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A Method for Generation of α-Halo Carbanions (Carbenoids) from Aryl α-Haloalkyl Sulfoxides with Alkylmetals

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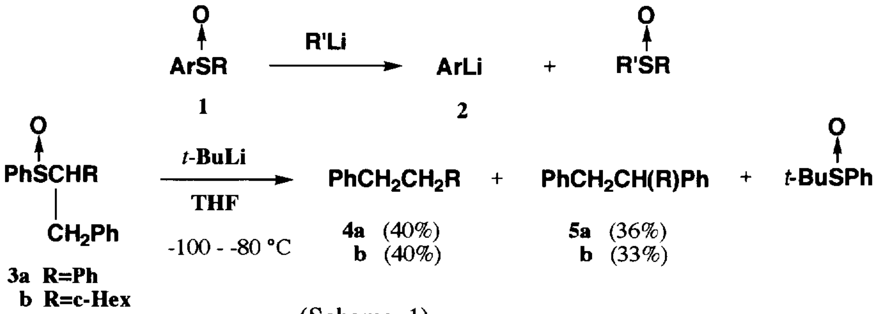
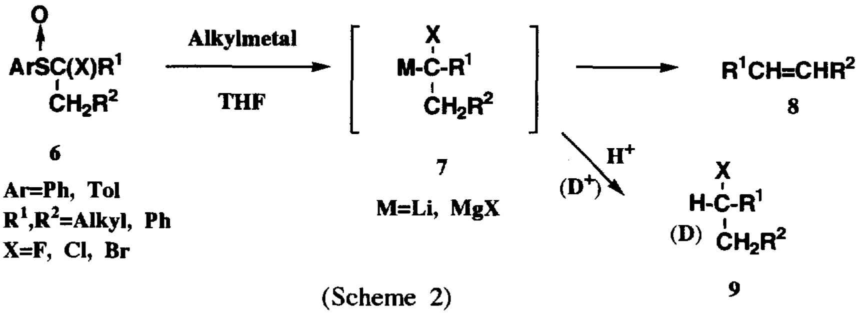
Abstract: *Ligand exchange reaction of simple aryl α-haloalkyl sulfoxides with alkyllithium and ethylmagnesium halide at low temperature was investigated. On treatment of aryl α-haloalkyl sulfoxide with n-BuLi, t-BuLi, or EtMgX exclusively sulfur-alkyl bond-cleavage took prace to afford α-halo carbanion (carbenoid). When this reaction was carried out without a proton source, the intermediate α-halo carbanion decomposed to give olefines in good yield. The ligand exchange reaction of sulfoxide was found to be very fast and the reaction could be carried out with a proton or a deuterium source (internal quench) to afford alkyl halide. This procedure offers a new method for preparing α-deuterated halides (the halogen is F, Cl, or Br).*

It has been known that on treatment of alkyl aryl sulfoxide **1** with alkyllithium sulfur-aryl bond-cleavage takes place to give aryllithium **2** (ligand exchange reaction of sulfoxides).[1] However, this is not always a straightforward process. For example, in our own experiment, treatment of alkyl phenyl sulfoxide **3** with *tert*-butyllithium (*t*-BuLi) gave **4** (sulfur-alkyl bond-cleavage) in 40% yield with ligand coupling product **5** and *tert*-butyl phenyl sulfoxide.



(Scheme 1)

