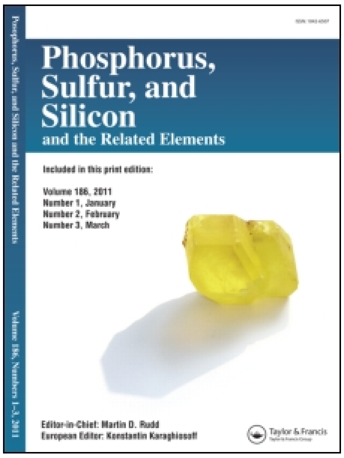

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Thionyl Chloride-A Good Ligand Coupling Reagent-

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THIONYL CHLORIDE -A GOOD LIGAND COUPLING REAGENT-

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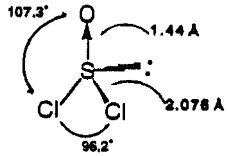
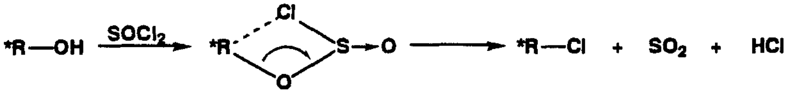
A. INTRODUCTION

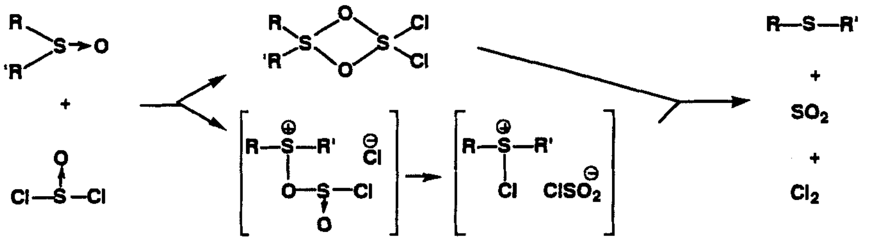
Thionyl chloride is known to be a pyramidal structure as show below[1)]



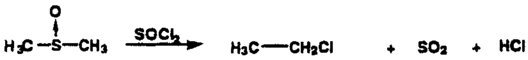
and has been known to be a good chlorinating reagent of aliphatic alcohols, amides, carbonylates, epoxides, oximes and sulfonic acids and various others.[2)] It reacts with phenols to afford phenolic diaryl sulfides.[3)] A good example would be the reaction of a seconary alcohol with thionyl chloride, shown below, which has been known to proceed with a partial retention of configuration as shown below.



Thionyl chloride has been known to be a good deoxygenation reagent for the sulfoxides as shown below.[4)] Two mechanisms have been suggested but no clear discrimination has been made.

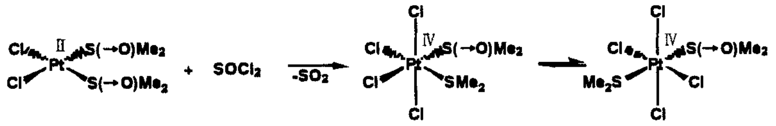


The following is another deoxygenation but involves rearrangement.[5)]

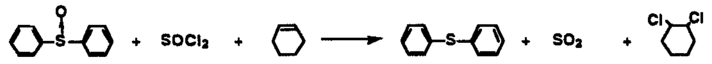


$$H_3C-\overset{O}{\overset{\uparrow}{S}}-CH_3 \xrightarrow{SOCl_2} H_3C-CH_2Cl + SO_2 + HCl$$

Another example of deoxygenation is the following.[6]



Thionyl chloride was shown to be deoxygenated as well as chlorinating olefine as shown below.[7]



Few reactions have been known for the reactions of organometallic reagents with thionyl chloride. Representive reactions are shown below.[8]

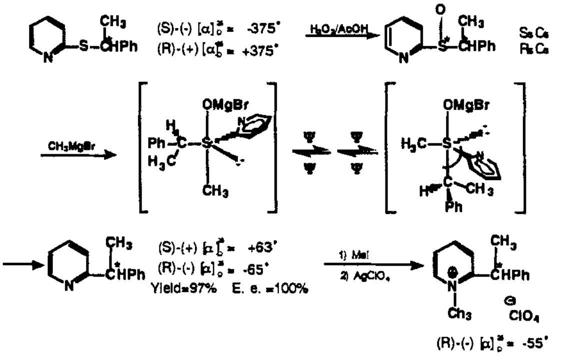
$$R_4Pb \xrightarrow{SOCl_2} R_3PbCl + R_2PbCl_2 + RSOCl + R\text{-}S(O)\text{-}R$$

$$Hg(SCF_3)_2 \xrightarrow{SOCl_2} CF_3SSCF_3 + SO_2 + HgCl_2$$

$$2RMgBr \xrightarrow{SOCl_2} R\text{-}S(O)\text{-}R + MgCl_2 + MgBr_2$$

B. LIGAND COUPLING

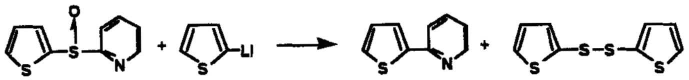
In the meantime, we have shown the stereochemistry of the reactions,[9] and



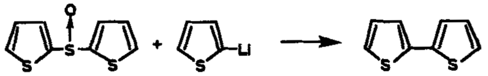
elucidated the concept of ligand coupling within hypervalent species as shown above.

