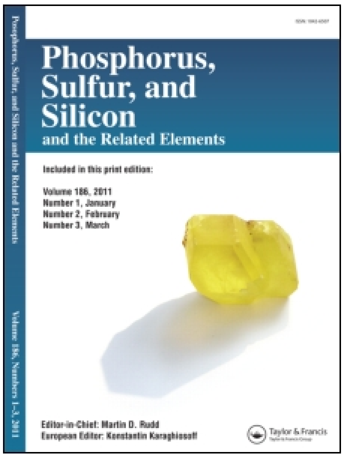


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

LIGAND COUPLING THROUGH HYPERVALENT INTERMEDIATES. REACTION OF HETEROARYL SULFOXIDES WITH ORGANOMETALLICS REAGENTS AND THEIR IMPLICATIONS

S. Oae[a]
[a] Okayama University of Science, Okayama, Japan

To cite this Article Oae, S.(1986) 'LIGAND COUPLING THROUGH HYPERVALENT INTERMEDIATES. REACTION OF HETEROARYL SULFOXIDES WITH ORGANOMETALLICS REAGENTS AND THEIR IMPLICATIONS', Phosphorus, Sulfur, and Silicon and the Related Elements, 27: 1, 13 — 29

To link to this Article: DOI: 10.1080/03086648608072755

URL: http://dx.doi.org/10.1080/03086648608072755

Phosphorus and Sulfur, 1986, Vol. 27, pp. 13–29
0308-664X/86/2702-0013/$20.00/0

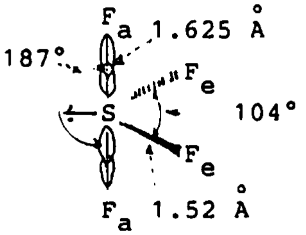
LIGAND COUPLING THROUGH HYPERVALENT INTERMEDIATES. REACTION OF HETEROARYL SULFOXIDES WITH ORGANOMETALLICS REAGENTS AND THEIR IMPLICATIONS

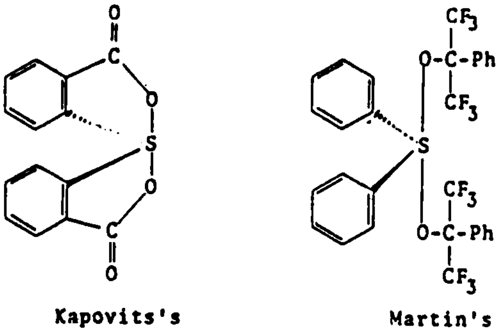
S. OAE

Okayama University of Science, Ridai-cho 1-1, Okayama 700, Japan

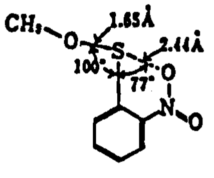
INTRODUCTION

Earlier, pentacoordinate phosphorus and sulfur compounds were presumed to be of 3sp^{3}d hybridization.[1] However, a three-centered-four-electron bond, called a hypervalent bond by Musher,[2] was suggested by Rundle and others[3] to be consistent with p-orbitals in the early 1950s. The structure of one such compound, SF_4, is shown below. Although the original theoretical treatment of hypervalent structure using three sp^2- and a p-orbital was modified slightly by introduction of 3d orbitals into the calculation,[4,5] the structural feature of such hypervalent compounds has remained the same. Following two stable sulfuranes, one by Kapovits *et al.*[6] and another by Martin and his coworkers[7], are the first organic σ-sulfuranes which have both two polar and longer S—O bonds nearly at 180°. Hypervalent interaction was noticed in the extremely short distance between the neutral divalent sulfenyl sulfur

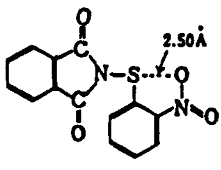




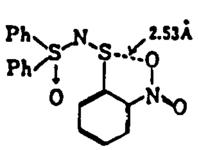
atom and the weakly nucleophilic oxygen atom of nitro group of the following compounds, we prepared for X-ray crystallographic analyses. Thus the hypervalent



8



9



9

bonding is considered to be quite common and readily formed.

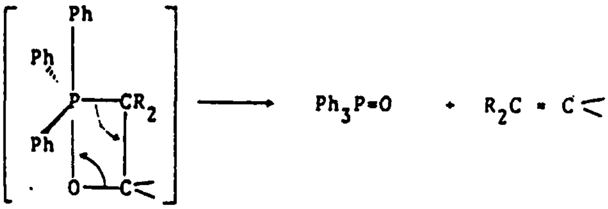
Another important concept in the chemistry of hypervalent compounds is pseudo- and/or turnstile rotation which controls the steric course of the reaction.

The most essential feature of the hypervalent compounds or intermediates is that the central atom is valence-shell expanded; e.g., the sulfur atom in the σ-sulfurane assumes decet. Therefore, the hypervalent species are relatively unstable and the central atom tends to resume the normal valency by extruding a ligand bearing a pair of electrons or a pair of ligands which couple with a pair of electrons, eventually affording stable compounds.

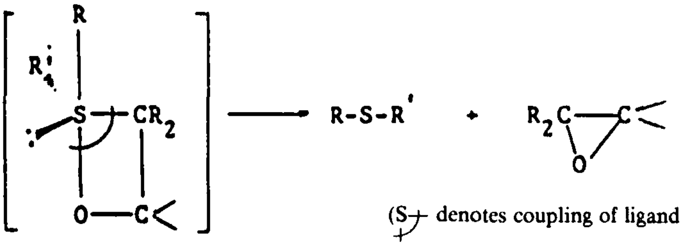
There are three conceivable ways for hypervalent species to undergo transformation to stable compounds, namely, self-decomposition, ligand exchange and ligand coupling.

One example of self-decomposition may be the following reaction.[10]

Another is the Wittig reaction,[11] in which the high energy gained by formation of P=O bond, ca. 536–578 KJ, would outweigh other possible reactions. A similar reaction does not proceed with an analogous sulfurane in the same manner, but

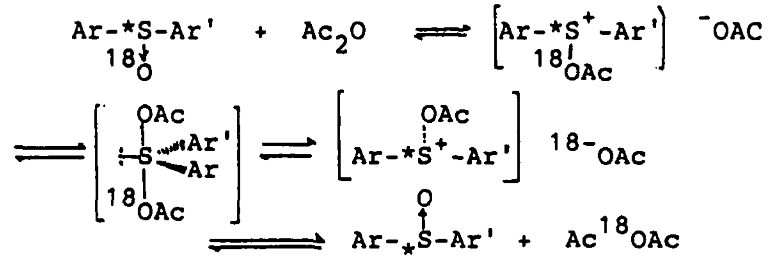


ligand coupling takes place, as shown below,[12] due mainly to the weak S—O bond, ca. 377 KJ,[13] affording an epoxide.[14]

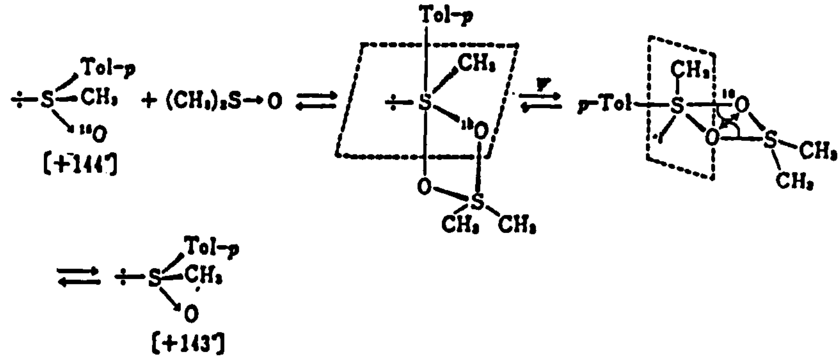


(S denotes coupling of ligands on S atom.)