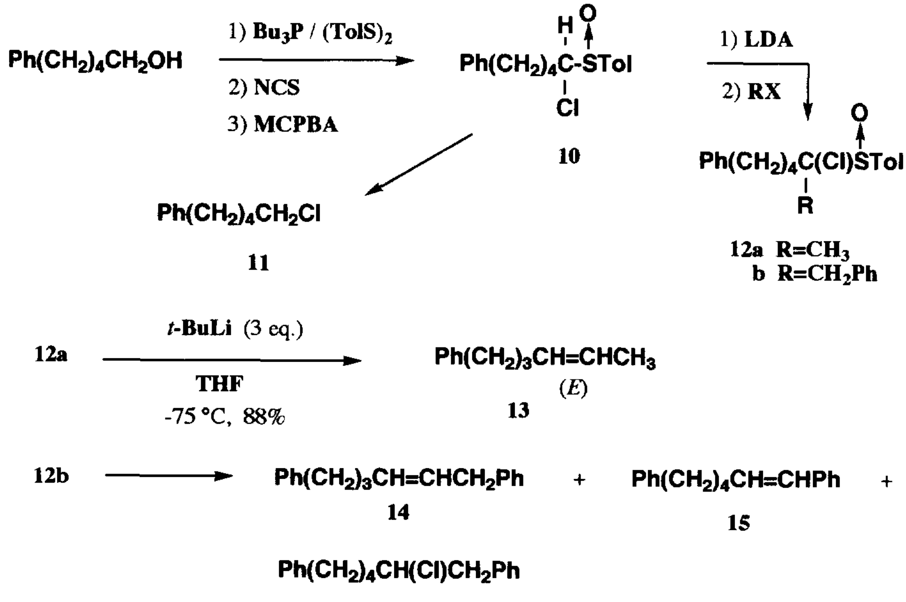
We and other chemists recently reported some examples of sulfur-alkyl[2] and sulfur-alkenyl[3] bond-cleavage by ligand exchange reaction of sulfoxides with alkylmetals. In particular, in the case of alkyl aryl sulfoxides having a 1-haloalkyl group a sulfur-alkyl bond was cleaved predominantly.[4] We have reported some results for the ligand exchange reaction of various kinds of alkyl aryl sulfoxides and their application to new synthetic methods.[3f,g, 4] However, the reaction with the simplest alkyl aryl sulfoxides having an α-haloalkyl group remains to be investigated. In this paper, we report results for the treatment of simple aryl α-haloalkyl sulfoxides **6** with alkylmetal to give α-halo carbanions **7** (carbenoid) in good yields (Scheme 2).



(Scheme 2)

Results and Discussion

First, 1-chloro-5-phenylpentyl *p*-tolyl sulfoxide **10** was synthesized from 5-phenyl-1-pentanol (Scheme 3). Sulfoxide **10** was treated with *t*-BuLi in THF at -70 °C for 3 min. In this reaction all the starting material was consumed; however, a very complex mixture was obtained, in which some amount of chloride **11** was obtained as a less polar product. This complexity was assumed to be due to the presence of an acidic hydrogen on the carbon bearing the sulfoxide.

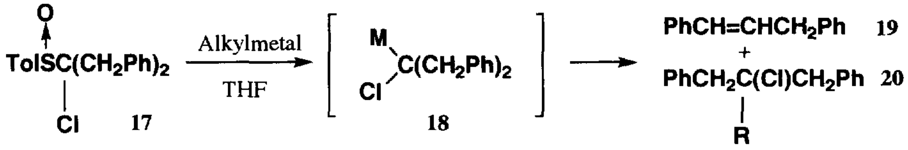


(Scheme 3)

Next, **10** was alkylated in the usual way to give **12** in quantitative yield. The sulfoxide **12a** was treated with three equivalents of *t*-BuLi in THF at -75 °C for 5 min. In contrast to the result with **10**, this reaction was shown to be very clean and (*E*)-6-phenyl-2-hexene **13** was obtained in 88% yield with *tert*-butyl *p*-tolyl sulfoxide. Interestingly, no Z-isomer nor 6-phenyl-1-hexene was observed on ^{1}H NMR. Obviously, the intermediate of this reaction was thought to be a lithium carbenoid **7**[5] derived from **12a** via the ligand exchange reaction of sulfoxide.[6] Similar treatment of **12b** with *t*-BuLi at -90 °C for 5 min gave a mixture of olefines **14** and **15** (**14**/**15**=3.5/1) in 65% yield with chloride **16** (35%). When this reaction was carried out at -70 °C for 30 min the yield of the olefines increased to 76% with chloride **16** (15%). The formation of the chloride **16** was thought to be protonation of the intermediate, α-chloro carbanion, with some acidic hydrogen in the reaction mixture.