Earlier, we thought that ligand coupling reaction proceeds between aryl methyl sulfoxides and benzylmagnesium halides when the ipso-carbon of the aryl group is between 177 and 150 ppm by ^{13}C nmr scale,[11] however, in the rection without using benzylmagnesium halides, it is rather inconvenient to diagnose the reaction path, particularly when we use other organometallics , such as 2-thienyllithium. Thus, we have shifted to pKa value of the ipso position of the sulfoxide, and partially succeeded.

However, we do not delineate this idea here. The following ligand coupling reaction was found to take place.12)



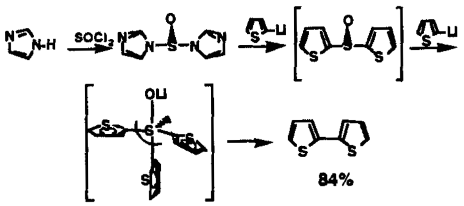
Since pKa value of the 2-position thiophene is 33.0 while ^{13}C chemical shift of 2-thienyl sulfoxide is just in the range of ligand coupling, we have treated di-2-thienyl sulfoxide with 2-thienyllithium and indeed a nice ligand coupling took place, as shown below.



C. THIONYL CHLORIDE -GOOD LIGAND COUPLIG REAGENT-

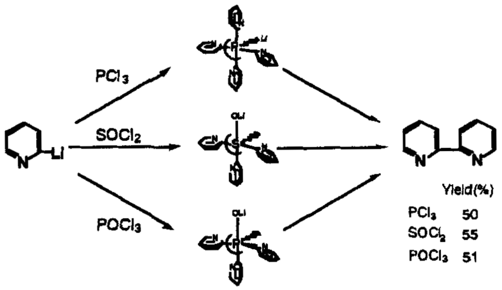
In order to make the sulfoxide, we used a standard procedure13), of using

imidazole, as shown above, however we found instead of having



di-2-thienyl sulfoxide, a direct ligand coupling reaction took place, as shown above. As one expects the yield of the coupling , 2-bithieny increased as the mole ratio increases, attaining the maximum yield when 3 moles of 2-thienyllithium was used.

The following reactions indicated that one can use not only thionyl chloride but also other chlorinating agents,14) as shown below.



Meanwhile, we attempted to study the streochemistry and treated both cis and trans β-bromostyrene with thionyl chloride, however, we found that the first step to be the formation of phenylacetylene, which then further treatment with n-BuLi to form ω-lithiated-phenylacetylene that reacted with thionyl chloride, as shown below. Here again, as in the case of 2-thienyllithium, 3 moles of the lithium compound incresed the yield of ligand coupling product, di-1, 4-phenyl-butadiyne, as shown in Table I.

Table I

$$\mathrm{PhC{=}CH{-}Br} \xrightarrow{^{n}\mathrm{BuLi}} \mathrm{PhC{\equiv}C{-}H} \xrightarrow{^{n}\mathrm{BuLi}} \mathrm{PhC{\equiv}C{-}Li} \xrightarrow{\mathrm{SOCl_2}} \mathrm{PhC{\equiv}C{-}C{\equiv}CPh}$$

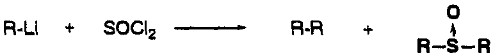
Phenylacetylene (eq.)[1]	^{n}BuLi (eq.)[1]	Product(%)[2]
1	1	12
2	2	24
3	3	96

1) Equimolar to $SOCl_2$ 2) Determined by glc analysis

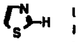
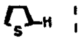
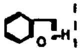
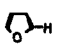
Some years ago, phenylethynylmagnesium halides was treated with thionyl chloride and a similar coupling was observed.[15)]

Other examples of both ligand coupling and exchange are listed in Table II.

