(t, 1 H, SH), 2.2 (s, 3 H, CH_3), 3.8 (d, 2 H, CH_2), 6.8 (d, 1 H, Ar), 7.1 (d, 1 H, Ar). Anal. Calcd for $C_6H_8S_2$: C, 50.00; H, 5.60. Found: C, 50.4; H, 5.8.

The alcohols used to obtain the thiols and to produce the corresponding aldehyde anion radicals were obtained by reduction of the analogous aldehydes with $NaBH_4$, except in the case of the commercially available precursors of **3a**, **3b**, **4a**, and **4b**. The alcohols that yield the following radical anions have been reported: **5c**,[32] **6c**,[31] **7a**,[33] **7b**,[34] and **7c**.[34] The remaining alcohols that yield, respectively, the radical anions listed below were identified as follows.

Precursor of **5d**: ^1H NMR ($CDCl_3$) 1.8 (s br, 1 H, OH), 2.5 (s, 3 H, CH_3), 4.8 (d, 2 H, CH_2), 6.65 (d, 1 H, Ar), 6.8 (d, 1 H, Ar). Anal. Calcd for C_6H_8OS: C, 56.24; H, 6.29. Found: C, 56.9; H, 5.8. Precursor of **6d**: ^1H NMR ($CDCl_3$) 1.6 (s br, 1 H, OH), 2.2 (s, 3 H, CH_3), 4.8 (d, 2 H, CH_2), 6.8 (d, 1 H, Ar), 7.15 (d, 1 H, Ar). Anal. Calcd for C_6H_8OS: C, 56.24; H, 6.29. Found: C, 56.4; H, 6.5.

Spectral Measurements. The ESR spectra were obtained by photolyzing the samples in the cavity of the spectrometer (Varian E 3) by means of a carefully focused 500-W high-pressure Hg lamp. The samples were prepared by dissolving the thiols or the alcohols in EtOK/EtOH with the addition of *t*-BuOOBu-*t*. The solutions were degassed and sealed in vacuo. The temperatures reported in the tables are those where the best signal to noise ratio was achieved; the conformer ratio, however, did not change in an appreciable manner within the temperature range examined.

Acknowledgment. The work was carried out with the financial support of MURST and CNR (Rome). We are indebted to Dr. K. U. Ingold (Ottawa, Canada) for helpful comments.

(32) Trahanovski, W. S.; Park, M.-G. *J. Org. Chem.* **1974**, *39*, 1449.
(33) Brown, H. C.; Vara Prasad, J. V. N.; Zee, S. H.; Richard, B. *J. Org. Chem.* **1986**, *51*, 439.
(34) Sjoholm, R.; Woerlund, K. *Acta Chem. Scand.* **1980**, *B34*, 435.

Extremely Facile Ligand-Exchange and Disproportionation Reactions of Diaryl Sulfoxides, Selenoxides, and Triarylphosphine Oxides with Organolithium and Grignard Reagents

Naomichi Furukawa,* Satoshi Ogawa, Kazunori Matsumura, and Hisashi Fujihara

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Received March 13, 1991

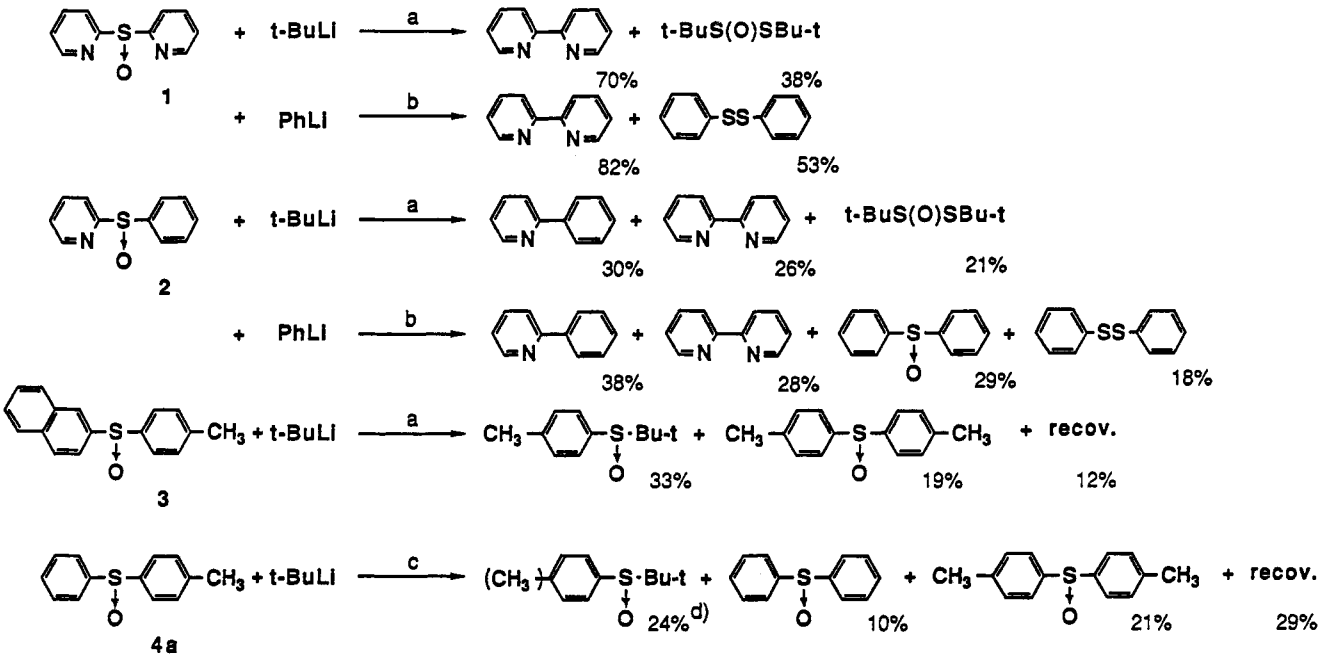
Diaryl sulfoxides undergo unusually rapid ligand-exchange reaction upon treatment with organolithium reagents at −95 °C. Optically pure phenyl *p*-tolyl sulfoxide (**4b**) reacted with organolithium reagents at the range from −20 to −95 °C to give facile ligand-exchange and disproportionation products, i.e., diphenyl sulfoxide (**7**), recovered **4b**, and di-*p*-tolyl sulfoxide (**8**) in a statistical ratio of 1:2:1 in quantitative yields, and the recovered **4b** was completely racemized. This facile ligand exchange was observed in the similar reactions using only diaryl selenoxides and triarylphosphine oxides. The reactions of ^{18}O-labeled phenyl *p*-tolyl sulfoxide (**4c**) with organolithium reagents gave products in a statistical ratio without ^{18}O scrambling, indicating that only the C–S bond cleavage took place under low temperature. It is suggested that the ligand exchange reactions occur by the nucleophilic attack by organolithium reagent at the sulfinyl sulfur atom, giving σ-sulfurane as an intermediate that collapses rapidly. These results suggest that the treatment of arylic sulfoxides, selenoxides, and phosphine oxides with strong bases should be effected with caution.