From a synthetic point of view, this reaction is a new method for preparing alkyl halides and/or olefinic compounds, if the α-halo carbanion can be trapped with electrophiles. To investigate this feasibility we selected α-chloroalkyl *p*-tolyl sulfoxide **17** and reacted **17** with alkylmetals and electrophiles (Table 1).

Table 1. Treatment of α-Chloroalkyl *p*-Tolyl Sulfoxide **17** with Alkylmetal



Entry	Alkylmetal (eq.)	Temp. (°C)	Time (min)	Yield (%)[a]	
				19	**20**
1	*t*-**BuLi** (2.2)	-100	5	86 (E/Z=13:1)	trace
2	*n*-**BuLi** (1.5)	-78	5	32	34 (R=H)
3	**EtMgBr** (1.5)	-78	5	___[b]	73 (R=H)
4	**EtMgCl** (1.5)	-78	30	11	82 (R=H)
5	**EtMgCl** (1.5)	-78	120	17	80 (R=H)
6	**EtMgCl** (1.5)	-78 - -30[c]	120	55	32 (R=H)
7	**EtMgCl** (2)[d]	-78	30	15	85 (R=H)
8	**EtMgCl** (2)[d]	-78	120	15	85 (R=H)
9	**EtMgCl** (2)[d]	-78 - -30[c]	70	70	26 (R=H)
10	**EtMgCl** (2)	-78	5 (CD_3OD)[e]	8	88 (R=D; 61%[f])
11	**EtMgCl** (2)[d]	-78	5 (CD_3OD)[e]	8	90 (R=D; 66%[f])

a) Isolated yield after silica gel column chromatography. b) Some amount of **19** was observed on TLC. We did not isolate it. c) Temperature of the reaction mixture was gradually allowed to warm to -30 °C. d) A solution of **17** in THF was added to a solution of EtMgCl (inverse addition). e) Large excess deuterated methanol was added to the reaction mixture and stirred at -78 °C for 5 min. f) The deuterium incorporation was measured from ^{1}H NMR.

First, **17** was treated with *t*-BuLi at -100 °C (entry 1). The product was olefine **19** with a trace of chloride **20**. This is a similar result compared to the treatment of **12** with *t*-BuLi. Changing the alkylmetal to *n*-BuLi gave olefine **19** (32%) and equal amount of chloride **20** (34%) (entry 2). The reason for this difference in comparison of the result with *t*-BuLi was thought to be as follows. The reaction of **17** with *n*-BuLi affords α-lithiated chloride **18** and *n*-butyl *p*-tolyl sulfoxide via the ligand exchange reaction of sulfoxides. As *n*-butyl *p*-tolyl sulfoxide has an acidic hydrogen on the carbon bearing the sulfinyl group, the α-lithiated chloride **18** quickly picks up the acidic hydrogen to give the chloride **20**. In contrast to this, when this reaction was carried out with *t*-BuLi, the produced *t*-butyl *p*-tolyl sulfoxide has no acidic hydrogen and the produced α-lithiated chloride **18** decomposed to olefine **19** via the hydrogen migration of the carbenoid.

This reaction was investigated with Grignard reagent (entries 3-6). Interestingly, this simple α-chloroalkyl *p*-tolyl sulfoxide reacted smoothly with EtMgBr in THF at low temperature to give chloride **20** as the main product in 73% yield. Entries 3-5 show that prolonging the reaction time to 2 h gave almost the same results within experimental error. Entry 6 shows that warming up the reaction temperature gave olefine **19** as the main product. These results implied that the intermediate α-chloro Grignard reagent prepared by this method is rather stable below -78 °C. The above mentioned reaction was carried out in an inverse manner; the sulfoxide **17** was added to a solution of EtMgBr (entries 7-9). The results were quite similar to those shown in entries 4-6.