Ligand exchange is the most common reaction for hypervalent compounds or intermediates and proceeds through a typical S_N2 type stereochemical path with inversion of configuration in most cases as illustrated by the following oxygen exchange reaction of sulfoxides.[15] However, if there is any cohesive interaction between an axial and an equatorial ligand, such as a dipole interaction, oxygen exchange reaction does proceed with retention of configuration through a hypervalent intermediate which undergoes pseudorotation prior to elimination of a leaving group, as shown by the following reaction.[16]



krac. = 2kex.



Ligand coupling reaction is the last and the least known reaction of hypervalent species and hence will be dealt with at this time.

LIGAND COUPLING REACTION

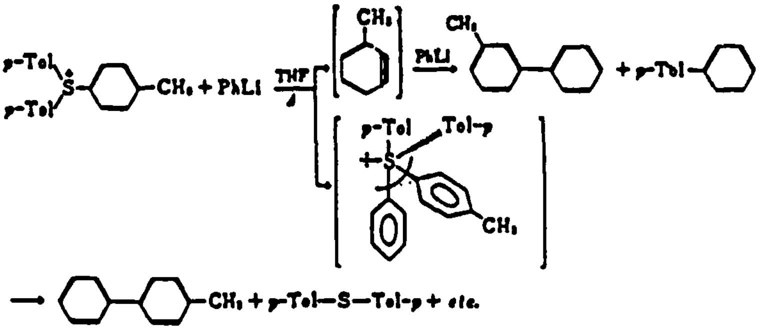
Hypervalent species are rather unstable and hence tend to transform, by extruding a ligand or two with a pair of electrons, to stable compounds in which the central atom resumes a normal valency. If there is any cohesive interaction between an axial and an equatorial ligand, the two ligands would be eliminated from the central valence-shell expanded atom concertedly to afford a ligand coupling product. The main cohesive interaction would result by the overlapping of orbitals of both axial and equatorial ligands. If the coupling reaction proceeds concertedly between an axial and an equatorial ligand, holding an angle of nearly 90°, the configuration of both ligands in the resulting coupling product should be retained completely. This has been shown by us in the reaction of optically active 1-phenylethyl 2-pyridyl sulfoxide with methyl Grignard reagent to form 2-(1-phenylethyl)-pyridine.[17]

Similar ligand coupling reactions are numerous in the reactions of tricoordinate sulfur compounds and tetracoordinate phosphorus compounds with nucleophiles, while hypervalent selenium and iodine compounds also seem to undergo similar coupling reactions. This concept of ligand coupling appears to be applied also to many reactions of organometallic compounds with nucleophiles and some oxidation reactions with metal oxides.

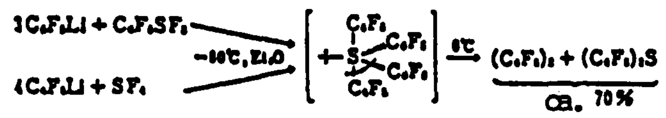
This lecture will deal first with our experimental work which has led to the concept of ligand coupling reaction in the hypervalent species and then some selected examples among many plausible ligand coupling reactions found in the literature.

A. On Sulfur Atom

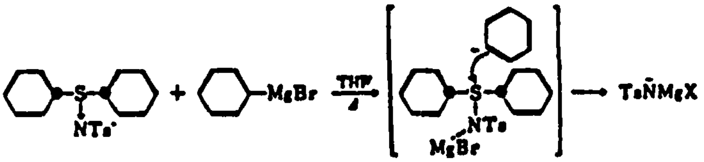
One of the earliest examples is the following reaction.[18,19]

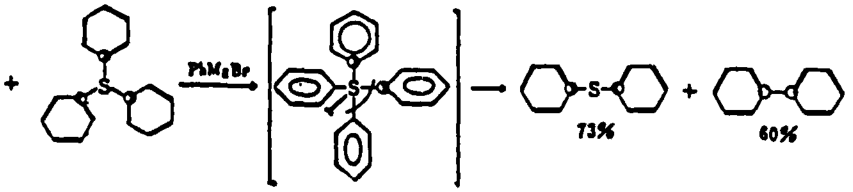


Although a part of the reaction proceeds through the formation of an aryne intermediate, ligand coupling products were obtained in a small yield, while the yields of the coupling products increased substantially under milder conditions.[20,21] Meanwhile, Sheppard observed the n.m.r. spectrum of what seems to be the intermediary sulfurane, which upon warming, gave a coupling product, as shown below.[22]



The following reaction is another example, in which the coupling product, biphenyl and diphenyl sulfide were found to have 1/3 and 2/3 of the original ^{14}C of the starting sulfilimine at their ipso positions.[23] In this reaction, the ligand coupling

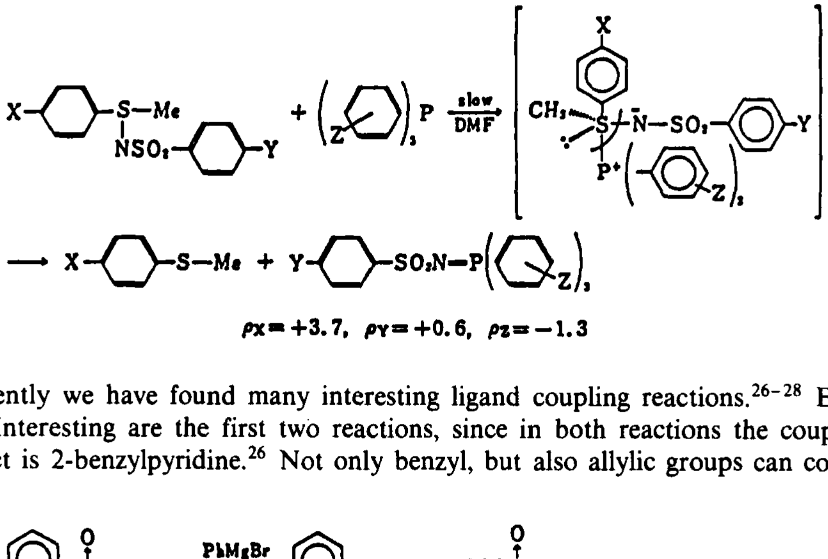




k (● ^{14}C, ◉ 2/3 ^{14}C, ○ 1/3 ^{14}C)