It has been known that alkyl aryl or haloalkyl aryl sulfoxides undergo simple substitution reaction on the sulfinyl sulfur atom upon treatment with Grignard or organolithium reagents to afford the sulfoxides in which the more electronegative ligand is usually replaced with organometallic reagents.[1] These reactions proceed with inversion of configuration at sulfur via a σ-sulfurane by analogy to the oxygen-exchange reaction of sulfoxides.[2] The procedures have been used for desulfinylation from organic compounds as well as the preparation of new Grignard or organolithium reagents,[3] and hence, these reactions have found application to various asymmetric syntheses.[4] It was found that azaheteroaryl sulfoxides react with Grignard or organolithium reagents to afford biaryls in high yields.[5] These ligand-coupling reactions have generally been observed in the reactions of sulfonium salts with organometallic reagents providing new methods of carbon–carbon bond formation. The mechanism is believed to involve a σ-sulfurane.[6] Meanwhile, a few diaryl sulfoxides have been demonstrated to give triaryl sulfonium salts on treatment with Grignard or organolithium reagents, indicating that the oxygen atom of the sulfoxides becomes a leaving group.[7] Thus, although the ligand exchange or coupling reactions of sulfoxides with organometallic reagents have been studied, whether the σ-sulfuranes [10-S-4(C_3O_1)][8] are intermediates or transition states remain unresolved. In order to detect and investigate the nature of σ-sulfuranes, we reacted diaryl sulfoxides with organolithium or Grignard reagents under various temperatures, since it has been known that attachment of aryl ligands stabilizes the hypervalent compounds such as

(1) (a) Jacobus, J.; Mislow, K. *J. Am. Chem. Soc.* **1967**, *89*, 5228. (b) Andersen, K. K. *Tetrahedron Lett.* **1970**, 2485. (c) Lockard, J. P.; Schroeck, C. W.; Johnson, C. R. *Synthesis* **1973**, 485. (d) Durst, T.; LeBelle, M. J.; Elzen, R.; Tin, K. C. *Can. J. Chem.* **1974**, *52*, 761. (e) Nokami, J.; Kunieda, N.; Kinoshita, M. *Chem. Lett.* **1977**, 249. (f) Hojo, M.; Masuda, R.; Saeki, T.; Fujimori, K.; Tsutsumi, S. *Synthesis* **1977**, 789.
(2) Kunieda, N.; Sakai, K.; Oae, S. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1090. Kunieda, N.; Oae, S. *Ibid.* **1969**, *42*, 1324. Kunieda, N.; Oae, S. *Ibid.* **1973**, *46*, 1745.
(3) Furukawa, N.; Shibutani, T.; Fujihara, H. *Tetrahedron Lett.* **1986**, *27*, 3899.
(4) Satoh, T.; Kaneko, Y.; Yamakawa, K. *Tetrahedron Lett.* **1986**, *27*, 2379. Satoh, T.; Oohara, T.; Ueda, Y.; Yamakawa, K. *Ibid.* **1988**, *29*, 313, 4093. Theobald, P. G.; Okamura, W. H. *Ibid.* **1987**, *28*, 6565.
(5) Furukawa, N.; Shibutani, T.; Fujihara, H. *Tetrahedron Lett.* **1987**, *28*, 5848.
(6) Oae, S.; Kawai, T.; Furukawa, N.; Iwasaki, F. *J. Chem. Soc., Perkin Trans. 2*, **1987**, 405.
(7) (a) Wildi, B. S.; Taylor, S. W.; Potratz, H. A. *J. Am. Chem. Soc.* **1951**, *73*, 1965. (b) Ackerman, B. K.; Andersen, K. K.; Nielsen, I. K.; Peynircioglu, N. B.; Yeager, S. A. *J. Org. Chem.* **1974**, *39*, 964.
(8) Martin, J. C. *Science* **1983**, *221*, 509.

0022-3263/91/1956-6341$02.50/0

Scheme I[a]



[a] Key: a, tetrahydrofuran/−95 °C; b, tetrahydrofuran/−78 °C; c, tetrahydrofuran/−85 °C; d, mixture of phenyl and tolyl.

pentaphenylphosphorane (Ph_5P)[9] and tetraphenyltellurane (Ph_4Te).[10] Indeed, in the case of sulfur compounds, Sheppard reported the formation of tetra(pentafluorophenyl)sulfurane as an unstable intermediate in the reaction of SF_4 and C_6F_5Li at −80 °C.[11] This result suggests that the σ-sulfuranes might become detectable intermediates. Unexpectedly, we observed extremely facile ligand exchange and disproportionation reactions of diaryl sulfoxides with organolithium reagents. These facile ligand exchange and disproportionation reactions were also observed even in the similar reactions of diaryl selenoxides and triarylphosphine oxides with organometallic reagents. In this paper, we report these unusually facile ligand-exchange reactions and propose a mechanism for the exchange reaction via a σ-sulfurane on the basis of stereochemical and ^{18}O isotopic labeling experiments.

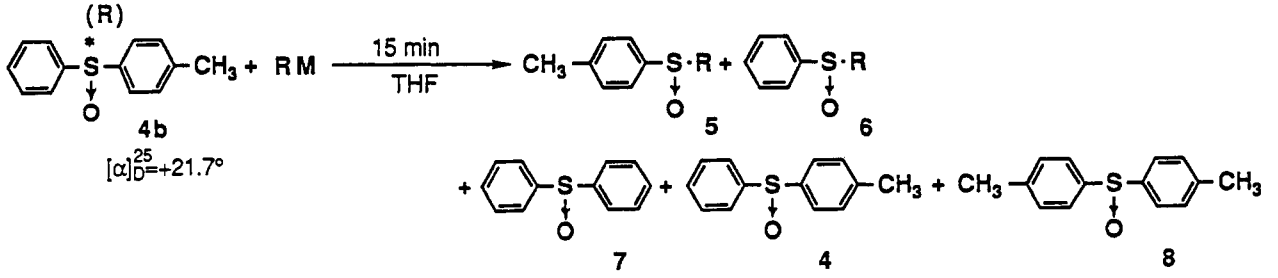
Results and Discussion

Ligand Coupling and Exchange Reactions of Diaryl Sulfoxides. This investigation was started aiming to synthesize ortho-lithiated diphenyl sulfoxide using lithium diisopropylamide (LDA) in tetrahydrofuran (THF) solution. This reaction was performed readily, and the ortho-lithiated sulfoxide reacted with aldehydes to afford desired ortho-substituted diphenyl sulfoxides in moderate yield.[12] However, when phenyl *p*-tolyl sulfoxide (**4a**) was similarly treated with LDA and then with aldehyde, diphenyl, phenyl *p*-tolyl, and di-*p*-tolyl sulfoxides were obtained in substantial yields together with the desired ortho-substituted phenyl *p*-tolyl sulfoxides. Since this disproportionation was undesirable for synthetic purposes, we investigated its origin and found that it was initiated by a small excess amount of unconsumed *n*-butyllithium (*n*-BuLi). Therefore, in order to elucidate clearly the nature of this unusual disproportionation reaction of diaryl sulfoxides, several diaryl sulfoxides having electron-withdrawing and -donating aryl groups were synthesized and reacted with alkyl- or aryllithium reagents. When di-2-pyridyl sulfoxide (**1**) was treated with alkyl- or aryllithium, only ligand-coupling reaction took place to afford 2,2′-bipyridine in moderate yield. However, when phenyl 2-pyridyl sulfoxide (**2**) was treated similarly, both ligand-coupling and ligand-exchange products were obtained, but no disproportionation was observed at all.[13] On the other hand, when 2-naphthyl *p*-tolyl sulfoxide (**3**) or phenyl *p*-tolyl sulfoxide (**4a**) was treated with *t*-BuLi, the facile ligand-exchange and disproportionation reactions proceeded at the range from −78 to −95 °C (Scheme I).