In order to trap the intermediate α-chloro carbanion the reaction was quenched with CD_3OD (entry 10). The produced chloride was deuterated; however, deuterium incorporation was 61%. This reaction in an inverse manner gave deuterated chloride **20** in good yield, but deuterium incorporation was still less than 70% (entry 11). The reason why the deuterium incorporation was not perfect is somewhat obscure at present.

Okamura[3a] and we[4h] reported that the rate of the ligand exchange reaction of sulfoxides is quite fast and internal quench of the intermediate is possible with a proton source. In order to get alkyl halides or deuterated alkyl halides we investigated the above mentioned reaction in the presence of an internal proton (deuterium) source (Table 2).

Entries 1-3 show the results of the reaction of **17** with EtMgBr in the presence of a proton source. The results are similar to those shown in Table 1, entries 3-5. This implies that the ligand exchange reaction with EtMgBr is not so fast that after all the proton source is quenched **17** reacted with EtMgBr. In the case with DMSO (entry 3) the produced α-chloro Grignard reagent reacts very slowly with DMSO. This assumption is supported by the results shown in entries 4 and 5. The reaction in the presence of the compounds having an acidic deuterium gave the chloride in over 80% yield; however, deuterium incorporation was quite low.

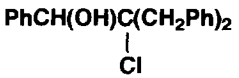
In contrast to the results with Grignard reagent, the reaction with *t*-BuLi is interesting. Sulfoxide **17** was reacted with *t*-BuLi in the presence of DMSO as a proton source to afford chloride **20** as the main product (entry 6). The same reaction without DMSO gave olefine **19** with a trace of **20** as shown in Table 1, entry 1. This result showed that the produced intermediate α-lithiated chloride was obviously protonated by DMSO. Next, this reaction was investigated with two deuterium sources, CD_3OD or DMSO-d_6, and the results are shown in Table 2, entries 7 and 8. Careful experiment (entry 8) showed that this reaction gave an almost quantitative yield of chloride **20** with 86% deuterium incorporation. Quenching this reaction with CD_3OD (entry 9) gave almost the same result. These results implied that about 10% of the protonation was due to a trace of the proton source in the reaction mixture (probably a trace of moisture in the solvent and DMSO-d_6). Entry 10 is an experiment of the reaction with DMSO followed by CD_3OD quench. No deuterium incorporation was observed. This result showed that the internal proton quench was complete before the CD_3OD quench.

Table 2. Treatment of **17** with Alkylmetals in the Presence of an Internal Proton (Deuterium) Source

Entry	Alkylmetal (eq.)	Time (min)	Proton (Deuterium) source[b]	Yield (%)[a]	
				19	**20**
1	**EtMgBr** (5)	120	***t*-BuOH**	37	63 (R=H)
2	**EtMgBr** (5)	120	**EtOH**	18	82 (R=H)
3	**EtMgBr** (5)	5	**DMSO**	25	75 (R=H)
4	**EtMgCl** (4)	30	$\mathbf{CD_3OD}$	10	83 (R=D; 8%)[c]
5	**EtMgCl** (4)	10	**DMSO-**$\mathbf{d_6}$	——[d]	87 (R=D; 6%)[c]
6	***t*-BuLi** (4)	10	**DMSO**	21	68 (R=H)
7	***t*-BuLi** (4)	30	$\mathbf{CD_3OD}$	18	78 (R=D; 61%)[c]
8	***t*-BuLi** (4)	10	**DMSO-**$\mathbf{d_6}$	——[d]	96 (R=D; 86%)[c]
9	***t*-BuLi** (4)	10	**DMSO-**$\mathbf{d_6}$ ($\mathbf{CD_3OD}$)[e]	——[d]	96 (R=D; 88%)[c]
10	***t*-BuLi** (4)	10	**DMSO** ($\mathbf{CD_3OD}$)[e]	——[d]	68 (R=H)

a) All the reactions were carried out in THF at -78 °C. Isolated yield after silica gel column chromatography. b) All the reactions were carried out with 2.5 equivalents of proton (deuterium) source. c) The yield in parenthesis is the rate of deuterium incorporation measured from ^{1}H NMR. d) Some amount of olefine **19** was observed on TLC; however, we did not isolate it. e) The reaction was quenched with CD_3OD.