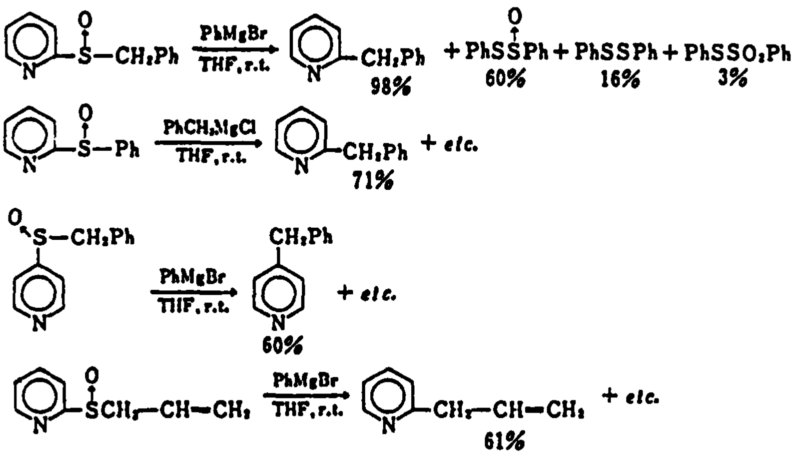
took place faster than the pseudorotation within σ-sulfurane. If the pseudorotation would be faster than the coupling, the resulting products should both contain 1/2 of ^{14}C at their ipso positions.

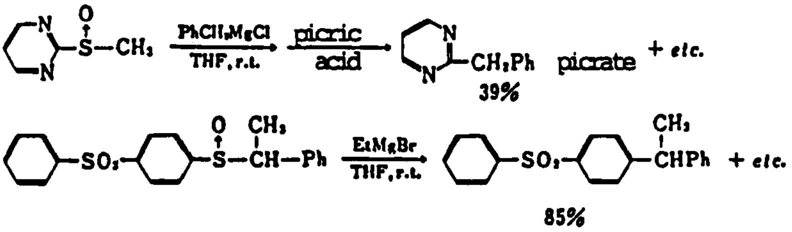
Ligand coupling reaction seems to be more pronounced when the central atoms of two coupling ligands are heteroatoms of high polarizabilities. The following is one such example.[24] The rate-determining step of this reaction is obviously the nucleophilic attack of the phosphine on the central sulfur atom, while the sulfurane formed can be trapped by protic solvents.[25]



$\rho_X = +3.7$, $\rho_Y = +0.6$, $\rho_Z = -1.3$

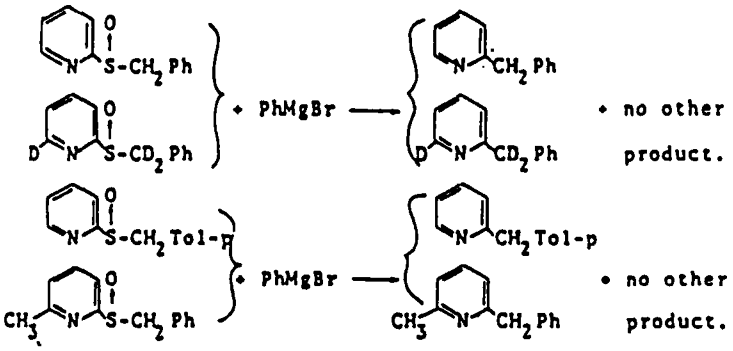
Recently we have found many interesting ligand coupling reactions.[26–28] Especially interesting are the first two reactions, since in both reactions the coupling product is 2-benzylpyridine.[26] Not only benzyl, but also allylic groups can couple



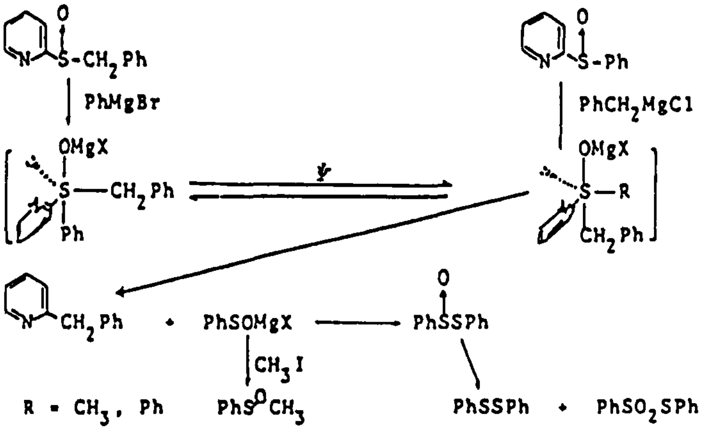


with pyridyl group, while an aromatic ligand bearing an electron-withdrawing group can also replace an heteroaromatic group to achieve a smooth coupling as shown above.

The following cross-over experiments revealed the intramolecular nature of the coupling reaction. Thus, the ligand coupling reaction to form 2-benzylpyridine may



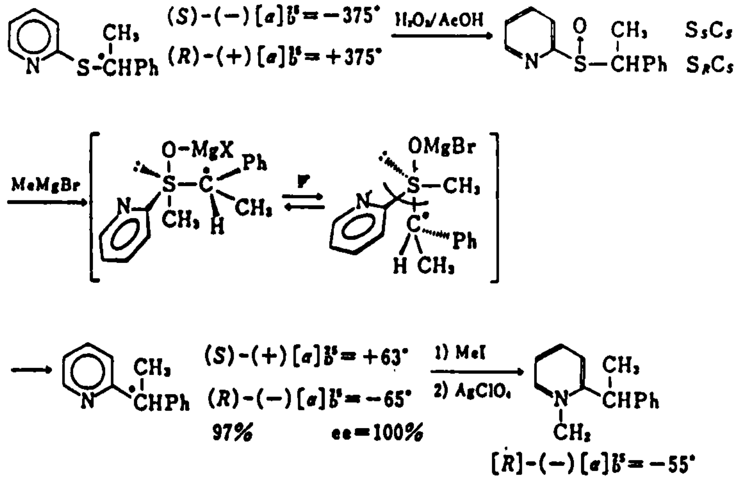
be as shown below.[26] The remaining organic sulfur species is PhSOMgX, which can



be converted by treating with methyl iodide to phenyl methyl sulfoxide or is quenched with water to give diphenyl thiosulfinate and its disproportionation products, as shown above.