Reactions of Optically Active Diaryl Sulfoxides with Organolithium and Grignard Reagents. Careful treatment of optically pure phenyl *p*-tolyl sulfoxide (**4b**) with an equimolar amount of *n*-BuLi or *t*-BuLi at −78 °C afforded a mixture of diphenyl sulfoxide (**7**), phenyl *p*-tolyl sulfoxide (**4**), and di-*p*-tolyl sulfoxide (**8**) together with (*n*- or *tert*-)butyl *p*-tolyl sulfoxide (**5**) and (*n*- or *tert*-)butyl phenyl sulfoxide (**6**) within 15 min. The aryl *n*-butyl sulfoxide or aryl *tert*-butyl sulfoxide initially obtained was found to be nearly racemized unlike other reactions of alkyl aryl sulfoxides with Grignard or organolithium reagents,[1] whereas the recovered sulfoxide **4** was found to be completely racemized. However, upon treatment of (*R*)-(+)-sulfoxide **4b** with ethylmagnesium bromide at −78 °C (*S*)-(−)-ethyl *p*-tolyl sulfoxide (**5**) and (*R*)-(+)-ethyl phenyl sulfoxide (**6**) resulting from ligand exchange were obtained with complete inversion of the configuration. Partial racemization occurs at room temperature. These results indicate a lower reactivity of Grignard reagents than organolithium reagents. Indeed, when optically active (*R*)-(+)-sulfoxide **4b** was treated with phenylmagnesium bromide in the range from −78 °C to the refluxing of THF,

(9) Wittig, G.; Rieber, M. *Liebigs Ann. Chem.* **1949**, *562*, 187. Wittig, G.; Geissler, G. *Ibid.* **1953**, *580*, 44. Wheatley, P. J. *J. Chem. Soc.* **1964**, 2206.
(10) Wittig, G.; Fritz, H. *Liebigs Ann. Chem.* **1952**, *577*, 39. Glover, S. A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1338. Smith, C. S.; Lee, J. S.; Titus, D. D.; Ziolo, R. F. *Organometallics* **1982**, *1*, 350.
(11) Sheppard, W. A. *J. Am. Chem. Soc.* **1971**, *93*, 5597. Sheppard, W. A.; Foster, S. S. *J. Fluorine Chem.* **1972/73**, *2*, 58.
(12) Ogawa, S.; Furukawa, N. *J. Org. Chem.*, in press.
(13) Furukawa, N.; Shibutani, T.; Fujihara, H. *Tetrahedron Lett.* **1989**, *30*, 7091.

Scheme II



Scheme III

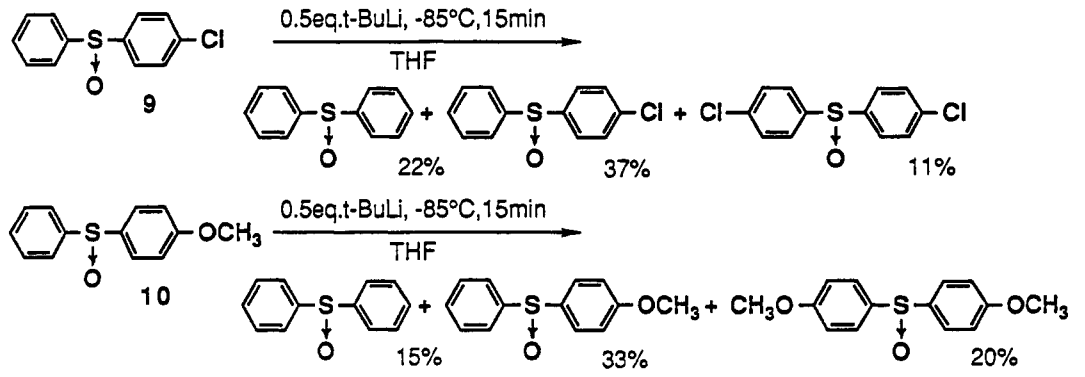


Table I. Reactions of Optically Active (*R*)-(+)-Phenyl *p*-Tolyl Sulfoxide (4b) with Organometallic Reagents

RM	equiv	temp (°C)	time (min)	yield (%) 5	6	7	4	8	$[\alpha]_D^{25}$ (deg) 5	6	4	
n-BuLi	2.0	−85	15	20	13	0	0	0				*a*
	1.0	−78	15	20	13	7	18	22	−10.0[b]	+10.6[c]	0	
t-BuLi	4.0	−85	15		29		0	0	0			*d*
	2.0	−85	15		30		0	0	0			*d*, *e*
	1.0	−78	15	30		6	8	17	19	−3.0[f]	+3.5[g]	0
	0.5	−85	15		15		14	35	22			0 *d*
	0.2	−85	15		7		17	41	21			0 *d*
	0.5	−80	15		15		15	38	24			0 *d*
	0.5	−60	15		15		17	39	22			0 *d*
	0.5	−40	15		14		17	39	21			0 *d*
	0.5	−20	15		16		19	41	21			0 *d*
PhLi	1.0	−95	60	0		0	22	41	22			0
	0.2	−85	15	0		0	24	48	22			0
EtMgBr	1.0	−78	15	20	13		7	18	22	−202.0[h]		+21.5[i]
	1.0	rt	15	55	32		0	0	0	−160.2[j]	+160.8[k]	
PhMgBr	1.0	−78	15	0	0		0	95	0			+21.2
	1.0	rt	15	0	0		3	74	10			+11.6[l]
	1.0	reflux	15	0	0		31	42	16			0

[a] $(n\text{-Bu})_2S{\rightarrow}O$, 55%. [b] Optical purity (op) = 5%, *S* configuration. [c] *R* configuration. [d] Mixture of 5 and 6. [e] *t*-BuS(O)SBu-*t*, 21%. [f] op = 2%, *S* configuration. [g] op = 2%, *R* configuration. [h] op = 99%, *S* configuration. [i] op = 98%. [j] op = 79%, *S* configuration. [k] op = 86%, *R* configuration. [l] op = 53%.

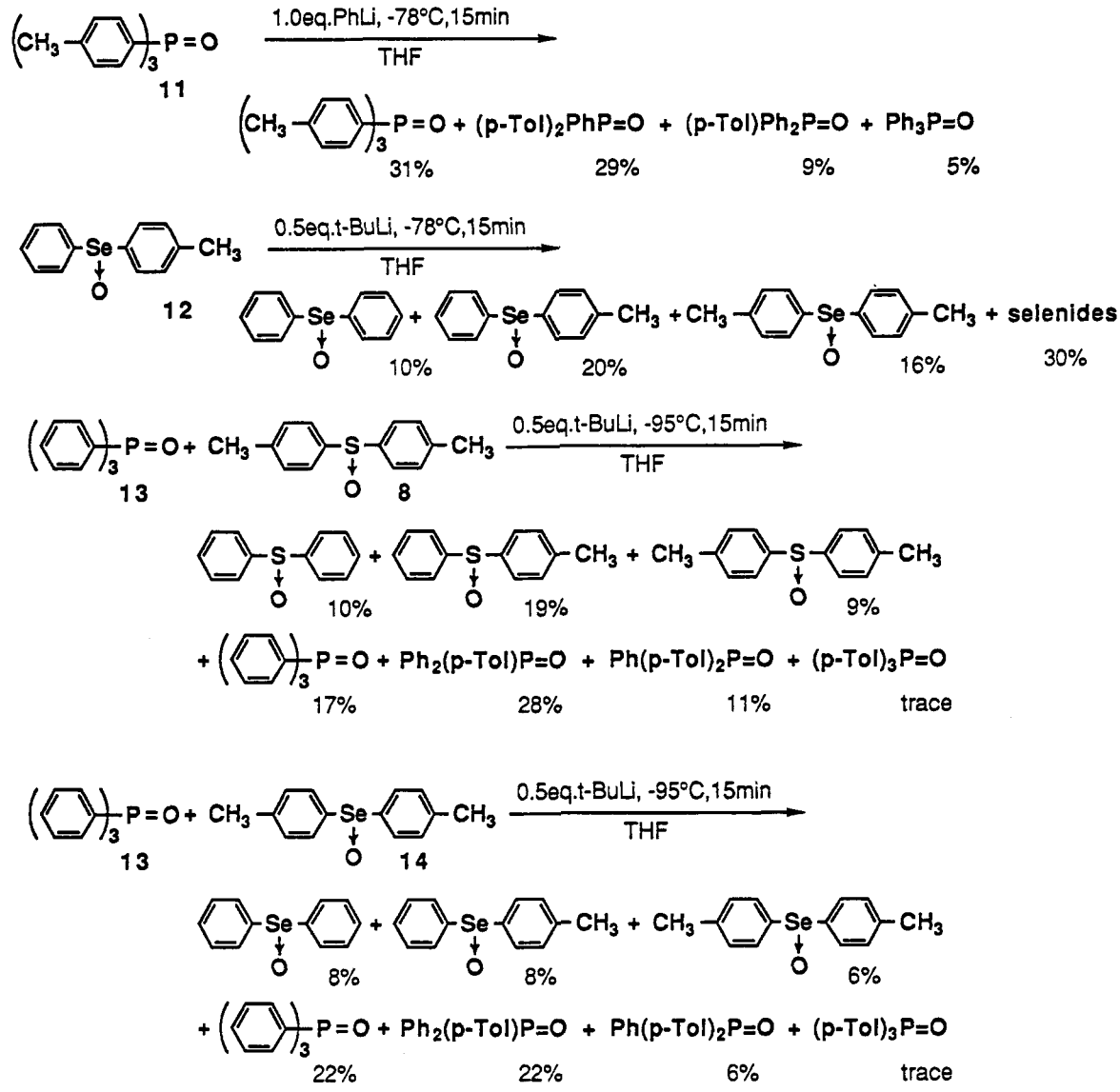
the disproportionation–racemization ratio increased with elevating temperature. Furthermore, when (*R*)-(+)-sulfoxide **4b** was treated with several organolithium reagents the recovered sulfoxide **4** was found to racemize even at −95 °C and less than 0.2 molar equiv of organolithium reagent initiated the complete statistical disproportionation of sulfoxide **4b** (Scheme II and Table I).