In order to investigate the feasibility for trapping the α-halo carbanion with electrophiles other than proton, **17** was treated with *t*-BuLi followed by iodomethane; however, no methylated product was observed. This reaction was carried out with benzaldehyde; an inseparable mixture of the adduct **21** and **22** (**21**:**22**=1:3.5) was obtained. Silylation was investigated as follows. To a mixture of **17** with chlorotrimethylsilane was added *t*-BuLi to give an inseparable mixture of sililated chloride **23** and the chloride **20** (**23**:**20**=1.2: 1).

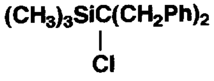


$PhCH(OH)\underset{\displaystyle Cl}{\underset{|}{C}}(CH_2Ph)_2$

21

$PhCH(OH)C(CH_3)_3$

22



$(CH_3)_3Si\underset{\displaystyle Cl}{\underset{|}{C}}(CH_2Ph)_2$

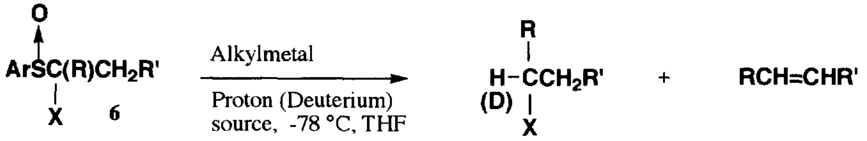
23

The above mentioned internal quench reaction was investigated with other α-haloganated sulfoxides (the halogen is Cl, F, Br) and the results are summarized in Table 3. Entries 1-3 show that the sulfoxide having a phenyl group on the carbon bearing sulfinyl group gave moderate yield of chloride and for the deuteration

DMSO-d_6 is a better reagent. Entries 5-10 show the results of some α-fluoro sulfoxides. By this method a synthesis of deuterated alkyl fluoride with deuterium incorporation up to 89% was realized.

Finally, this method was applied to the sulfoxide having bromine (entries 12-15). Under similar conditions all the starting material was consumed; however, this reaction gave a rather complex mixture, in which about 20% of alkyl bromide was obtained. Interestingly, in these cases the deuterium incorporation was higher than in other reactions. We thought that the produced bromides are unstable in these conditions.

Table 3. Treatment of α-Haloalkyl Aryl Sulfoxide with Alkylmetal under Internal Quench Conditions



Entry	6				Alkyl-metal[a]	Proton (Deuterium) source[a]	Alkyl halide (Yield/%; D-content)[c]	Olefine
	Ar	R	R'	X				
1	Ph	Ph	Ph	Cl	*t*-BuLi	DMSO	**24** (58)	—[b]
2					*t*-BuLi	DMSO-d_6	**25** (56; 77)	—[b]
3					*t*-BuLi	CD_3OD	**25** (35; 67)	—[b]
4	Tol	CH_3	$(CH_3)_3Ph$	Cl	*t*-BuLi	CD_3OD	**26** (69; 72)	30
5	Tol	CH_2Ph	Ph	F	*t*-BuLi	DMSO	**27** (73)	17
6					*t*-BuLi	DMSO-d_6	**28** (81; 58)	17
7					*t*-BuLi	CD_3OD	**28** (69; 78)	29
8	Ph	Ph	Ph	F	EtMgBr	EtOH	**29** (41)	6
9					*t*-BuLi	DMSO	**29** (72)	10
10					*t*-BuLi	DMSO-d_6	**30** (64;89)	—[b]
11	Ph	$(CH_2)_9CH_3$	$(CH_3)_3Ph$	F	*t*-BuLi	CD_3OD	**31** (43; 78)	—[b]
12				F	*t*-BuLi	DMSO-d_6	**31** (55; 85)	—[b]
13	Ph	CH_2Ph	Ph	Br	*t*-BuLi	CD_3OD	**32** (28; 72)	—[b]
14	Ph	CH_2Ph	$(CH_3)_3Ph$	Br	*t*-BuLi	DMSO-d_6	**33** (22; 87)	24
15	Ph	$(CH_2)_9CH_3$	$(CH_3)_3Ph$	Br	*t*-BuLi	DMSO-d_6	**34** (22; 89)	34