B. Stereochemistry of Ligand Coupling on Sulfur Atom

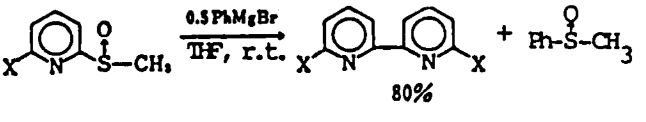
Since the coupling was found to proceed nearly quantitatively, we have carried out a stereochemical study of the coupling reaction using optically active 1-phenylethyl 2-pyridyl sulfoxide as shown in the following equation.

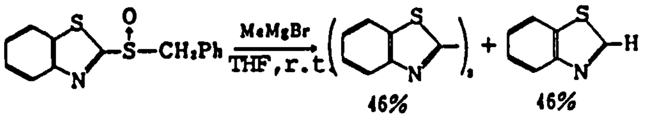


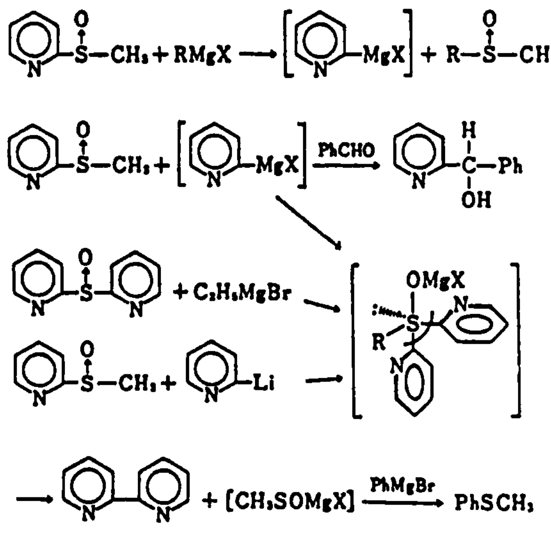
When the (S) isomer was converted to crystalline *N*-methyl perchlorate for X-ray crystallographic analysis, the compound was found to have retained the configuration completely.[29] This stereochemical study together with other accumulated observations clearly indicate that the ligand coupling within the σ-sulfurane is a concerted process.

C. Ligand Coupling and Ligand Exchange on Sulfur Atom

In the following reactions, the initial step is ligand exchange and the subsequent step involves ligand coupling of two identical heteroaromatic groups.[30] This was verified by trapping of 2-pyridylmagnesium bromide in the former reaction. Namely, in the presence of benzaldehyde, 2-pyridyl phenyl carbinol was obtained in 15% yield, along with 2,2′-bipyridine, the coupling product. Similar reactions, summarized in the following equations, are also found to proceed smoothly.



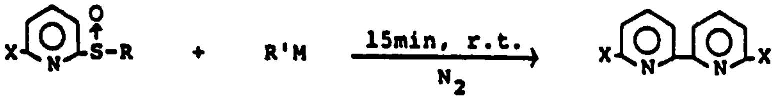




This is a very convenient method for preparing various 6.6′-substituted 2,2′-dipyridyls, as shown in Table I.[30]

It is interesting to see the change of yield of 2,2′-dipyridyl when R group changes from methyl to *t*-butyl in Table II.[31] As the bulkiness of R group increases, direct coupling between 2-pyridyl and phenyl group starts to compete with the consecutive reaction of ligand exchange and coupling. When R is *t*-butyl, the only reaction occurring was the direct coupling between 2-pyridyl and phenyl group. This would be expected due mainly to the bulky *t*-butyl group which would be placed at an axial position rather than at an equatorial position where the readily exchangeable 2-pyridyl group would be placed for facile ligand coupling.

TABLE I



X	R	R′M	Solvent	Time (min)	Yield (%)	X	R	R′M	Solvent	Time (min)	Yield (%)
H	CH_3	CH_3MgBr	THF	15	73	H		C_2H_5MgBr	THF	15	63
H	CH_3	C_2H_5MgBr	THF	15	57	Cl	CH_3	CH_3MgI	Et_2O	12h	24
H	CH_3	C_2H_5MgBr	Et_2O	15	30	Cl	CH_3	C_2H_5MgBr	THF	12h	33
H	CH_3	PhMgBr	THF	15	79	Cl	CH_3	C_2H_5MgBr	Et_2O	1h	55
H	CH_3	 Li	THF	15	59	Br	CH_3	C_2H_5MgBr	Et_2O	1h	50
H	C_2H_5	C_2H_5MgBr	THF	15	55	SCH_3	CH_3	C_2H_5MgBr	Et_2O	1h	61
H	Ph	C_2H_5MgBr	THF	15	42						

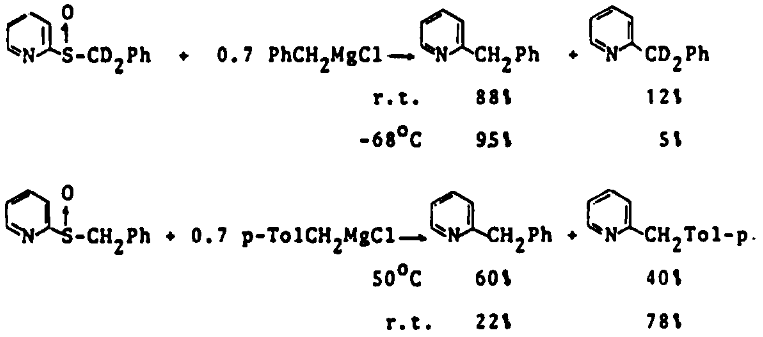
TABLE II

R	PhMgBr	Products	(%)			
Me	0.5		79[a]			PhS(=0)Me 36[a]
Me	1		78[a]			PhS(=0)Me 39[a]
Me	1		68		9	PhS(=0)Me 30 PhSMe 23
Et	0.5		56		4	PhS(=0)Et 30 EtSS(=0)Et 8
Et	1		56		6	PhS(=0)Et 52 PhSEt 20
i-Pr	1		59		17	PhS(=0)*i*-Pr 42
						*i*-PrSS(=0)*i*-Pr 23
t-Bu	1		0		85	*t*-BuSS(=0)*t*-Bu 63

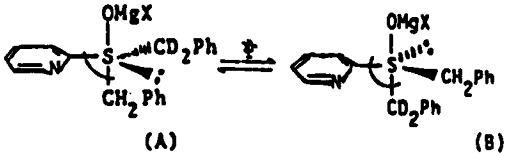
[a]) by g.l.c. analysis. In all reactions, 2-alkyl pyridine was not obtained.