Similarly, other substituted diaryl sulfoxides **9** and **10** bearing electron-withdrawing or -donating groups underwent the facile disproportionation reactions on treatment with organolithium reagents (Scheme III). These rapid ligand exchanges and disproportionations were observed in diaryl selenoxides or triarylphosphine oxides. When tri-*p*-tolylphosphine oxide (**11**) and phenyl *p*-tolyl selenoxide (**12**) reacted with PhLi or *t*-BuLi, disproportionated mixtures of phosphine oxides and selenoxides were obtained, respectively. Furthermore, rapid intermolecular ligand exchange and disproportionation reactions were observed upon treatment of an equimolar mixture of triphenylphosphine oxide (**13**) and di-*p*-tolyl sulfoxide (**8**) or di-*p*-tolyl selenoxide (**14**) with alkyllithium (Scheme IV).

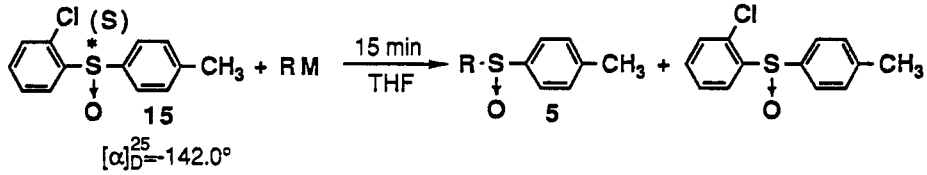
To investigate further the stereochemistry of the ligand exchanges, optically pure (*S*)-(−)-*o*-chlorophenyl *p*-tolyl sulfoxide (**15**) was synthesized and reacted with organolithium or Grignard reagents. In the reaction of sulfoxide **15** with less than 1 equiv of organolithium reagents, both sulfoxide **5** and recovered **15** were found to racemize completely even at −78 °C. On the other hand, in the reactions of (*S*)-(−)-sulfoxide **15** with ethyl Grignard reagent, the sulfoxides **5** and **15** were found to be partially racemized (Scheme V and Table II).

It is surprising that the aryl group is eliminated rather than lithium oxide or bromomagnesium oxide anion, which should have a better leaving ability than the aryl group. In fact, Wildi et al.[7a] and Andersen et al.[7b] reported that in the reactions of diaryl sulfoxides with aryllithium or aryl

Scheme IV



Scheme V



Grignard reagents, the OM (M = Li or MgBr) group is removed exclusively to give the corresponding sulfonium salts. These distinctly different modes of the reactivity cannot be explained by the present experiments, although they would not have detected the facile ligand-exchange reactions due to their choice of reagent and substrate. Itoh et al. reported that aryl sulfoxides undergo the ligand exchange in their paper on the preparation of sulfonium salts.[14] It is well-known that in the reactions of alkyl aryl sulfoxides with organolithium or Grignard reagents, the electronegative aryl group is substituted preferentially while in the oxygen-exchange reactions under acidic conditions the C–S bond is not cleaved at all.[2] These different results on the substitutions on the sulfur atom can be explained in terms of the difference between the bond energy of the C–S bond (60–70 kcal/mol) and the semipolar S–O bond (85–90 kcal/mol).[15] However, the energy

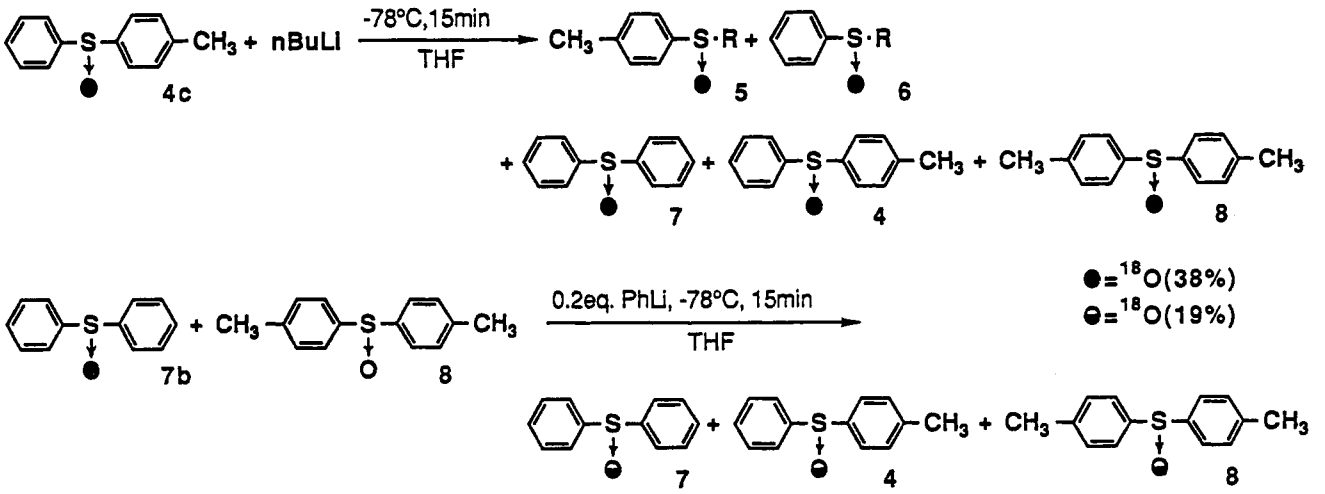
Table II. Reactions of Optically Active (*S*)-(−)-*o*-Chlorophenyl *p*-Tolyl Sulfoxide (15) with Organometallic Reagents

			yield (%) and $[\alpha]_D^{25}$ (deg)			
RM	equiv	temp (°C)	5	$[\alpha]_D^{25}$	15 (recov)	$[\alpha]_D^{25}$
n-BuLi	0.2	−78	13		83	0
	0.5	−78	25		42	−3.2
t-BuLi	0.2	−78	21		54	0
	0.2	−78	26	0	45	0
PhLi	0.5	−78	*a*		40	0
EtMgBr	0.5	rt	41	−199.8[b]	45	−127.5[c]

[a] Disproportionated mixture. [b] Optical purity (op) = 98%, *S* configuration. [c] op = 90%.

(14) Miller, R. D.; Renaldo, A. F.; Ito, H. *J. Org. Chem.* **1988**, *53*, 5571.

Scheme VI



differences between S–O and C–S is not much different and hence both the S–O and C–S bond fission could compete at high temperature. In fact, when the present reactions were carried out in refluxing THF for an extended period the sulfonium salts were formed, showing concurrence with the resulting of Wildi and Andersen.

