/z 370 (M^+).

Benzyl 2-quinolyl sulfoxide: yield 43%, mp 117.0–118.0°C; IR (KBr) 1025, 1480, 1570 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 4.26$ (AB –q, 2 H, $J = 12$ Hz), 6.55–8.36 (m, 11 H); ^{13}C NMR ($CDCl_3$) $\delta = 60.6$(t), 116.0 (d), 127.7 (d), 127.8 (s), 127.9 (d), 128.2 (d), 129.0 (d), 129.4 (s), 130.2 (d), 130.5 (d), 137.7 (d), 147.1 (s), 164.0 (s); MS m/z 267 (M^+).

Benzyl 2-pyrimidyl sulfoxide: yield 58%, mp 72.5–73.5°C; IR (KBr) 1040, 1380, 1560 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 4.48$ (AB –q, 2 H, $J = 16$ Hz), 7.00–7.70 (m, 6 H), 8.33 (d, 2 H, $J = 5$ Hz); ^{13}C NMR ($CDCl_3$) $\delta = 172.6$ (s), 158.2 (d), 132.7 (s), 130.8 (d), 128.6 (d), 128.3 (d), 121.6 (d), 60.1 (t); MS m/z 218 (M^+, 58.4%), 92 (69.5), 89 (17.0), 79 (34.6), 65 (100).

General Procedure for the Reaction of Sulfides, Sulfoxides, Sulfones and Sulfilimines with Grignard reagents. Reaction of benzyl 2-pyridyl sulfoxide with C_6H_5MgBr—To a solution of benzyl 2-pyridyl sulfoxide (200 mg, 0.92 mmol) in 10 ml THF, C_6H_5MgBr (0.93 ml, 0.93 mmol) in 1.0 mmol/ml THF solution was added through a 1 ml syringe with stirring under nitrogen atmosphere at room temperature. Stirring was continued for 15 min. Then, 5 ml water was added to the reaction mixture and the solution was neutralized with dil. HCl solution and extracted three times with CH_2Cl_2. The combined CH_2Cl_2 layer was washed with water and dried over anhydrous $MgSO_4$. After the solvent was evaporated, the resulting residue was separated on a silica-gel column using benzene as an eluent. First fraction was found to contain $C_6H_5SSC_6H_5$ (16 mg, 60%) together with a trace of $C_6H_5S(O)_2SC_6H_5$ upon g.l.c. analysis. 2-Benzylpyridine was obtained in 154 mg in 98% yield on changing from benzene to acetone as an eluent.

Reaction of benzyl-2-pyridyl-N-*p*-tosylsulfilimine with C_6H_5MgBr—In the reaction of benzyl-2-pyridyl-N-*p*-tosyl-sulfilimine (199 mg, 0.54 mmol) with C_6H_5MgBr (0.64 ml, 0.64 mmol in 8 ml THF, benzyl 2-pyridyl sulfoxide of 71 mg and diphenylmethyl 2-pyridyl sulfide of 13.6 mg were obtained in 7% and 9% yields, respectively. Benzyl 2-pyridyl sulfide and benzaldehyde were observed using g.l.c. analysis among various unknown products.

Reaction of benzyl 2-pyridyl sulfoxide with BuLi. To a stirred solution of benzyl 2-pyridyl sulfoxide (188 mg, 0.87 mmol) in 10 ml THF, 0.78 ml BuLi of 15% solution in hexane was added using 1 ml syringe under nitrogen atmosphere at −72°C in a dry ice-acetone bath. After the reaction mixture was warmed at room temperature, the solution was stirred for 15 min. Then, water was added to the solution and the solution was extracted three times with CH_2Cl_2. The combined CH_2Cl_2 layer was dried over anhydrous magnesium sulfate and the solvent was evaporated. The residue was separated through silica-gel column chromatography using a mixture of hexane : acetone = 5 : 2 as an eluent. 2-Benzylpyridine of 58 mg and recovered sulfoxide of 52 mg were obtained in 46% and 28% yields, respectively.

All the sulfoxides reacted with the Grignard reagents in the same way, as shown in Equations 1–10 and Tables I, II. Reaction products 2-ethylpyridine, 2-*t*-butylpyridine, 2-allylpyridine, 4-benzylpyridine, 2-benzylpyridine, 2,2′-bipyridine, diphenyl sulfoxide and benzyl phenyl sulfoxide were identified by comparing the spectra with those of authentic samples.

p-Benzyl-phenylsulfonylbenzene and *p*-(1-phenylethyl)-phenylsulfonylbenzene, 2-benzylquinoline and 2-benzylpyrimidine were identified by NMR, mass spectrometry and elemental analysis.

p-Benzyl-phenylsulfonylbenzene: mp 163.5–164.5°C; IR (KBr) 1150, 1300 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 4.00$ (s, 2 H), 6.93 –8.22 (m, 14 H); MS m/z 308 (M^+); Found: C, 74.23, H, 5.29%. Calcd for $C_{19}H_{16}SO_2$: C, 73.99, H, 5.22%.

p-(1-Phenylethyl)-phenylsulfonylbenzene: mp 118.5–119.5°C; IR (KBr) 1150, 1310 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 1.67$ (d, 3 H, $J = 8$ Hz), 3.78 (q, 1 H, $J = 8$ Hz), 6.80–8.08 (m, 14 H); MS m/z 322 (M^+); Found: C, 74.06, H, 5.71%. Calcd for $C_{20}H_{18}SO_2$: C, 74.53, H, 5.59%.

2-*benzylquinoline*: pale yellow oil; IR (neat) 1420, 1450, 1500, 1560, 1595 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 4.29$ (s, 2 H), 7.06–8.18 (m, 11 H); MS m/z 219 (M^+); Found: C, 87.28, H, 6.15%. Calcd for $C_{16}H_{13}N$: C, 87.67, H, 5.94%.

2-benzylpyrimidine: brown oil; IR (neat) 1410, 1560 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 4.28$ (s, 2H), 6.90–7.70 (m, 6 H), 8.59 (d, 2 H, $J = 5$ Hz); MS m/z 170 (M^+, 36.5%), 169 (100), 168 (14.3), 91 (9.0), 65 (8.3).

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