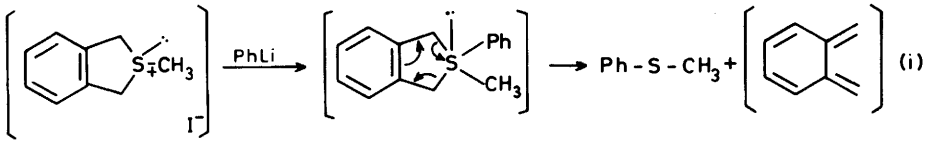
Ligand Coupling within σ-Sulphurane Intermediates formed in the Reaction of Benzyl 2-Pyridyl and Related Sulphoxides with Grignard Reagents[1,2]

Shigeru Oae *
Okayama University of Science, Ridai-cho 1-1, Okayama 700, Japan
Tsutomu Kawai and Naomichi Furukawa
Department of Chemistry, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 305, Japan
Fujiko Iwasaki
Department of Material Science, The University of Electrocommunications, Chofugaoka, Chofu-shi, Tokyo 182, Japan

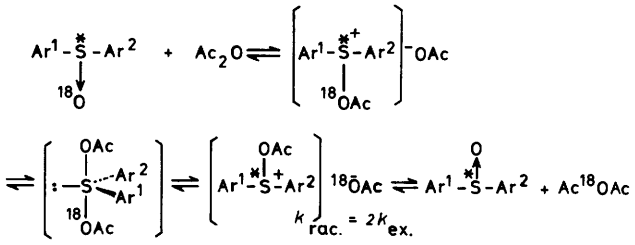
The reaction of benzyl or 1-phenylethyl 2-pyridyl sulphoxide (**1**) or (**18**) with a Grignard reagent was found to give the ligand-coupling product, *i.e.*, 2-benzylpyridine or 2-(1-phenylethyl)pyridine (**2**) or (**22**) in excellent yield. This coupling reaction was found to proceed within the σ-sulphurane formed as an intermediate upon treatment of benzyl 2-pyridyl and related sulphoxides with a Grignard reagent. The stereochemical course of this coupling reaction involves complete retention at the benzylic carbon.

When trico-ordinate organosulphur compounds react with nucleophiles, the latter usually attack the central sulphur atom, forming pentaco-ordinate species as intermediates. These hypervalent species are named σ-sulphuranes; they are relatively unstable, since the central sulphur atom is valence-shell expanded and hence tends to resume its normal valence by extruding a ligand bearing a pair of electrons or a pair of ligands coupled with a pair of electrons.

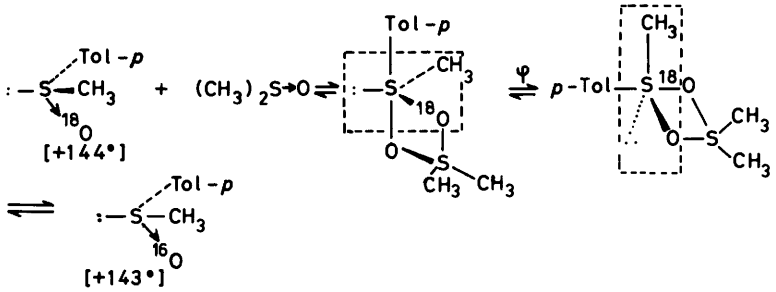
There are three conceivable ways for σ-sulphuranes to undergo transformation into stable compounds, in which the central sulphur atom assumes the normal valency, namely, self-decomposition, ligand exchange, and ligand coupling. One example of self-decomposition is reaction (i).[3] Ligand exchange is the most common reaction and proceeds typically through an S_N2-type stereochemical path with inversion of configuration in most cases as illustrated by the oxygen-exchange reaction of optically active diaryl sulphoxides with acetic anhydride, shown in Scheme 1.[4]



Oxygen exchange may proceed with retention of configuration *via* pseudo-rotation of the intermediate σ-sulphurane, (Scheme 2).[5] Ligand coupling is the last and least known reaction of σ-sulphuranes and the main theme of this paper. Earlier, we studied the reaction of triarylsulphonium salts with aryl-lithiums and found that although part of the reaction proceeds through the formation of an aryne intermediate, a ligand-coupling product was obtained in a fair yield.[6] The yield of the coupling product was found to increase substantially under mild conditions[7,8] (Scheme 3).



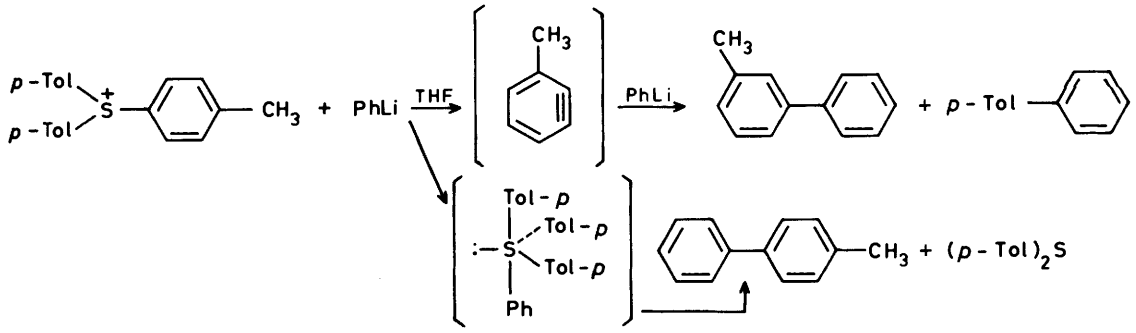
Scheme 1.