D. Ligand Coupling and Pseudorotation

In the reaction of 2-pyridyl benzyl sulfoxide with either alkyl or aryl Grignard reagent or in that of 2-pyridyl alkyl or aryl sulfoxide with benzylmagnesium halide, the ligand coupling takes place always between 2-pyridyl and benzyl groups. This means that regardless of the incoming nucleophile which approaches the sulfur atom from an axial direction, pseudorotation always puts a 2-pyridyl group at an equatorial position and benzyl group at an axial coordinate for facile ligand coupling. However, there are cases in which ligand coupling proceeds faster than pseudorotation, as shown previously in the reaction of N-p-tosyldiphenylsulfilimine with phenylmagnesium bromide by our ^{14}C experiment.[23] Another example may be our recent finding, shown below.[31] In the former reaction, the incoming benzyl



group couples preferentially with 2-pyridyl group, whereas in order for 2-pyridyl and benzyl-D_2 groups to couple, the original sulfoxide has to undergo pseudorotation from (A) to (B). However, in the latter reaction especially at a higher temperature,

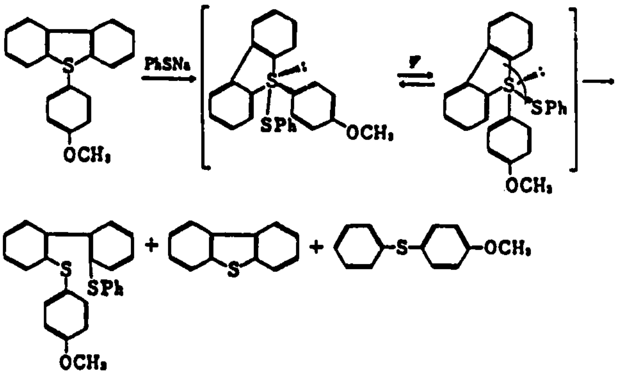


ca. 50 °C, pseudorotation seems to become relatively faster than ligand coupling. In view of the small values of free energies of activation for pseudorotation of sulfuranes, i.e., 7.4 Kcal (31.4 KJ)/mole to 13.5 Kcal (56.6 KJ)/mole for Martin's sulfuranes,[32] and 10.3 Kcal/mole for SF_4.[33] Ligand coupling would proceed much more readily than ligand exchange in most cases. The acid-catalyzed oxygen exchange, a typical ligand exchange reaction of sulfoxides, requires about 20 Kcal/mole of free energy of activation.[34] Thus, the ligand coupling is considered to be quite a common reaction for most hypervalent species.

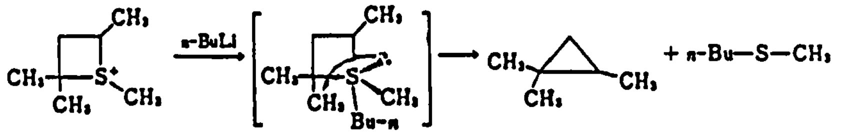
The scope and limitations of this coupling reaction of hypervalent species have not been well studied yet. However, in the reaction of sulfoxides with Grignard reagents, not only pyridyl group but also other heteroaryl groups, such as 2-thienyl and 2-furyl groups would undergo ligand coupling, based on our crude diagnosis of possible reactions on the basis of ^{13}C n.m.r. spectroscopic data. This crude diagnosis reveals that not only benzylic or allylic groups but also vinylic and electron-releasing alkyl groups such as ethyl, *t*-butyl groups can couple within the incipient σ-sulfurane formed in the reaction of sulfoxides with Grignard reagents.

E. Extension of Concept of Ligand Coupling on Various Reactions Involving Nucleophilic Attack on Tricoordinate Sulfur Atom

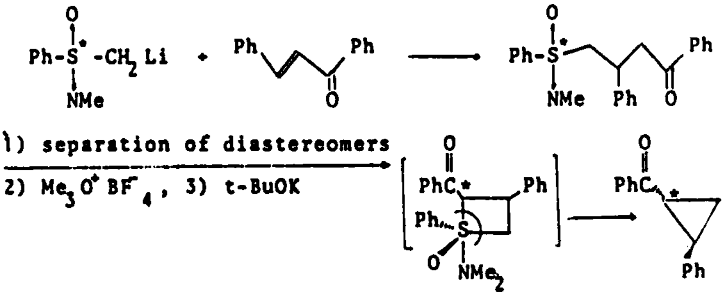
Since the concept of ligand coupling within the σ-sulfurane has now been fairly well substantiated, it is interesting to see how we can extend this concept to interpret mechanisms of hitherto known reactions and also to apply this concept for discovering many new reactions, useful for organic syntheses. Among so many examples, only a few reactions will be cited at this time. Hori et al. carried out many interesting reactions, which are typical ligand couplings,[35] among which only one example is shown below.

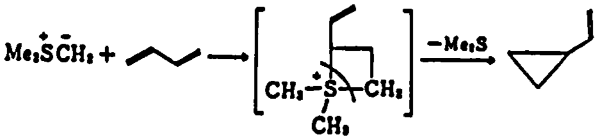


Another example is the following reaction.[36] Among numerous examples of

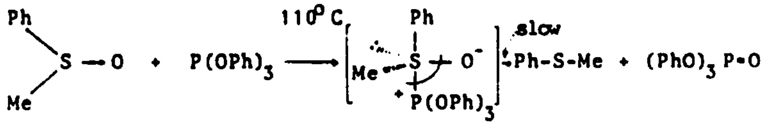


nucleophilic additions of sulfonium ylides to electrophilic conjugate olefins, only two works are chosen.[37,38]



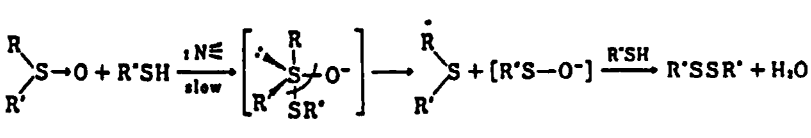


The following reductions of sulfoxides with either triphenyl phosphite[39] or thiols in the presence of amines[40] may be good examples of ligand coupling reactions.

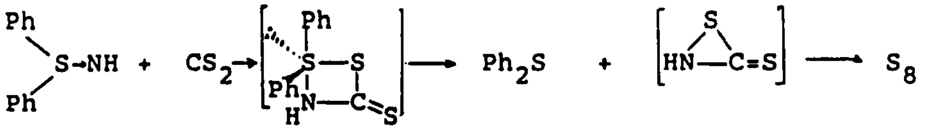


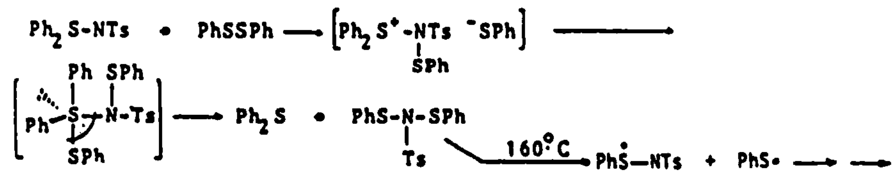
Reactivities : $MeC_6H_4S(O)Me > PhS(O)Me > ClC_6H_4S(O)Me$