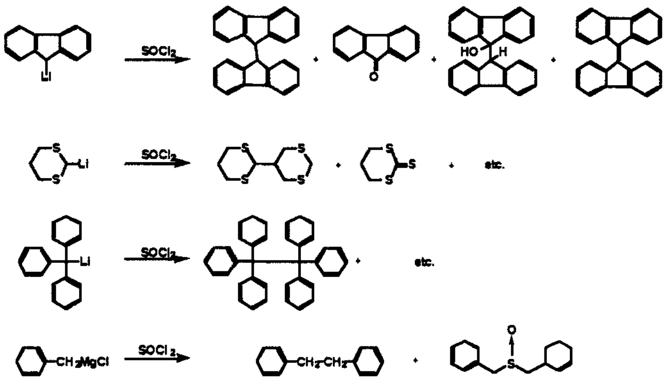
Table II Ligand Coupling and Exchange of Some Heterocycles with $SOCl_2$



$$\mathrm{R{-}Li} + \mathrm{SOCl_2} \longrightarrow \mathrm{R{-}R} + \mathrm{R{-}\overset{O}{\overset{\uparrow}{S}}{-}R}$$

R-H	pKa	Products (%) R-R	R-S-R	R-S(O)-R	Chemical Phenomenon
	28.3	33	15	17	L. C
	27.8 ~ 28.9	29	11	19	L. C
	33.0	48	-	-	L. C
	33.2	48	27	17	L. C
	32.4 ~ 33.5	-	-	34	L. E.
	35.6	-	-	45	L. E.

We believe that thionyl chloride is a good ligand coupling reagent for some heteroaromatic compounds and phenylacetylene, however, for lithiated carbon of sp^3 species whose pKa values are in the range of ligand couplig reaction, does not necesarily applicable. For example, lithiated fluorene reacts with thionyl chloride but the products are rather complicated. 2-Lithio-1, 3-dithiane reacts but gives a meager amount of the ligand coupling product, while benzyl Grignard reagent affords while benzyl



Grignard reagent affords dibenzyl, seemingly the coupling reaction but need some further study.

REFERENCE

1) I. Hargittai, *Acta. Chim.*, 60(3), 231(1969).

2) J. March, "Advanced Organic Chemistry", pp. 1490(1992).

3) S. Oae and C. Zalut, *J. Am. Chem. Soc.*, 62, 6359(1969).

4) T. Numata, K. Ikura, Y. Shimano and S. Oae, *Org. Prep. Proc. Int.*, 8, 119(1976); J. Drabowicz, T. Numata and S. Oae, *Org. Prep. Proc. Int.*, 9, 63(1977); J. Drabowicz, H. Togo, M. Mikolajcxyk and S. Oae, *Org. Prep. Proc. Int.*, 16, 171(1984); S. Oae, "Organic Sulfur Chemistry: Streucture and Mechanism", Boca Raton CRC Press pp.312 (1991).

5) F. G. Bordwell and B. M. Pitt, *J. Am. Chem. Soc.*, 77, 572(1955).

6) V. Yu. Kukushkin and E. Yu. Pankova., *Koord. Khim.*, 15, 531(1989); *Soc. J. Coor. Chem.* (Eng. Transl.)15, 331 (1989), acoord. to a private commun.

7) I. Granoth, J. Chem. Soc., Perkin Trans. II, 2166(974).

8) M. Davis, H. Szkuta and K. Krubsack, "Mechanism of Sulfur Compounds", 9, 7(1970).

9) S. Oae, T. Kawai and N. Furukawa, *Tetrahedron Lett.* 25, 69(1984); S. Oae, T. Kawai, N. Furukawa and F. Iwasaki, *J. Chem. Soc. Perkin Trans.*, 2, 405 (1987) and many others cited in S. Oae, *Rev. on Heteroatom Chem.*, 4, 195(1991).

10) S. Oae, *Croat. Chem. Acta.*, 59, 129(1986); S. Oae, *Phosphorous & Sulfur*, 27, 13(1986); see in detail S. Oae, "Organic Sulfur Chemistry-Streucture and Mechanism-" CRC Press, Boca Raton, Florida(1991), Chapter 5, pp.183-201.

11) T. Kawai, Y. Kotera, N. Furukawa, S. Oae, M. Isida, T. Takeda and S. Wakabayashi, *Phosphorous & Sulfur*, 34, 139(1987).

12) S. Oae, Y. Inubushi and M. Yoshihara, *Heteroatom Chem.*, 4, 185(1993); S. Oae, Y. Inubushi and M. Yoshihara, ibid. 5, (in publication) .

13) S. Bast and K. Andersen, *J. Org. Chem.*, 33, 846(1968).

14) Y. Uchida and S. Oae, *Heteroatom Chem.*, 5, (in publication) 65th Chem. Soc. Jpn. Spring Meeting in 1993.

15) A. Uchida, T. Nakazawa, I. Kondo, N. Iwata and S. Matsuda, *J. Org. Chem.*, 37, 3749(1972).