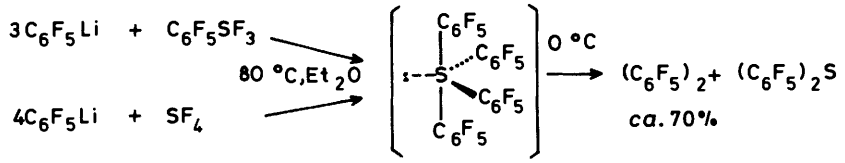
Scheme 2.

σ-Sulphuranes are quite stable when the axial ligands contain highly electronegative heteroatoms.[9,10] However, no σ-sulphurane with axial carbon ligands has ever been isolated in stable form. Sheppard, however, observed the n.m.r. spectrum of what seems to be an intermediate σ-sulphurane, which upon warming gave a coupling product as shown in Scheme 4.[11]

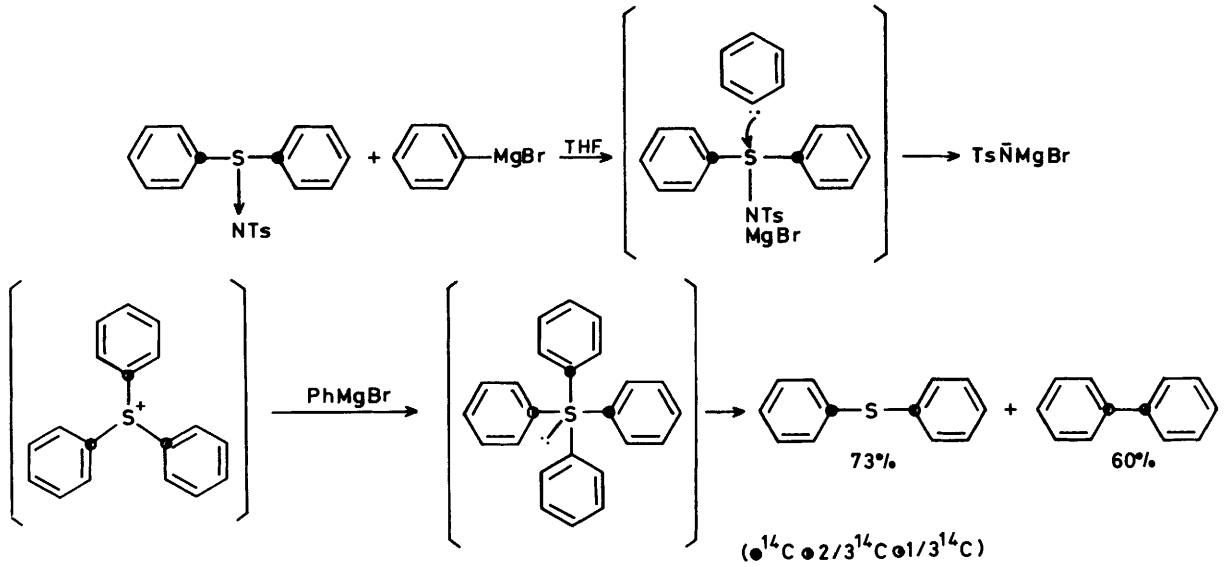
Another interesting example is the reaction of [^{14}C]-diphenyl-*N*-tosylsulphilimine with phenylmagnesium bromide in refluxing tetrahydrofuran (THF).[12] In this reaction, the ^{14}C distribution in the products, *i.e.* 1/3 in biphenyl and 2/3 in



Scheme 3. Reaction of sulphonium salt with PhLi



Scheme 4. Sulphurane as an intermediate



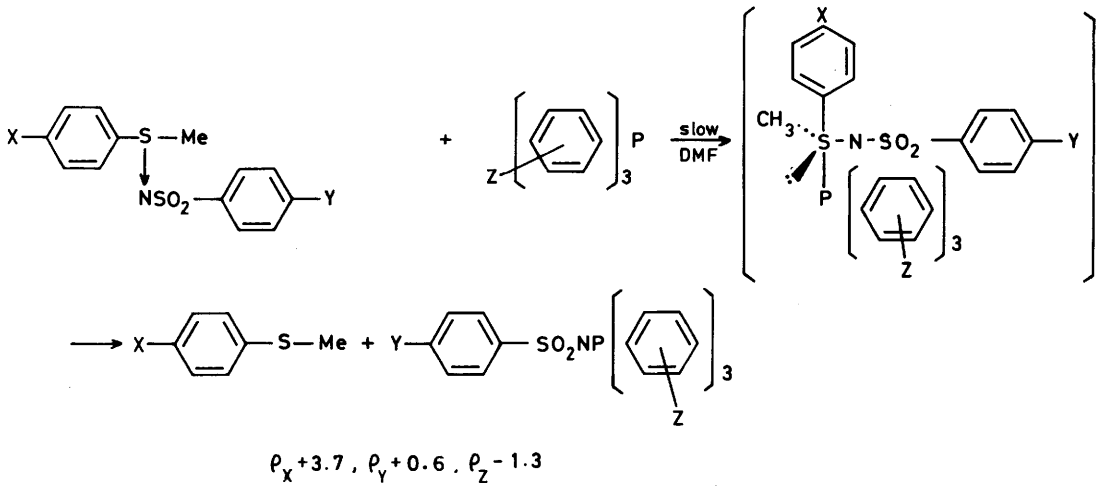
Scheme 5.

diphenyl sulphide of the original ^{14}C in the *ipso* position of the starting sulphilimine, suggests that ligand coupling took place faster than pseudo-rotation within the σ-sulphurane (Scheme 5).