$(ClC_6H_4)_3P > Ph_3P$

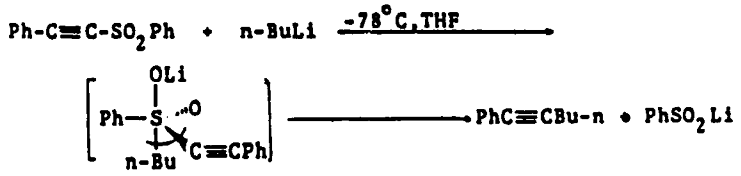


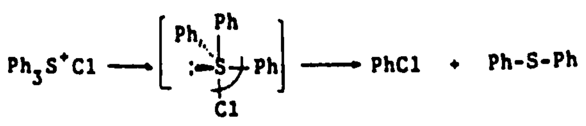
The following two reactions of sulfilimines would also proceed through ligand coupling.[41,42]





The following is another interesting example.[43] Pyrolysis of triphenylsulfonium chloride may also be another example.[44]





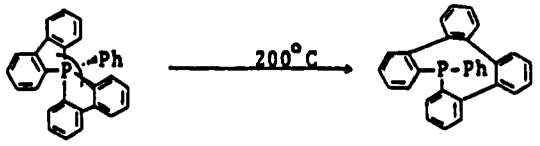
Among many analogous reactions carried out, the following two reactions of selenium and tellurium compounds are cited as examples.[45,46]

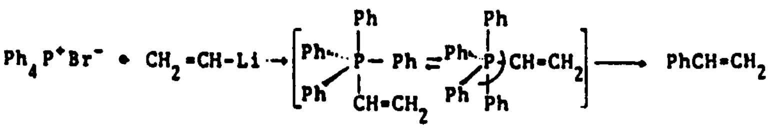
$$\mathrm{Ph_3Se^+Cl^-} + \mathrm{PhLi} \longrightarrow \mathrm{Ph\text{-}Ph} + \mathrm{Ph_2Se}$$

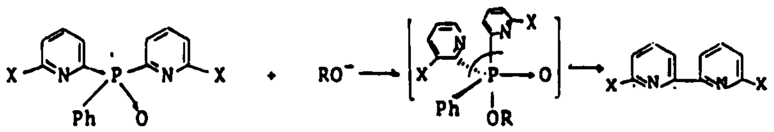
$$\mathrm{Ph_4Te} \xrightarrow{\Delta} \mathrm{Ph\text{-}Ph}\ 89\% + \mathrm{Ph_2Te}\ 92\%$$

F. Ligand Coupling on Phosphorus Atom

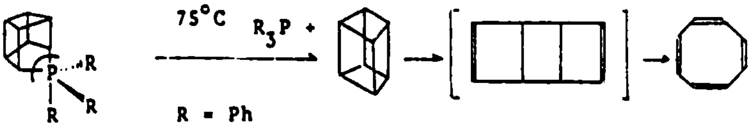
Pentacoordinate phosphoranes seem to be more stable than corresponding σ-sulfuranes, due probably to the neutral nature of the central P atom and hence have been often isolated; however, upon heating at a high temperature, they seem to undergo ligand coupling, as shown below.[47] Facile ligand couplings, found in the literature are the following two reactions.[48,49]

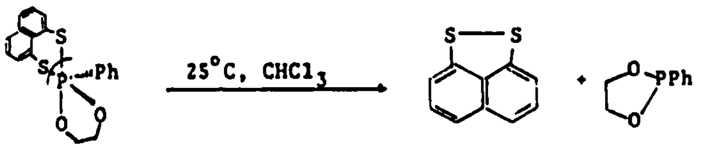






Two more examples[50, 51] are shown below.





Wittig *et al.* carried out the following reactions of hypervalent arsenic and antimony compounds.[52]

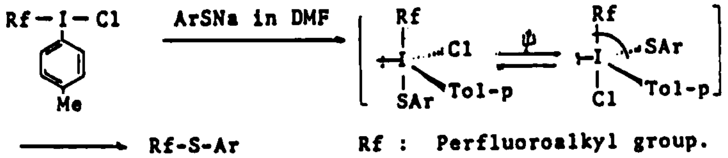
$$Ph_4As^+Br^- + PhLi \longrightarrow Ph_5As \longrightarrow Ph\text{-}Ph + Ph_3As$$

$$Ph_4Sb^+Br^- + PhLi \longrightarrow Ph_5Sb \longrightarrow Ph\text{-}Ph_{98.5\%} + Ph_3Sb_{96\%}$$

Unfortunately, no stereochemical study has been conducted to verify the coupling of axial and equatorial ligands.

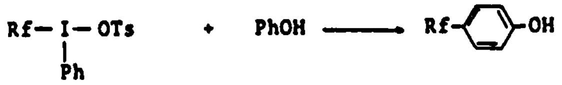
G. *Ligand Coupling on Iodine Atom*

Iodine-centered hypervalent compounds are also well known.[53] Interesting and quite useful reactions are the three following[54, 55] perfluorinations which are considered to be ligand couplings.

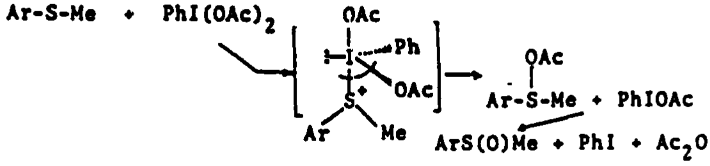


Rf : Perfluoroalkyl group.

$$Rf\text{—}\underset{\displaystyle Ph}{\underset{|}{I}}\text{—}OSO_3H + PhCH_2MgX \longrightarrow Rf\text{-}CH_2Ph$$



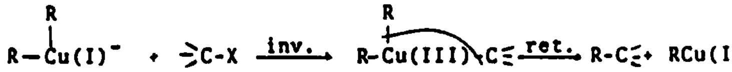
While many examples of pyrolyses of diaryl or diheteroaryl iodonium compounds would be ligand couplings,[56] oxidation of sulfides to sulfoxides by phenyliodoso diacetate is considered to be a ligand coupling reaction, as shown below, since the rates are nicely correlated by the Hammett σ-values, giving ρ-value of -0.8.[57]



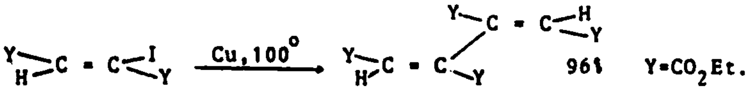
Similarly oxidation of sulfides by alkali metal periodates,[58,59] would also be ligand coupling reactions in view of the steric requirement of the reaction.