Proposed Mechanism. These extremely facile ligand-exchange and disproportionation reactions of diaryl sulfoxides, diaryl selenoxides, and triarylphosphine oxides with organolithium reagents cannot be explained by a simple S_N2-type mechanism known in the substitution reactions on the sulfur atoms.[1] The results obtained from the product analysis can eliminate two mechanisms involving electron transfer from the organometallic reagents to the sulfinyl group to give a sulfuranyl radical[1d] and formation of benzyne.[7b] Therefore, these results indicate that the mechanism should proceed via an initial nucleophilic attack on the sulfur atom by the organometallic reagent to form the σ-sulfurane as an intermediate or a transition state. The reaction thus affords the alkyl aryl sulfoxide with inversion of the configuration (an S_N2 type) together with an aryllithium (or Grignard) reagent that attacks again more readily than alkyllithium (or Grignard) reagent. Consistent with the mechanism (only C–S bond cleavage), we found that ^{18}O-labeled phenyl *p*-tolyl sulfoxide (**4c**) reacted with *n*-BuLi to afford exchanged and disproportionated sulfoxides without loss of their ^{18}O contents as shown in Scheme VI.

When one reacted optically pure phenyl *p*-tolyl sulfoxide (**4b**) with alkyllithium, the result obtained supports this mechanism since butyl phenyl and butyl *p*-tolyl sulfoxides thus obtained have the inverted configuration at the sulfur atom from phenyl *p*-tolyl sulfoxide though the optical purity decreased down to ca. 10%. These results indicate that the aryllithium generated from the exchange process should have higher reactivity to the sulfur atom than that of the starting alkyl lithium. These ligand exchange reactions between aryl groups would be repeated rapidly to attain an equilibration mixture of the three sulfoxides, and hence the recovered aryl sulfoxide was racemized completely. Furthermore, these three disproportionated sulfoxides would be attacked by the alkyllithium (or Grignard) reagent slowly to afford the corresponding racemized but partially inverted alkyl aryl sulfoxides. These unusual differences of the reactivity between alkyl- and aryllithium (or Grignard) reagents cannot be explained at all by the differences between the pK_a values of the conjugate acids.[16] In general, alkyllithium must react faster than aryllithium if the substitution or ligand exchange proceeds via an S_N2 process. Therefore, we propose that the intermediacy formation of a σ-sulfurane is involved in these ligand-exchange and disproportionation reactions because sulfurane A having three aryl ligands should be more stable than sulfurane B having two aryl ligands and one alkyl ligand due to an electronic effect that can stabilize the hypervalent structure and hence the reactions tend to proceed for the formation of A (Scheme VII).

The present investigations suggest that lithiation reactions of sulfoxides and related compounds using alkyllithium reagents require a careful handling.

Experimental Section

General. All melting points are uncorrected. IR spectra were recorded on a JASCO A-3 or a JASCO FT/IR-5000 spectrometer. ^1H NMR spectra were obtained with a Hitachi R-600. Mass spectra were taken with a Hitachi RMU-6MG mass spectrometer. Optical rotation was measured on a JASCO DIP-140 digital polarimeter. Preparative liquid chromatography was performed on a JAI Model LC-09 or a LC-908. All the reactions were monitored by gas–liquid chromatography (GLC) (Hitachi 163 or 263, using a 2% silicon OV-1 chromosorb WAW DMCS on 80–100 mesh in column) or thin-layer chromatography (TLC) (Merck Kieselgel 60 F_{254}). Silica gel used for column chromatography was Wako-gel C-200. Elemental analyses were carried out by Chemical Analysis Center at this University.

Materials. All reagents were obtained from Wako Pure Chemical Industries, Ltd., Tokyo Kasei Kogyo, Co., Ltd., or Aldrich Chemical Co. The reaction solvents were further purified by general methods.

Di-2-pyridyl Sulfoxide (1). To a stirred solution of sodium hydroxide (5.4 g, 135.0 mmol) in ethanol (100 mL) at room temperature was added 2-mercaptopyridine (10.0 g, 90.0 mmol). The mixture was stirred at room temperature for 30 min and the solvent removed under reduced pressure. The residue was dissolved in *N,N*-dimethylacetamide (80 mL) and added 2-chloropyridine (10.2 g, 90.0 mmol). The mixture was refluxed for 24 h. Then, the mixture was added into water (10 mL) and extracted with chloroform (3 × 100 mL). The extract was dried with anhydrous magnesium sulfate, and the solvent was evaporated under

(15) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.

(16) Cram, D. J. *Chem. Eng. News* **1963**, *41*, 94. Streitwieser, A., Jr.; Granger, M. R.; Mares, F.; Wolf, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 4257. Streitwieser, A., Jr.; Guibe, F. *Ibid.* **1978**, *100*, 4532. Algrim, D.; Bares, J. E.; Branca, J. C.; Bordwell, F. G. *J. Org. Chem.* **1978**, *43*, 5024. Streitwieser, A., Jr.; Scannon, P. J.; Niemeyer, H. M. *J. Am. Chem. Soc.* **1972**, *94*, 7936. Maskornick, M. J.; Streitwieser, A., Jr. *Tetrahedron Lett.* **1972**, 1625. Streitwieser, A., Jr.; Boerth, D. W. *J. Am. Chem. Soc.* **1978**, *100*, 755.

Scheme VII

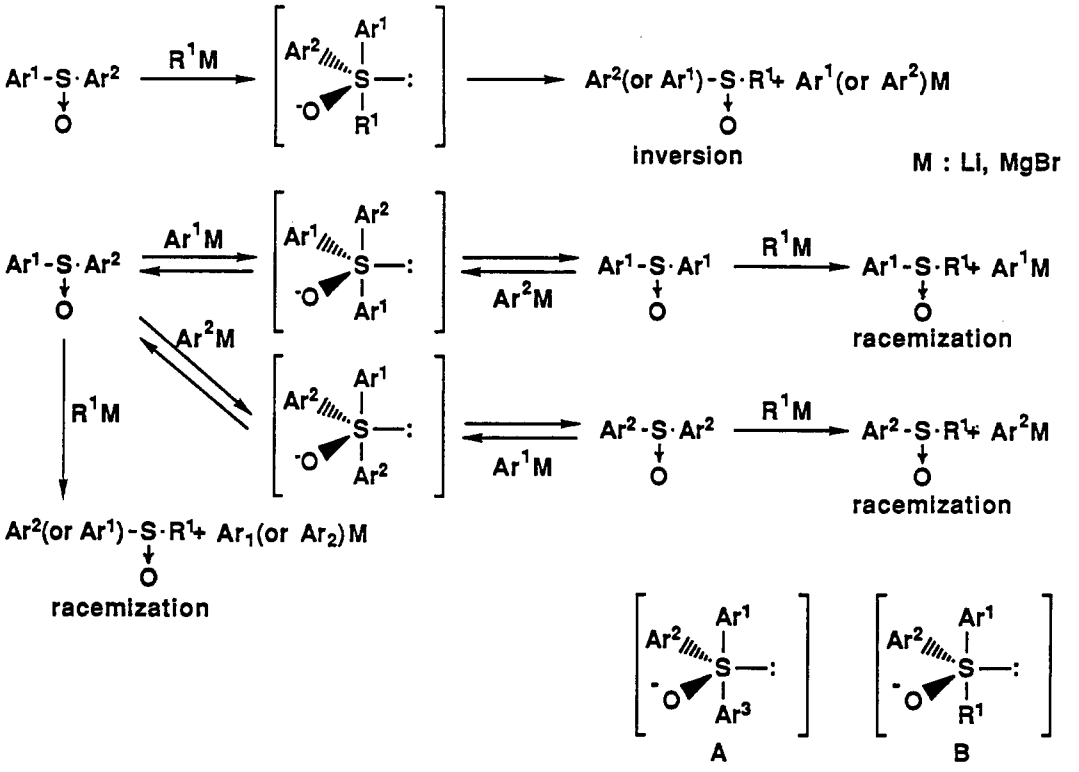


Table III. ^{1}H NMR Data of Sulfoxides (R^1-S(O)-R^2), Selenoxide, and Phosphine Oxide