Mislow *et al.* have also investigated a similar reaction of triphenylsulphonium salt with phenyl-lithium labelled with ^{14}C at −78 °C.[13] However, they obtained a different result, suggesting that ligand coupling is slower than pseudo-rotation at the lower temperature in this case.

Coupling of two heteroatom ligands around the central pentaco-ordinate sulphur atom has been considered to be more pronounced and indeed has been proposed in a few reactions of trico-ordinate sulphur compounds with various nucleophiles.[14,15] For example, the reaction of benzyl,aryl- or methyl,aryl-*N*-tosylsulphilimine in dimethylformamide (DMF) is considered to involve initial nucleophilic attack of triphenylphosphine on the trico-ordinate sulphur atom of the sulphilimine, to form a σ-sulphurane intermediate which upon ligand coupling finally affords the corresponding sulphide and phosphinimine,[14] as shown in Scheme 6.

Thus, all these results clearly reveal that in the reactions of trico-ordinate sulphur compounds with nucleophiles, ligand coupling within the σ-sulphurane intermediate is quite common. If there is any cohesive interaction between axial and equatorial ligands, the two ligands would be eliminated from the central valence-shell expanded sulphur atom concertedly to afford a ligand-coupling product. The main cohesive interaction would result from the overlap of orbitals of both axial and equatorial ligands. If the coupling proceeds concertedly between axial and equatorial ligands, at an angle of *ca.* 90°, the configuration of both ligands in the product should be retained completely. Indeed, there has been a report that in the reaction of triphenylsulphonium salt with *trans*- or *cis*-propenyl-lithium, either *trans*- or *cis*-propenylbenzene, obtained in *ca.* 65% yield, was found to retain the geometry of the propenyl group.[7] We



ρ_X +3.7 , ρ_Y +0.6 , ρ_Z - 1.3

Scheme 6. Reaction of sulphilimine with phosphine

have reported previously[1] that the optically active 1-phenylethyl group in 2-(1-phenylethyl)pyridine, obtained quantitatively in the reaction of optically active 1-phenylethyl 2-pyridyl sulphoxide with either methyl or phenyl Grignard reagent, retains its configuration completely. This paper describes the detail of the reaction and the mechanism involved.

Results and Discussion

When benzyl 2-pyridyl sulphoxide (**1**) was treated with an equimolar amount of phenylmagnesium bromide in THF at room temperature, 2-benzylpyridine (**2**) was obtained quantitatively along with a mixture of diphenyl disulphide (**4**), diphenyl thiosulphinate (**3**) and diphenyl thiosulphonate (**5**) [equation (1)].

When [$^2H_2$]benzyl 2-pyridyl sulphoxide [$^2H_2$]-(**1**), prepared by the usual base-catalysed H–D exchange reaction, was treated with phenylmagnesium bromide, the deuterium content of 2-[$^2H_2$]benzylpyridine [$^2H_2$]-(**2**), measured by ^1H n.m.r. spectroscopy, did not decrease at all. Similarly, when the undeuteriated sulphoxide (**1**) was treated with phenylmagnesium bromide and the reaction mixture was quenched with D_2O, compound (**2**) was found to have incorporated no deuterium at all