H. Ligand Coupling on Transition Metal Atoms

Among numerous investigations on the reactions of organometallic compounds, one finds many reactions in which retention of configuration of the coupling ligand is observed, similar to the ligand coupling in the hypervalent species. Indeed, in most these reactions, the intermediates are hypervalent species. Coupling with cuprates, R_2CuLi,[60–62] is most interesting, since coupling of two ligands on Cu is known to proceed with retention of configuration, after the initial S_N2 type reaction.[63]

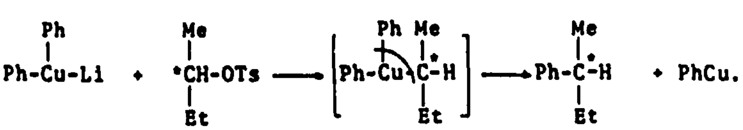


Even the Ullmann type reaction was shown to be stereoselective as shown below.[64]



Johnson *et al.* found two stereospecific reactions.[65,66]

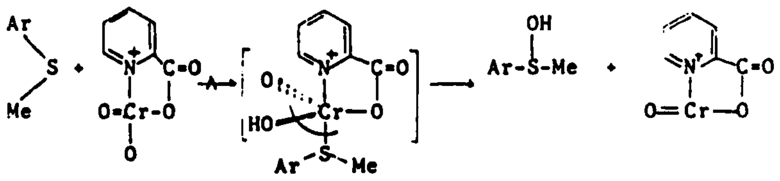
$$(-)(R)\text{-}2\text{-}C_4H_9\text{-}Br \xrightarrow{Ph_2CuLi} (+)(S)\text{-}2\text{-}C_4H_9\text{-}Ph \quad (87\%)$$



It is interesting to note that nucleophilic solvents such as ethers, amines and sometimes phosphines are used in these ligand coupling reactions on Cu atom. Perhaps by coordinating to the central Cu atom, which in turn becomes so rich with excess electrons, two ligands on Cu atom are readily extruded concertedly to afford the ligand coupling product. Many similar coupling reactions are found among Pd, Fe, Co and Ni catalyzed condensation reactions which are used for many industrial processes. However, these will be dealt with elsewhere.[67]

I. Oxidation of Heteroatoms with Metal Oxides

Certain metal oxides, such as MnO_4^- and acid chromate, $HCrO_4^-$, are strong oxygen transfer reagents to heteroatoms and the reactions are usually acid-catalyzed. One interesting example was selected to illustrate the oxygen transfer to be another ligand coupling reaction, as shown below.[68]



Although the oxidation was suggested to involve the initial rate-determining one electron transfer (SET) from sulfur atom to chromate, the large ρ-value, -1.66 at 40 °C, obtained by a nice correlation with the Hammett σ-values, seems to suggest that the rate-determining step to involve the nucleophilic attack of the divalent sulfur atom on the chromium atom, followed by fast ligand coupling, as shown above. The slow rate of oxidation of phenyl *t*-butyl sulfide, i.e., 1/10 of that of thioanisole, is in keeping with the mechanism. Oxidation of sulfides and olefins with other metal oxides, such as permanganate and osmium tetroxide are also considered to proceed through the same mechanistic path.

J. Conclusion

A new concept of ligand coupling within hypervalent intermediates has been presented with numerous experimental data, especially reactions involving the nucleophilic attack on the tricoordinate sulfur atom. Although this new concept has to be tested with numerous critical experiments, it would be quite interesting to see how this concept will be used for discovering many new reactions in the future.

K. Acknowledgement

From the beginning of this work, Professors N. Furukawa, Y. H. Kim, Drs. T. Aida and T. Yoshimura have contributed so much when the work began at Osaka City University. In recent years, Dr. T. Kawai devoted much to this work at the University of Tsukuba. Mr. Y. Kotera at U. T. and Mr. T. Takeda at O.U.S have also worked on this project earnestly. I am so grateful for their enthusiastic efforts. I would like to mention that so many old and new friends have offered me their kind suggestions and criticisms throughout this study and am so thankful for that.