compd no.	R^1	R^2	δ (ppm)	ref
1	2-pyridyl	2-pyridyl	7.10–8.10 (m, 6 H, 3,4,5-PyH), 8.45–8.55 (m, 2 H, 6-PyH)	
2	Ph	2-pyridyl	7.19–8.17 (m, 8 H, 3,4,5-PyH, ArH), 8.51–8.63 (m, 1 H, 6-PyH)	3, 5
3	2-naphthyl	*p*-Tol	2.26 (s, 3 H, CH_3), 6.90–8.25 (m, 11 H, ArH)	
4a–c	Ph	*p*-Tol	2.39 (s, 3 H, CH_3), 7.00–7.75 (m, 9 H, ArH)	17, 19
5a	*n*-Bu	*p*-Tol	0.70–3.00 (m, 9 H, *n*-Bu), 2.40 (s, 3 H, CH_3), 7.30, 7.54 (ABq, J = 8 Hz, 4 H, ArH)	25
5b	*t*-Bu	*p*-Tol	1.20 (s, 9 H, *t*-Bu), 2.45 (s, 3 H, CH_3), 7.36, 7.49 (ABq, J = 8 Hz, 4 H, ArH)	26
5c	Et	*p*-Tol	1.17 (t, J = 7 Hz, 3 H, CH_3), 2.40 (s, 3 H, CH_3Ph), 2.80 (q, J = 7 Hz, 2 H, CH_2), 7.29, 7.52 (ABq, J = 8 Hz, 4 H, ArH)	24
6a	*n*-Bu	Ph	0.70–3.00 (m, 9 H, *n*-Bu), 7.00–7.80 (m, 5 H, ArH)	1d
6b	*t*-Bu	Ph	1.17 (s, 9 H, *t*-Bu), 7.10–7.76 (m, 5 H, ArH)	27
6c	Et	Ph	1.19 (t, J = 7 Hz, 3 H, CH_3), 2.82 (q, J = 7 Hz, 2 H, CH_2), 7.00–7.75 (m, 5 H, ArH)	24
7a–b	Ph	Ph	7.31–7.81 (m, ArH)	*a*, 20
8	*p*-Tol	*p*-Tol	2.39 (s, 6 H, CH_3), 7.26, 7.56 (ABq, J = 8 Hz, 8 H, ArH)	*a*
9	*p*-ClC_6H_4	Ph	7.31–7.74 (m, ArH)	17
10	*p*-$CH_3OC_6H_4$	Ph	3.82 (s, 3 H, CH_3O), 6.85–7.70 (m, 9 H, ArH)	17
11	(tri-*p*-tolylphosphine oxide)		2.40 (s, 9 H, CH_3), 7.20–7.58 (m, 12 H, ArH)	21
12	(phenyl *p*-tolyl selenoxide)		2.36 (s, 3 H, CH_3), 7.18–7.70 (m, 9 H, ArH)	22
13	(triphenylphosphine oxide)		7.30–7.95 (m, ArH)	*a*
14	(di-*p*-tolyl selenoxide)		2.39 (s, 6 H, CH_3), 7.27, 7.57 (ABq, J = 8 Hz, 8 H, ArH)	23
15	*o*-ClC_6H_4	*p*-Tol	2.37 (s, 3 H, CH_3), 7.00–8.15 (m, 8 H, ArH)	

[a] Commercially available.

Table IV. ^{1}H NMR and Mass Data of Products

product	δ (ppm)	M^+
bipyridine	7.10–8.60 (m, 6 H, 3,4,5-PyH), 8.60–8.80 (m, 2 H, 6-PyH)	156
diphenyl disulfide	7.14–7.61 (m, ArH)	218
tert-butylthiosulfinate	1.43 (s, 9 H, CH_3S), 1.61 (s, 9 H, CH_3SO)	*a*
2-phenylpyridine	7.00–8.30 (m, 8 H, 3,4,5-PyH, ArH), 8.30–8.80 (m, 1 H, 6-PyH)	155
di-*n*-butyl sulfoxide	0.70–3.00 (m, *n*-Bu)	162
diphenyl *p*-tolyl phosphine oxide	2.39 (s, 3 H, CH_3), 7.00–7.90 (m, 14 H, ArH)	292
phenyl di-*p*-tolyl phosphine oxide	2.40 (s, 6 H, CH_3), 7.00–7.90 (m, 13 H, ArH)	306
diphenyl selenoxide	7.40–7.68 (m, ArH)	234 (M^+ – 16)[b]

[a] IR (neat) 1078 cm^{-1} (SO). [b] IR (KBr) 823 cm^{-1} (SeO).

reduced pressure. The residue was purified by vacuum distillation to give di-2-pyridyl sulfide in 59% yield: bp 161–162 °C, (4 Torr); ^{1}H NMR ($CDCl_3$) δ 6.85–7.80 (m, 6 H, 3,4,5-PyH), 8.35–8.70 (m, 2 H, 6-PyH). To a stirred solution of the sulfide (5.0 g, 26.6 mmol) in chloroform (50 mL) at 0 °C was added *m*-chloroperoxybenzoic acid (4.58 g, 26.5 mmol). The mixture was stirred at 0 °C for 12 h and treated with anhydrous ammonia. The resulting solid was separated by filtration, and the filtrate was evaporated under reduced pressure to afford crude sulfoxide, which was purified by column chromatography (silica gel; eluent, hexane/EtOAc =

1/4) to give sulfoxide 1 in 56% yield. Recrystallization from benzene/hexane gave colorless crystals: mp 100.5–101.0 °C; IR (KBr) 1048 cm^{-1} (SO); MS (m/z) 204 (M^+). Anal. Calcd for $C_{10}H_8N_2OS$: C, 58.81; H, 3.95; N, 13.72. Found: C, 58.65; H, 3.87; N, 13.46.

Phenyl 2-Pyridyl Sulfoxide (2). Title sulfoxide was prepared from 2-chloropyridine and sodium thiophenolate by the same procedure as sulfoxide 1. 2:[3,5] mp 70–71 °C; IR (KBr) 1042 cm^{-1} (SO); MS (m/z) 203 (M^+).

2-Naphthyl *p*-tolyl sulfoxide (3): mp 135–136 °C; IR (KBr) 1044 cm^{-1} (SO); MS (m/z) 266 (M^+). Anal. Calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30. Found: C, 76.54; H, 5.31.

Phenyl *p*-tolyl sulfoxide (4a): mp 70–71 °C (lit.[17] mp 71–72 °C); IR (KBr) 1046 cm^{-1} (SO); MS (m/z) 216 (M^+).

(*R*)-(+)-Phenyl *p*-Tolyl Sulfoxide (4b). A solution of *l*-menthyl *p*-toluenesulfinate[18] [$[\alpha]_D^{25}$ = −190.8° (*c* = 2.0, acetone) (15.0 g, 51.0 mmol)] in ether (130 mL) was treated dropwise with 2.16 M phenylmagnesium bromide (50 mL, 108.0 mmol) for 1 h at 0 °C. After the addition was complete, the reaction mixture was stirred for 1 h at 0 °C. The mixture was added to saturated aqueous ammonium chloride until the inorganic salts precipitated, leaving a clear ether solution. The ether layer was separated. The inorganic residue was extracted with ether (3 × 200 mL). The combined ether solution was dried over anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, hexane/EtOAc = 3/2) to give sulfoxide **4b** in 72% yield. Recrystallization from benzene/hexane gave colorless crystals: mp 92–93 °C (lit.[19] mp 92–93 °C); IR (KBr) 1064 cm^{-1} (SO); MS (m/z) 216 (M^+); $[\alpha]_D^{25}$ = +21.7° (*c* = 2, acetone); op (optical purity) = 100%. Anal. Calcd for $C_{13}H_{12}OS$: C, 72.19; H, 5.59; S, 14.82. Found: C, 72.29; H, 5.62; S, 14.66.

^{18}O-Labeled Phenyl *p*-Tolyl Sulfoxide (4c). To a solution of ^{18}O-labeled diphenyl sulfoxide **7b** (38 atom %, 406 mg, 2.0 mmol) in THF (20 mL) was added 0.8 M *p*-tolylmagnesium bromide (2.7 mL, 2.2 mmol). After the mixture was refluxed for 1 h and treated with water (10 mL), the mixture was extracted with chloroform (3 × 20 mL). The extract was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by preparative liquid chromatography to give ^{18}O-labeled phenyl *p*-tolyl sulfoxide **4c** in 35% yield together with ^{18}O-labeled di-*p*-tolyl sulfoxide in 60% yield. Recrystallization from benzene/hexane gave colorless crystals of ^{18}O-labeled sulfoxide **4c**. The ^{18}O content was 38 atom % by mass spectrometry.