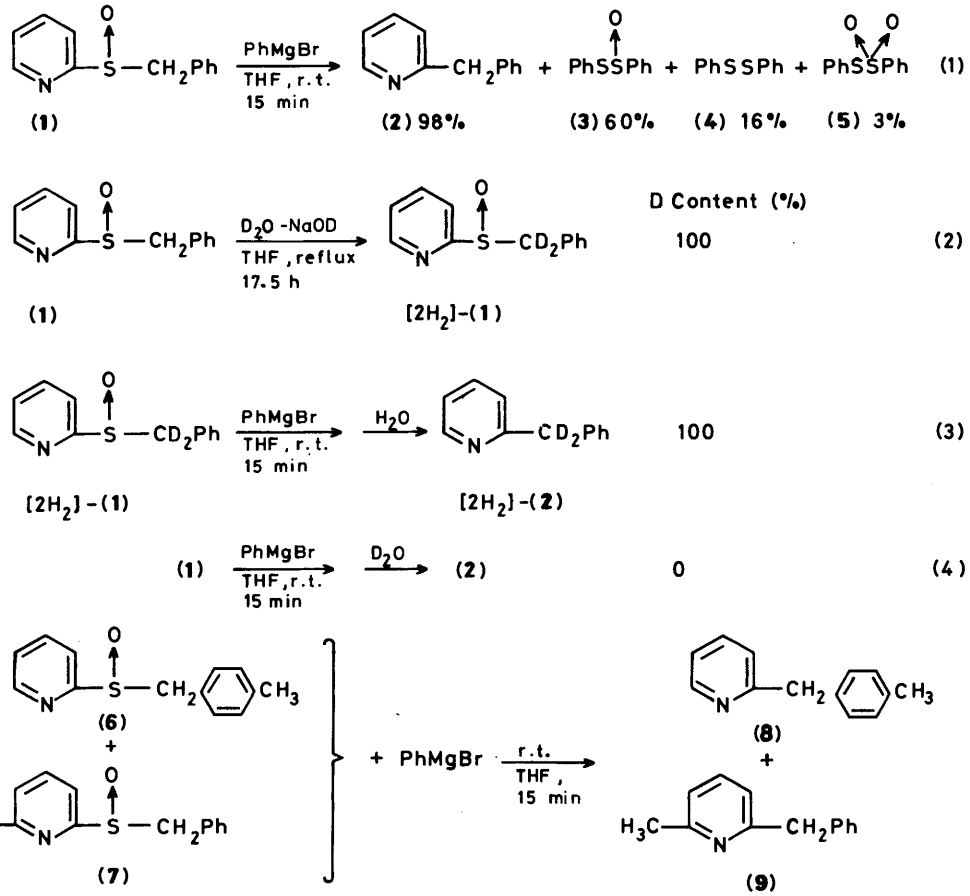
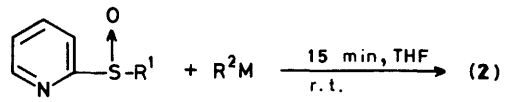
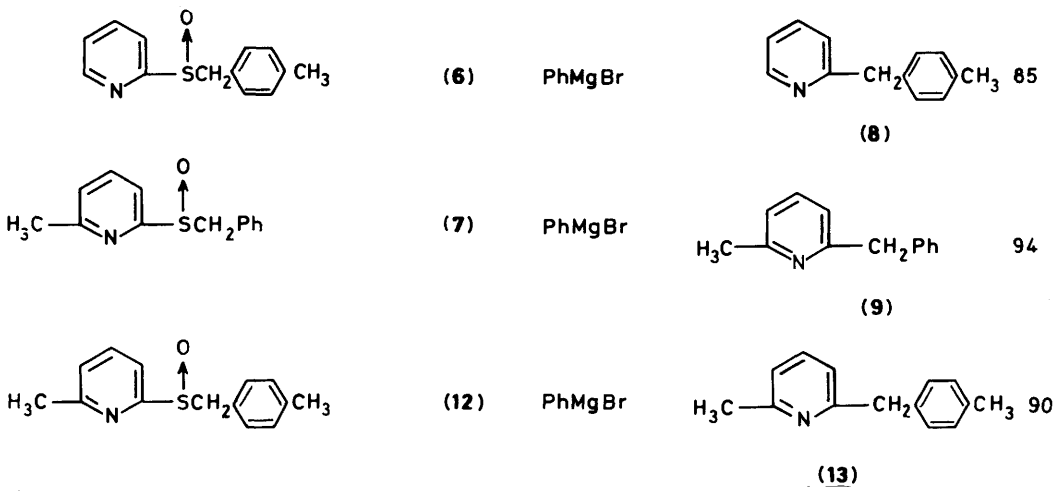


Table 1. Reaction of sulphoxides with R^2M



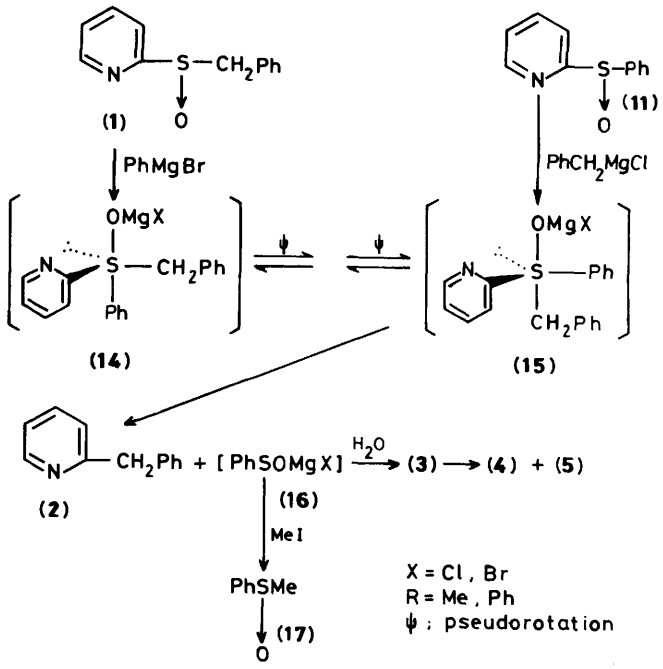
R^1	R^2M	Yield of (2) (%)
CH_2Ph (1)	PhMgBr	98
CH_2Ph (1)	MeMgBr	83
CH_2Ph (1)	Bu^nLi	46
CH_3 (10)	$PhCH_2MgCl$	79[a]
Ph (11)	$PhCH_2MgCl$	71[a]



[a] By g.l.c. analysis.