REFERENCES

1. L. Pauling, *The Nature of the Chemical Bond*, 1st. Ed., Cornell University Press, Ithaca, New York, (1939).

2. J. I. Musher, *Angew. Chem., Int. Ed.*, **8**, 54 (1969).
3. R. J. Hoh and R. E. Rundle, *J. Am. Chem. Soc.*, **71**, 48 (1951); G. C. Pimentel, *J. Chem. Phys.*, **19** 446 (1951); See also S. Oae, "Historical Development of Sulfur Bonding", a chapter in *Theoretical and Experimental Advances in Organic Sulphur Chemistry*, ed. by A. Mangini, F. Bernardi and I. G. Csizmadia, Elsevier, Amsterdam, (1985).
4. V. B. Koutecky and J. I. Musher, *Theor. Chem. Acta*, **33**, 227 (1974).
5. M. M. Chen and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 1647 (1976).
6. I. Kapovits and A. Kalman, *Chem. Commun.*, **1971**, 649.
7. J. C. Martin and R. J. Arhart, *J. Am. Chem. Soc.*, **93**, 2339 (1971).
8. W. C. Hamilton and S. J. LaPlaca, *J. Am. Chem. Soc.*, **86**, 2289 (1964).
9. F. Iwasaki, private communication.
10. J. Bornstein and J. H. Supple, *Chem. & Ind.* (London), **1960**, 1333.
11. For the historical background, see G. Wittig, *Pure Appl. Chem.*, **9**, 245–254 (1964).
12. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 3782 (1962).
13. S. Oae, "Yuki-Io-Kagaku," *Organic Sulfur Chemistry, Reaction Mechanism*, Kagaku Dojin, Kyoto, (1982), p. 5.
14. E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).
15. S. Oae and M. Kise, *Tetrahedron Lett.*, **1967**, 1409.
16. S. Oae, M. Yokoyama, M. Kise, and N. Furukawa, *Tetrahedron Lett.*, **1968**, 4131.
17. S. Oae, T. Kawai and N. Furukawa, *Tetrahedron Lett.*, **1984**, 69.
18. Y. H. Khim and S. Oae, *Bull. Chem. Soc. Jpn.*, **42**, 1968 (1969).
19. B. M. Trost, R. LaRochelle and R. C. Atkins, *J. Am. Chem. Soc.*, **91**, 2175 (1969); **93**, 6077 (1971).
20. B. M. Trost and H. C. Arndt, *ibid.*, **95**, 5288 (1973).
21. K. K. Andersen, S. A. Yeager and N. B. Peynircioglu, *Tetrahedron Lett.*, **1970**, 2485; H. Harrington, J. Weston, J. Jacobus and K. Mislow, *Chem. Commun.*, **1972**, 1079.
22. W. A. Sheppard, *J. Am. Chem. Soc.*, **93**, 5597 (1971).
23. S. Oae, T. Yoshimura and N. Furukawa, *Bull. Chem. Soc. Jpn.*, **45**, 2019 (1972).
24. T. Aida, N. Furukawa and S. Oae, *Chem. Lett.*, 805 (1973); **29** (1976); *J. Chem. Soc., Perkin II*, **1976**, 1438.
25. S. Oae, T. Aida and N. Furukawa, *Chem. Pharm. Bull.*, **1975** 3011; *Int'l. J. Sulfur Chem.*, **1973**, 401.
26. S. Oae, T. Kawai and N. Furukawa, *Bull. Chem. Soc. Jpn.*, in press.
27. Y. Kotera and T. Takeda, unpublished work from this laboratory.
28. T. Kawai, Ph. D. Thesis at The University of Tsukuba, (1985).
29. F. Iwasaki, private communication.
30. T. Kawai, N. Furukawa and S. Oae, *Tetrahedron Lett.*, **25**, 2549 (1984).
31. T. Kawai and T. Takeda, unpublished work from this laboratory.
32. J. C. Martin and E. Perozzi, *Science*, **191**, 154 (1976); G. W. Astrologes and J. C. Martin, *J. Am. Chem. Soc.*, **98**, 2895 (1976).
33. I. W. Levin and W. C. Harris, *J. Chem. Phys.*, **55**, 3078 (1971).
34. N. Kunieda, K. Sakai and S. Oae, *Bull. Chem. Soc. Jpn.*, **42**, 1090 (1969); N. Kunieda and S. Oae, *ibid.*, **42**, 1324 (1969); N. Kunieda and S. Oae, *ibid.*, **46**, 1745 (1973).
35. M. Hori, T. Kataoka and H. Shimizu, *Chem. Pharm. Bull.*, **22**, 1711, 2004, 2014, 2020, 2030 (1974).
36. B. M. Trost, W. L. Schinski and J. T. Manz, *J. Am. Chem. Soc.*, **91**, 4320 (1969), *ibid.*, 93, 676 (1971).
37. C. R. Johnson, C. W. Schroeck and J. R. Shauklin, *J. Am. Chem. Soc.*, **95**, 7424 (1973).
38. J. Kiji and M. Iwamoto, *Tetrahedron Lett.*, 2749 (1966).
39. S. Oae, A. Nakanishi and S. Kozuka, *Tetrahedron*, **28**, 549 (1972).
40. T. J. Wallace and J. J. Mahon, *J. Org. Chem.*, **30**, 1502 (1965).
41. R. Appel and W. Buchner, *Chem. Ber.*, **95**, 2220 (1962).
42. S. Oae, Y. Tsuchida, K. Tsujihara and N. Furukawa, *Bull. Chem. Soc. Jpn.*, **45**, 2856 (1972).
43. R. L. Smorada and W. E. Truce, *J. Org. Chem.*, **44**, 3444 (1979).
44. G. H. Wiegant and W. E. McEwen, *J. Org. Chem.*, **33**, 2671 (1968).
45. G. Wittig and H. Fritz, *Liebig Ann.*, **577**, 39 (1952).
46. D. H. R. Barton, S. A. Glover and S. V. Ley, *Chem. Commun.*, 266 (1977).
47. G. Wittig and A. Maercker, *Chem. Ber.*, **97**, 747 (1964).
48. D. Seyferth, J. Fogel and J. K. Heeren, *J. Am. Chem. Soc.*, **88**, 2207 (1966).
49. G. R. Newkome and D. C. Hager, *J. Am. Chem. Soc.*, **100**, 5567 (1978).
50. T. J. Katz and E. W. Turnblom, *J. Am. Chem. Soc.*, **92**, 6701 (1970); E. W. Turnblom and T. J. Katz, *Chem. Commun.*, 1270 (1972).
51. Y. Kimura, T. Kokura and T. Saegusa, *J. Org. Chem.*, **47**, 3815 (1983).
52. G. Wittig and K. Claus, *Liebig Ann.*, **577**, 26 (1952).
53. S. Tamagaki and S. Oae, "Electronic Structures of σ-Hypervalent Sulfur Compounds—Three Center Four Electron σ-Bonding", Part 2. Kagaku-no Ryoiki (*J. Jpn. Chem.*), **31**, 218–223 (1977); W. Agosta, *Tetrahedron Lett.*, 2681 (1965); A. T. Balaban, *Rev. Roumaine Chim.*, **14**, 1281 (1969).

54. V. V. Lyalim, V. V. Orda, L. A. Alekseeva and L. M. Yagupolskii, *Zh. Org. Khim.*, **7**, 1473 (1971); L. M. Yagupolskii, I. I. Maletina, N. V. Kondratenko and V. V. Orda, *Synthesis*, 835 (1978).
55. T. Umemoto, *Yukigosei-Kagaku*, **41**, 251–265 (1983); T. Umemoto and Y. Kuriu, *Tetrahedron Lett.*, **22**, 5197 (1981); T. Umemoto and O. Miyano, *Bull. Chem. Soc. Jpn.*, **57**, 3361 (1984).
56. A. J. Margida and G. F. Koser, *J. Org. Chem.*, **49**, 3643 (1984).
57. C. Srinivasan, A. Chellamani and P. Kuthalingam, *J. Org. Chem.*, **47**, 428 (1982); see also Ph.D. Thesis of S. Rajagopal at Madurai Kamaraj Univ. (1984).
58. Y. H. Kim, T. Takata and S. Oae, *Tetrahedron Lett.*, 2305 (1978); T. Takata, Y. H. Kim and S. Oae, *Bull. Chem. Soc., Jpn.*, **54**, 1443 (1981).
59. K. W. Buch, T. A. Hamor and D. J. Watkin, *Chem. Commun.*, 759 (1966).
60. G. H. Posner, "Substitution Reactions using Organocopper Reagents", *Org. Reactions*, **22**, Chapter 2, 252–400 (1975).
61. G. H. Posner, "Conjugative Addition Reactions of Organocopper Reagents", *Org. Reactions*, **19**, Chapter 1, 1–114 (1972).
62. B. H. Lipshutz, R. S. Wilhelm and J. A. Kozlowski, "The Chemistry of Higher Order Organocuprates", *Tetrahedron Report, No. 176*, *Tetrahedron*, **40**, 5005–5038 (1984).
63. G. M. Whitesides, J. S. Filippo, E. R. Stredronsky and C. P. Casey, *J. Am. Chem. Soc.*, **91**, 6542 (1969).
64. T. Cohen and T. Poeth, *J. Am. Chem. Soc.*, **94**, 4363 (1972).
65. C. R. Johnson and G. A. Dutra, *J. Am. Chem. Soc.*, **95**, 7783 (1973).
66. C. R. Johnson and G. A. Dutra, *J. Am. Chem. Soc.*, **95**, 7777 (1973).
67. S. Oae, *Croatica Chem. Acta*, in press.
68. S. Rajagopal, *Kinetics and Mechanism of Oxidation of Organic Compounds*, Ph.D. Thesis at Madurai Kumaraj University (1984).