^{18}O-Labeled Diphenyl Sulfoxide (7b). The title compound was prepared according to the known method.[20] To a suspension of diphenyl sulfide (2.5 g, 13.4 mmol) in methanol (3 mL) was added $H_2{}^{18}O$ (98.4 atom %, 400 mg, 20.0 mmol) under Ar atmosphere. The mixture was stirred vigorously, and N-bromosuccinimide (2.5 g, 14.0 mmol) was added slowly. The mixture was stirred at room temperature for 1 h and extracted with ether (3 × 20 mL). The extract was washed with water (50 mL), aqueous potassium carbonate (50 mL), and water. Then, the ether layer was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, hexane/EtOAc = 3/2) to give sulfoxide **7b** in 79% yield. Recrystallization from benzene/hexane gave colorless crystals of the ^{18}O-labeled sulfoxide **7b**. The ^{18}O content was 38 atom % by mass spectrometry.

***p*-Chlorophenyl phenyl sulfoxide (9):** mp 44–44.5 °C (lit.[17] mp 45–46 °C); IR (KBr) 1036 cm^{-1} (SO); MS (m/z) 236 (M^+).

***p*-Methoxyphenyl phenyl sulfoxide (10):** mp 59–61 °C (lit.[17] mp 57–59 °C); IR (KBr) 1025 cm^{-1} (SO); MS (m/z) 232 (M^+).

Tri-*p*-tolylphosphine oxide (11): mp 146–147 °C (lit.[21] mp 146 °C); IR (KBr) 1180 cm^{-1} (PO); MS (m/z) 320 (M^+).

Phenyl *p*-Tolyl Selenoxide (12) mp 131–132 °C dec (lit.[22] mp 131–133 °C); IR (KBr) 812 cm^{-1} (SeO); MS (m/z) 248 (M^+ − 16). Anal. Calcd for $C_{13}H_{12}OSe$: C, 59.33; H, 4.60. Found: C, 59.51; H, 4.57.

Di-*p*-tolyl selenoxide (14): mp 89–90 °C dec (lit.[23] mp 90 °C); IR (KBr) 813 cm^{-1} (SeO); MS (m/z) 262 (M^+ − 16). Anal. Calcd for $C_{14}H_{14}OSe$: C, 60.66; H, 5.09. Found: C, 60.76; H, 5.11.

(*S*)-(−)-*o*-Chlorophenyl *p*-Tolyl Sulfoxide (15). The title sulfoxide was prepared from *l*-menthyl *p*-toluenesulfinate and (*o*-chlorophenyl)magnesium bromide by the same procedure as **4b**. **15**: mp 90.5–91 °C; IR (KBr) 1049 cm^{-1} (SO); MS (m/z) 250 (M^+); $[\alpha]_D^{25}$ = −142.0° (*c* = 2, acetone); op (optical purity) = 100%). Anal. Calcd for $C_{13}H_{11}ClOS$: C, 62.27; H, 4.42. Found: C, 61.97; H, 4.35. Optical purity was calculated on the basis of the optical rotation of ethyl *p*-tolyl sulfoxide,[24] which was obtained by the reaction of the sulfoxide **15** with ethylmagnesium bromide at 0 °C.

Reactions of Sulfoxides 1–3 and 4a with Organolithium Reagents. A typical run is as follows. To a stirred solution of di-2-pyridyl sulfoxide (1; 204 mg, 1.0 mmol) in THF (10 mL) at −78 °C was added 2.0 M phenyllithium (0.5 mL, 1.0 mmol) in ether/cyclohexane solution under N_2 atmosphere at −78 °C for 15 min. After hydrolysis and extraction with dichloromethane (3 × 20 mL), the extract was dried with anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, $CHCl_3$) to give bipyridyl in 82% and diphenyl disulfide in 53% yields.

Reactions of (*R*)-(+)-Phenyl *p*-Tolyl Sulfoxide (4b) with Organolithium or Grignard Reagents. A typical run is as follows. To a stirred solution of sulfoxide **4b** (216 mg, 1.0 mmol) in THF (10 mL) at −78 °C was added 1.58 M *n*-butyllithium (0.63 mL, 1.0 mmol) in hexane solution under N_2 atmosphere at −78 °C for 15 min. After hydrolysis and extraction with dichloromethane (3 × 20 mL), the extract was dried with anhydrous magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified with column chromatography (silica gel; eluent hexane/EtOAc = 3/2) and then liquid chromatography to give *n*-butyl *p*-tolyl sulfoxide (**5a**; 20%, $[\alpha]_D^{25}$ = −10.0°), *n*-butyl phenyl sulfoxide (**6a**; 13%, $[\alpha]_D^{25}$ = +10.6°), diphenyl sulfoxide (7; 7%), phenyl *p*-tolyl sulfoxide (4; 18%, $[\alpha]_D^{25}$ = 0°), and di-*p*-tolyl sulfoxide (8; 22%). Optical purities were determined by the highest values reported in the literature.[1b,19,25-27]

Reactions of 9–12 with Organolithium Reagents. The title reactions were carried out according to the similar procedure as sulfoxide **4b** with organolithium reagent. The product yields were obtained by GLC. Mass spectra were in satisfactory agreement with those of authentic samples.

Cross-Over Reactions. A typical experimental procedure is as follows. To a solution of triphenylphosphine oxide (**13**; 139 mg, 0.5 mmol) and di-*p*-tolyl sulfoxide (**8**, 115 mg, 0.5 mmol) in THF (10 mL) was added 1.55 M *tert*-butyllithium (0.32 mL, 0.5 mmol) under N_2 atmosphere at −95 °C. After 15 min, water was added and the mixture was extracted with dichloromethane (3 × 20 mL). The extract was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by preparative liquid chromatography to afford sulfoxide **7** in 10%, sulfoxide **4** in 19%, sulfoxide **8** in 9%, phosphine oxide **13** in 17%, diphenyl *p*-tolyl phosphine oxide in 28%, and phenyl di-*p*-tolyl phosphine oxide in 11% yield and a trace amount of phosphine oxide **11**.

Reactions of Optically Active (*S*)-(−)-*o*-Chlorophenyl *p*-Tolyl Sulfoxide (15) with Organolithium or Grignard

(17) Cerninani, A.; Modena, G. *Gazz. Chim. Ital.* **1959**, *89*, 834.
(18) Herbrandson, H. F.; Dickerson, R. T., Jr.; Weinstein, J. *J. Am. Chem. Soc.* **1959**, *81*, 4102.
(19) Andersen, K. K. *Tetrahedron Lett.* **1962**, 93. Andersen, K. K.; Gaffield, W.; Papanikolaou, N. E.; Foley, J. W.; Perkins, R. I. *J. Am. Chem. Soc.* **1964**, *86*, 5637.
(20) Tagaki, W.; Kikukawa, K.; Kunieda, N.; Oae, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 614.
(21) Michaelis, A. *Liebigs Ann. Chem.* **1901**, *315*, 43.
(22) Greenberg, B.; Gould, E. S.; Burlant, W. *J. Am. Chem. Soc.* **1956**, *78*, 4028.
(23) Zeiser, F. *Ber.* **1895**, *28*, 1670.
(24) Cope, A. L.; Caress, E. A. *J. Am. Chem. Soc.* **1966**, *88*, 1711. Kamiyama, K.; Minato, H.; Kobayashi, M. *Bull. Chem. Soc. Jpn* **1973**, *46*, 3895.
(25) Mislow, K.; Green, M. M.; Laur, P.; Melillo, J. T.; Simmons, T.; Ternay, A. L., Jr. *J. Am. Chem. Soc.*, **1965**, *87*, 1958. Auret, B. J.; Boyd, D. R.; Henbest, H. B.; Ross, S. *J. Chem. Soc. C* **1968**, 2371, 2374. Folli, U.; Iarossi, D.; Montanari, F.; Torre, G. *Ibid.* **1968**, 1317.
(26) Auret, B. J.; Boyd, D. R.; Henbest, H. B.; Ross, S. *J. Chem. Soc. C* **1968**, 2371.
(27) Barnard, D.; Fabian, J. M.; Koch, H. P. *J. Chem. Soc.* **1949**, 2442.