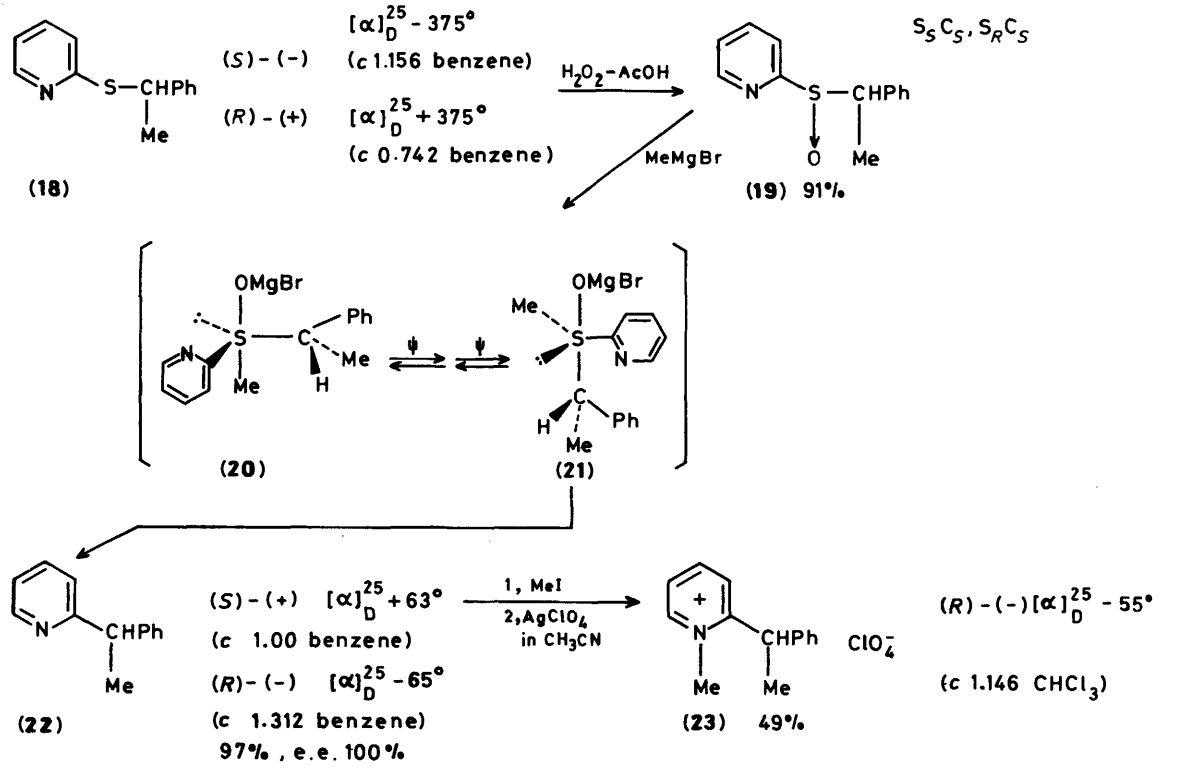
[equations (2)—(4)]. These results reveal that the reaction does not involve any initial α-deprotonation by the Grignard reagent, thus eliminating a possible Ramberg–Bäcklund-type reaction process.[16]

In order to establish whether the reaction proceeds through an intra- or inter-molecular route, a mixture of equal amounts of 4-methylbenzyl 2-pyridyl sulphoxide (**6**) and benzyl 6-methyl-2-pyridyl sulphoxide (**7**) was treated with phenylmagnesium bromide and the coupling products were analysed by g.l.c. However, in this reaction no cross-over coupling product was detected at all [equation (5)]. The result demonstrates clearly that this ligand-coupling reaction is an intramolecular process. Treatment of benzyl 2-pyridyl sulphoxide (**1**) with a few other Grignard reagents as well as Bu^nLi or of alkyl or aryl 2-pyridyl sulphoxide with benzyl Grignard reagent was found to afford similarly 2-benzylpyridine as the sole coupling product. The data are listed in Table 1. All these observations suggest that the ligand-coupling reaction proceeds through an intramolecular process *via* the formation of the same sulphurane intermediate. Thus, a plausible reaction mechanism is shown in Scheme 7. In the reaction of benzyl 2-pyridyl sulphoxide (**1**) with phenylmagnesium bromide, the Grignard reagent initially attacks the sulphinyl sulphur atom from the back side of the sulphinyl oxygen atom, forming the σ-sulphurane (**14**). Then, interconversion of the ligands takes place by pseudorotation to form the preferred stereoisomer (**15**) in which the aromatic 2-pyridyl group is placed at an equatorial position and the apicophilic[17] benzyl group becomes an axial ligand, keeping an angle between the two ligands of *ca.* 90° in the incipient σ-sulphurane (**15**). The reaction of phenyl 2-pyridyl sulphoxide (**11**) with benzylmagnesium chloride may afford the same σ-sulphurane (**15**) directly which can readily undergo a ligand-coupling reaction without pseudorotation. Beside the



Scheme 7.

coupling product, three sulphur-containing products (**3**)—(**5**) were obtained. These are undoubtedly derived from unisolable phenylsulphenoxylmagnesium bromide (**16**), which is readily converted into the thiosulphinate (**3**) upon quenching the



Scheme 8. Stereochemistry of the coupling reaction

reaction mixture with water. The formation of the sulphenyl species (**16**) was further confirmed by isolating methyl phenyl sulphoxide (**17**) upon treatment of the reaction mixture with an excess of methyl iodide.

On the basis of these product analyses and cross-over experiments, the reaction of 2-pyridyl sulphoxides with Grignard reagents is believed to involve the initial formation of a σ-sulphurane within which ligand coupling takes place intramolecularly.