Reagents. In a typical run, to a stirred solution of sulfoxide 15 (251 mg, 1.0 mmol) in THF (10 mL) was added 1.58 M *n*-butyllithium (0.13 mL, 0.2 mmol) under N_2 atmosphere at -78 °C. The mixture was stirred for 15 min at -78 °C. After hydrolysis and extraction with dichloromethane (3 × 20 mL), the extract was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, hexane/EtOAc = 7/3) to give *n*-butyl *p*-tolyl sulfoxide (**5a**) in 13% and recovered sulfoxide 15 in 83% yield. Optical rotation ($[\alpha]_D^{25}$) of the recovered sulfoxide 15 is 0° (*c* = 1.0, acetone).

Reactions of ^{18}O-Labeled Phenyl *p*-Tolyl Sulfoxide (4c) with *n*-Butyllithium. The reaction was carried out according to the same procedure of the optically active sulfoxide **4b** with *n*-butyllithium. The products were separated by column and preparative liquid chromatography, and their ^{18}O contents were determined by mass spectrometry. The ^{18}O content of each sulfoxide is 38 atom %.

Cross-Over Reaction of ^{18}O-Labeled Diphenyl Sulfoxide (7b) and Unlabeled Di-*p*-tolyl Sulfoxide (8) with Phenyllithium. To a solution of sulfoxide **7b** (101 mg, 0.5 mmol) and di-*p*-tolyl sulfoxide (8, 115 mg, 0.5 mmol) in THF (10 mL) under N_2 atmosphere at -78 °C was added 1.8 M phenyllithium (0.11 mL, 0.2 mmol) in ether/cyclohexane solution. After 15 min, water was added and the mixture was extracted with dichloromethane (3 × 20 mL). The extract was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by preparative liquid chromatography to afford diphenyl sulfoxide in 26%, phenyl *p*-tolyl sulfoxide in 51%, and di-*p*-tolyl sulfoxide in 17% yield. The ^{18}O contents of three sulfoxides are 19 atom % by mass spectrometry.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Area No. 02247101 from the Ministry of Education, Science and Culture of Japan.

Redox-Initiated Per(poly)fluoroalkylation of Olefins by Per(poly)fluoroalkyl Chlorides

Chang-Ming Hu* and Feng-Ling Qing

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, China

Received August 29, 1990

The per(poly)fluoroalkylation of olefins by per(poly)fluoroalkyl chlorides, initiated by ammonium persulfate/sodium formate ($(NH_4)_2S_2O_8/HCO_2Na$), is described. The reaction proceeds smoothly in polar aprotic solvents. The presence of functional groups like sodium carboxylate or sulfonate in the polyfluoroalkyl chloride appear to facilitate the reaction. The reaction appears to be initiated by a single-electron transfer, represents the first example of the reactivity of per(poly)fluoroalkyl chlorides, and also demonstrates their use as per(poly)fluoroalkylating agents. For α-chloro-ω-iodoperfluoroalkanes only the carbon–iodine bond is cleaved during the reaction. An explanation for the apparent stability of the carbon–chlorine bond in such compounds is given.

Introduction

The development of methods for introducing per(poly)fluoroalkyl groups into organic molecules is an important goal of synthetic organic chemistry. Traditional methods involve the addition of organofluorine compounds like R_fX (X = I, Br, CCl_3, SO_2Cl, SO_2Br, or SO_2Na) to alkenes and alkynes.[1] Such additions are commonly catalyzed by peroxides,[2] main-group metals,[3] transition-metal complexes,[4] or $Na_2S_2O_4$.[5] Whether the additions occur through a free-radical, ionic, or single-electron-transfer (SET) mechanism, the reactivity of $-CF_2X$ generally decreases in the following order:[6] $CF_2I > CCl_3 \sim CF_2Br > CFCl_2$. Until now, nearly all per(poly)fluoroalkylations have involved the use of R_fI, R_fBr, or R_fCCl_3.

Table I. Yields of the Adducts $R_fCH_2CH_2R$ (1-10) from the Per(poly)fluoroalkylation of Olefins (CH_2=CHR) by R_fCl

adduct[a]	R_fCl R_f =	CH_2=CHR R =	isolated yield (%)
1	$(CF_2)_8OCF_2CF_2SO_3Na$	*n*-C_4H_9	87
2	$(CF_2)_8OCF_2CF_2SO_3Na$	*n*-C_5H_{11}	79
3	$(CF_2)_8OCF_2CF_3$	*n*-C_5H_{11}	76
4	$(CF_2)_8OCF_2CF_3$	CH_2Br	52
5	$(CF_2)_8OCF_2CF_3$	CH_2OAc	74
6	$(CF_2)_6COONa$	*n*-C_5H_{11}	87[a]
7	$(CF_2)_7COONa$	CH_2OAc	74[a]
8	$(CF_2)_7COONa$	*n*-C_4H_9	85[a]
9	$(CF_2)_7COONa$	*n*-C_5H_{11}	67[a]
10	$(CF_2)_7COONa$	$CH_2Si(CH_3)_3$	69[a]

[a] The yield is that of the corresponding methyl ester $RCH_2CH_2(CF_2)_nCOOCH_3$ (*n* = 6, 7), formed by treating the initial product with methanolic H_2SO_4.

Because they apparently are stable in the presence of various initiators, few reports dealing with the use of R_fCFCl_2 as per(poly)fluoroalkylating agents have appeared in the literature. Perfluoroalkyl chlorides, R_fCF_2Cl, appear to be chemically inert and are thermally stable up to 600 °C, even in the presence of NO_2.[7] Thus, such compounds have never been reported to be useful for synthetic work.

Although the redox telomerization of fluorine-containing olefinic monomers is rather well-known, the redox-initiated

(1) (a) Sheppard, W. A.; Sharts, C. M. *Organic Fluorine Chemistry*; Benjamin W. A.: New York, 1969; Chapter 6. (b) Burton, D. J.; Rehoe, L. J. *J. Org. Chem.* **1970**, *35*, 1339. (c) Dudrhiri-Hassani, M.; Brunel, D.; Germain, A.; Commeyras, A. *J. Fluorine Chem.* **1984**, *25*, 49. (d) Huang, W.-Y.; Chen, J.-L.; Hu, L.-Q. *Bull. Soc. Chim. Fr.* **1986**, *6*, 681. (e) Huang, W.-Y.; Hu, L.-Q.; Xie, Y. *Acta Chim. Sin. (Engl. Ed.)* **1989**, 190.

(2) Hudlicky, M. *Chemistry of Organofluorine Compounds*, 2nd ed.; Ellis, Horwoord: Chichester, England, 1976.

(3) Chen, Q.-Y.; Qiu, Z-M.; Yang, Z.-Y. *J. Fluorine Chem.* **1987**, *36*, 149.

(4) Fuchikami, T.; Ojima, I. *Tetrahedron Lett.* **1984**, *3*, 303.

(5) Haung, W.-Y.; Wang, W.; Haung, B.-N. *Acta Chim. Sin.* **1986**, *44*, 488.

(6) (a) Moore, L. O. *Can. J. Chem.* **1971**, *49*, 666. (b) Rozhkov, I.; Becker, G.; Igumnov, S.; Pletnev, S.; Rempel, G.; Borisov, Yu. *J. Fluorine Chem.* **1989**, *45*, 114. (c) Kim, Y. K. *J. Org. Chem.* **1967**, *32*, 3673.

(7) Serverson, W. A.; Brice, T. J. *J. Am. Chem. Soc.* **1958**, *80*, 2313.

0022-3263/91/1956-6348$02.50/0