If the coupling of 2-pyridyl and benzyl groups takes place concertedly in one step, keeping the angle between the coupling ligands at *ca.* 90° in the incipient σ-sulphurane, the configuration around the benzylic carbon atom of the resulting 2-benzylpyridine (**2**) should be maintained. Thus optically active (*S*)-(−)-1-phenylethyl 2-pyridyl sulphoxide (**19**) was treated with the Grignard reagent. After the usual work-up, the original configuration of 1-phenylethyl group of the sulphoxide (**19**) was found to be retained completely in the product, 2-(1-phenylethyl)pyridine (**22**), (Scheme 8).

Optically pure (*S*)-(−)-1-phenylethyl 2-pyridyl sulphide (**18**) (e.e. 100%) was oxidized with H_2O_2–AcOH to give a diastereoisomeric mixture of the corresponding sulphoxide (**19**). The sulphoxide (**19**) was either separated into pure diastereoisomers or allowed to react directly without separation with an equimolar amount of methylmagnesium bromide. The coupling product, 2-(1-phenylethyl)pyridine (**22**), was isolated in 97% yield. The optical activity of (**22**) was $[\alpha]_D^{25}$ +65° in benzene, while the enantiomeric excess was determined as 100% by use of a ^1H n.m.r. shift reagent, regardless of the diastereoisomeric purity of the sulphoxide (**19**), as was anticipated. The other enantiomer, (*R*)-(+)-(**18**), has been found to afford the same stereochemical result only with the opposite optical activity. In order to confirm the absolute configuration, (**22**) was converted into (*R*)-(−)-2-(1-phenylethyl)-1-methylpyridinium perchlorate (**23**) by treatment with methyl iodide and silver perchlorate. The crystalline perchlorate (**23**) was subjected to *X*-ray crystallographic analysis which confirmed it to be of pure *R* configuration (Figure). Thus, the ligand coupling of the equatorially preferred 2-pyridyl group and the apicophilic 1-phenylethyl group has been found to proceed concertedly.

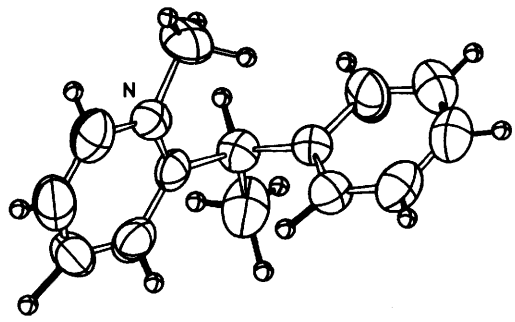


Figure. *R* Configuration of perchlorate (**23**)

Experimental

General.—M.p.s were uncorrected and were taken on a Yanaco mirco melting point apparatus. I.r. spectra were obtained on a JASCO A-3 spectrometer and n.m.r. spectra on a Hitachi R-600 FT-NMR or a JEOL LMN-MH-100 spectrometer, in $CDCl_3$ or CCl_4 solution, using tetramethylsilane as internal standard. Reactions were monitored by chromatography, *i.e.* t.l.c. (Merck Kieselgel 60-GF_{254}, aluminium oxide 60-GF_{254}), g.l.p.c. (Hitachi 163, using 5% silicon GE-30 on 60—80 mesh or 2% silicone OV-1 Chromosorb W on 80—100 mesh column). Silica gel used for column chromatography was Merck Kieselgel 60. Alumina used for column chromatography was

Wako activated aluminium oxide, *ca.* 200 mesh. Mass spectra were taken with a Hitachi RMU-6MG mass spectrometer. Elemental analyses were carried out at the Chemical Analysis Center, Tsukuba University.

Materials.—All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co., or Aldrich Chemical Co. Solvents were further purified by general methods. Starting sulphoxides were prepared from the corresponding sulphides on treatment with hydrogen peroxide or *m*-chloroperbenzoic acid, according to our procedure.[18]

Reaction of (**1**) *with* PhMgBr.—To a solution of (**1**) (200 mg, 0.92 mmol) in THF (10 ml), PhMgBr (0.93 ml, 0.93 mmol) in THF solution (1 mmol ml^{-1}) was added through a 1 ml syringe with stirring under nitrogen at room temperature. After 15 min, water (5 ml) was added and THF was evaporated. Water (10 ml) was added again and the solution was extracted three times with CH_2Cl_2. The combined CH_2Cl_2 layer was dried ($MgSO_4$) and the solvent was evaporated. The residue was separated through column chromatography using benzene as eluant. The first fraction contained (**4**) (16 mg, 16%) together with a trace of (**5**) based on g.l.c. analysis. The second fraction contained (**3**) (65 mg, 60%). Compound (**2**) (154 mg, 98%) was obtained on changing from benzene to acetone as eluant.

Preparation of [$^2H_2$]-(**1**).—A solution of (**1**) (250 mg, 1.15 mmol) in D_2O (0.5 ml) and THF (10 ml) with NaOD (0.25 ml) (40% solution in D_2O) as base was stirred at 70 °C for 17.5 h under nitrogen. After the solution was cooled at room temperature, CH_2Cl_2 and then water was added. The solution was extracted with CH_2Cl_2 three times and dried ($MgSO_4$). After removing the solvent, the residue was recrystallized from hexane and benzene. [$^2H_2$]Benzyl 2-pyridyl sulphoxide [$^2H_2$]-(**1**) (190 mg, 75%) was obtained, m.p. 85—86 °C. The deuterium content of the benzyl protons of [$^2H_2$]-(**1**) was nearly 100% (n.m.r.).

Reactions of (**1**) *and* [$^2H_2$]-(**1**) *with* PhMgBr.—To a solution of [$^2H_2$]-(**1**) (50 mg, 0.23 mmol) in THF (2 ml), PhMgBr (0.23 ml, 0.23 mmol) in THF solution (1.0 mmol ml^{-1}) was added through a 1 ml syringe with stirring under nitrogen at room temperature. After 15 min, water was added and the solution was extracted three times with CH_2Cl_2. The combined CH_2Cl_2 layer was dried ($MgSO_4$) and the solvent evaporated. Crude (**2**) (59 mg) was obtained. The benzyl protons of (**2**) were not detected (n.m.r.).

On the other hand, when nondeuteriated sulphoxide (**1**) (50 mg, 0.23 mmol) was treated similarly with PhMgBr (0.23 ml, 0.23 mmol) and the mixture was quenched with D_2O (1 ml), crude (**2**) (50 mg) was obtained. When this was subjected to ^1H n.m.r. measurement, no deuterium incorporation of (**2**) was observed.

Cross-over Experiment.—To a solution of (**6**) (100 mg, 0.43 mmol) and (**7**) (100 mg, 0.43 mmol) in THF (8 ml), PhMgBr (0.95 ml, 0.95 mmol) in THF solution (1 mmol ml^{-1}) was added with stirring under nitrogen at room temperature. After 15 min, water was added and the solution was extracted three times with CH_2Cl_2. The combined CH_2Cl_2 layer was dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography using benzene as eluant. A mixture of (**8**) and (**9**) of (140 mg, 88%) was obtained. The ratio of (**8**) and (**9**) was *ca.* 1:1 upon examining the integration of their methyl proton signals at δ 2.31 and 2.52, respectively. There are four conceivable coupling products, (**2**), (**8**), (**9**), and (**13**); (**2**) was commerically available and (**8**), (**9**), and (**13**) were synthesized by the reaction of the corresponding sulphoxides (**6**), (**7**), and (**12**) with PhMgBr. The ^1H n.m.r. data of these products together with the starting sulphoxides are shown in Table 2. The ^1H n.m.r. spectrum of the products obtained in this experiment was consistent with that of a mixture authentic (**8**) and (**9**) and the cross-over products (**2**) and (**13**) were not detected at all.

Reaction of (**1**) *with BuLi.*—To a stirred solution of (**1**) (188 mg, 0.87 mmol) in THF (10 ml), BuLi (0.78 ml, 15% solution in hexane) was added under nitrogen at −72 °C in a dry ice–acetone bath. The mixture was then warmed to room temperature, water was added, and the aqueous solution was extracted three times with CH_2Cl_2. The combined CH_2Cl_2 layer was dried ($MgSO_4$), the solvent was evaporated, and the residue was separated through silica-gel column chromatography using hexane–acetone 5:2 as eluant. Compound (**2**) (58 mg, 46%) and recovered (**1**) (52 mg, 28%) were obtained.

Table 2. Analytical data for sulphoxides (**6**), (**7**), and (**12**) and the corresponding coupling products (**8**), (**9**), and (**13**)

Compound (formula)	Yield (%)	Solvent	M.p. (°C)	Found (%) (required) C	H	N	Chemical shift δ ($CDCl_3$, p.p.m.)
(**6**) ($C_{13}H_{13}NOS$)	88	Cyclohexane	72—73	67.5 (67.5)	5.7 (5.7)	6.05 (6.05)	2.29 (3 H, s, Me), 4.00, 4.37 (2 H, dd, *J* 13.3 Hz, CH_2), 6.81—7.82 (7 H, m, 3,4,5-PyrH, ArH), 8.61—8.72 (1 H, m, 6-PyrH)
(**7**) ($C_{13}H_{13}NOS$)	46	Cyclohexane	88—89	67.5 (67.5)	5.7 (5.7)	6.0 (6.05)	2.62 (3 H, s, Me), 4.02, 4.39 (2 H, dd, *J* 13.8 Hz, CH_2), 6.95—7.82 (8 H, m, 3,4,5-PyrH, ArH)
(**12**) ($C_{14}H_{15}NOS$)	47	Cyclohexane	56—57	68.5 (68.5)	6.1 (6.2)	5.7 (5.7)	2.29 (3 H, s, ArMe), 2.60 (3 H, s, PyrMe), 4.00, 4.37 (2 H, dd, *J* 14.4 Hz, CH_2), 6.85—7.82 (7 H, m, 3,4,5-PyrH, ArH)
(**8**)	85						2.31 (3 H, s, Me), 4.11 (2 H, s, CH_2), 6.93—7.73 (7 H, m, 3,4,5-PyrH, ArH), 8.43—8.63 (1 H, m, 6-PyrH)
Picrate of (**8**) ($C_{19}H_{16}N_4O_7$)		EtOH	155—156	55.3 (55.3)	3.9 (3.9)	13.6 (13.6)	
(**9**)	95						2.52 (3 H, s, Me), 4.12 (2 H, s, CH_2), 6.70—7.43 (7 H, m, 3,4,5-PyrH, ArH)
Picrate of (**9**) ($C_{19}H_{16}N_4O_7$)		EtOH	149—150[a]	55.3 (55.3)	3.9 (3.9)	13.6 (13.6)	
(**13**)	90						2.31 (3 H, s, ArMe), 2.55 (3 H, s, PyrMe), 4.09 (2 H, s, CH_2), 6.63—7.53 (7 H, m, 3,4,5-PyrH, ArH)
Picrate of (**13**) ($C_{20}H_{18}N_4O_7$)		EtOH	175.5—176.5	56.4 (56.3)	4.2 (4.25)	13.2 (13.1)	

[a] Lit.,[19] m.p. 145—147 °C.

Preparation of 4-Methylbenzyl 2-Pyridyl Sulphoxide (**6**), *Benzyl 6-Methyl-2-pyridyl Sulphoxide* (**8**) *and 4-Methylbenzyl 6-Methyl-2-pyridyl Sulphoxide* (**12**).—The title sulphoxides were prepared from the corresponding sulphides with hydrogen peroxide, according to our previous procedure.[18] Analytical data of sulphoxides (**6**), (**8**), and (**12**) are shown in Table 2.

Reaction of Sulphoxides with Grignard Reagents.—A typical experimental procedure is as follows.

Reaction of (**7**) *with* PhMgBr. To a stirred solution of (**7**) (198 mg, 0.86 mmol) in THF (8 ml), PhMgBr (0.94 ml, 0.94 mmol) in THF solution (1 mmol ml^{-1}) was added under nitrogen at room temperature. Stirring was continued for 15 min. Water was added and the solution was neutralized with dilute HCl solution and extracted three times with CH_2Cl_2. The combined CH_2Cl_2 layer was washed with water and dried ($MgSO_4$). After the solvent was evaporated, the residue was separated through an activated alumina column using benzene as eluant. Compound (**9**) (138 mg, 95%) was obtained. Sulphoxides (**6**) and (**12**) reacted with PhMgBr in the same way and the results are shown in Table 2.

Reaction of (**1**) *with* MeMgBr. In the reaction of (**1**) (100 mg, 0.46 mmol) with MeMgBr (0.5 ml, 0.5 mmol) in THF (5 ml), (**2**) (65 mg, 83%) was obtained.

Reaction of (**10**) *with* $PhCH_2MgCl$. In the reaction of (**10**) (52 mg, 0.36 mmol) with $PhCH_2MgCl$ (0.7 ml, 0.35 mmol) in THF (2 ml), (**2**) was obtained in 79% yield. The yield was determined by g.l.c. analysis using biphenyl as internal standard. Sulphoxide (**11**) reacted with $PhCH_2MgCl$ in the way as shown in Table 1.

Reaction of optically active 1-phenylethyl 2-pyridyl sulphoxide (**19**)[20] *with* MeMgBr. MeMgBr (4.4 ml, 2.2 mmol) was added to a stirred solution of optically active (**19**) (500 mg, 2.16 mmol) which was prepared from (−)-(*S*)-(**18**) ($[\alpha]_D$ −375°[20]) in THF (10 ml) under nitrogen at room temperature. After the solution was stirred for 15 min, water was added. The solution was neutralized with dilute HCl solution and extracted three times with CH_2Cl_2. The combined CH_2Cl_2 layer was washed with water and dried ($MgSO_4$). After the solvent was evaporated the residue was separated through an activated alumina column using benzene as eluant and optically active 1-phenylethylpyridine (**22**) was obtained, $[\alpha]_D^{25}$ +63° (*c* 1.00 benzene). In the reaction of optically active 1-phenylethyl 2-pyridyl sulphoxide (**19**) prepared from (+)-(*R*)-(**18**) ($[\alpha]_D$ +375°) with MeMgBr, optically active 1-phenylethylpyridine (**22**) was obtained in 75% yield, $[\alpha]_D^{25}$ −65° (*c* 1.312 benzene). The enantiomeric excess was determined by integration of the methyl signal of the sample by ^1H n.m.r. using tris-[3-(2,2,2-trifluoro-1-hydroxyethylidene)camphorato]europium as shift reagent in CCl_4.

Preparation of (R)-2-(1-*Phenylethyl*)-1-*methylpyridinium Perchlorate* (**23**).—(−)-1-Phenylethyl-2-pyridine ($[\alpha]_D$ −65°) (**22**) (402 mg) was added to excess of MeI. This mixture was stirred in the dark and a precipitate appeared overnight. This precipitate was filtered and washed with cold acetone. (*R*)-2-(1-Phenylethyl)-1-methylpyridinium iodide (392 mg) was obtained. Immediately, a solution of this precipitate and $AgClO_4$ (255 mg, 1.23 mmol) in CH_3CN (10 ml) was stirred in the dark for 1 h, since (*R*)-2-(1-phenylethyl)-1-methylpyridinium iodide was found to decompose under light. The reaction mixture was filtered and the solvent removed. The residue was recrystallized from CH_2Cl_2–hexane, and (**23**) (318 mg, 49%) was obtained, m.p. 115—116 °C, $[\alpha]_D^{25}$ −55° (*c* 1.146, $CHCl_3$) (Found: C, 56.4; H, 5.4; N, 4.8. Calc. for $C_{14}H_{16}ClNO_4$: C, 56.5; H, 5.4; N, 4.7%), δ($CDCl_3$) 1.78 (3 H, d, *J* 7 Hz, CH_3), 4.22 (3 H, s, NCH_3), 4.75 (1 H, q, *J* 6.7 Hz, CH), 7.00—7.40 (5 H, m, ArH), and 7.75—8.83 (4 H, m, PyrH).

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