a) All reactions were carried out at -78 °C in THF with 4 equivalents of alkylmetal in the presence of 2.5 equivalents of proton (deuterium) source. b) Some amount of olefine was observed on TLC; however, we did not isolate it. c) The deuterium incorporation was measured from ^{1}H NMR.

In conclusion, we have found that sulfur-alkyl bond-cleavage took place in the ligand exchange reaction of sulfoxides of simple alkyl aryl sulfoxides having an α-haloalkyl group with alkylmetals to give α-halo carbanions in good yields. The produced lithiated haloalkanes are, as expected, unstable to give olefines via carbenoids.

The produced α-halo Grignard reagents were found to be somewhat more stable than lithiated haloalkanes. The ligand exchange reaction with *t*-BuLi was found to be very fast and the reaction was possible with a proton (or deuterium) source. In this reaction α-protonated or α-deuterated haloalkanes were produced though the deuterium incorporation was not perfect. This procedure offers a new method for preparing α-deuterated alkyl halides.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were measured in a $CDCl_3$ solution with JEOL GX-270 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel BW-127 ZH (Fuji-Silicia) containing 2% fluorescence reagent 254 and a quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry solvent, THF was distilled from diphenylketyl; diisopropylamine, HMPA, and chlorotrimethylsilane were dried over CaH_2 and distilled.

1-Chloro-5-phenylpentyl *p*-tolyl sulfoxide (10). A solution of 5-phenyl-1-pentanol (3.29 g; 20 mmol) and *p*-tolyl disulfide (6.41 g; 26 mmol) in 25 ml of THF was cooled in an ice bath. To this solution was added with stirring 5.26 g (26 mmol) of freshly distilled tributylphosphine.[7] The reaction mixture was stirred at 0 °C for 20 min and at room temperature for 18 h. The reaction mixture was diluted with benzene and the solution was washed twice with 5% NaOH (50 ml) followed by sat. NH_4Cl. The solution was dried over $MgSO_4$ and the solvent was evaporated. The residue was purified by silica gel column chromatography (hexane:AcOEt=200:1) to afford 5.38 g (99 %) of 5-phenylpentyl *p*-tolyl sulfide as a colorless oil. ^{1}H NMR δ 1.4-1.7 (6H, m), 2.31 (3H, s), 2.59 (2H, t, *J*=7 Hz), 2.86 (2H, t, *J*=7 Hz), 7.1-7.3 (9H, m).

N-Chlorosuccinimide (NCS; 1.47 g; 11 mmol) was added to a solution of the sulfide (2.7 g; 10 mmol) in 20 ml of carbon tetrachloride and the suspension was stirred at room temperature for 2 h. The precipitate (succinimide) was filtered off and the solvent was evaporated to give a yellow oil. The oil was dissolved in 40 ml of CH_2Cl_2 and the solution was cooled to -50 °C. To this solution was added *m*-chloroperbenzoic acid (80%; 2.3 g; 10.5 mmol) by portions with stirring and the reaction mixture was stirred for 1 h. The reaction mixture was diluted with CH_2Cl_2 and the solution was washed twice with 5% NaOH (50 ml), then with sat NH_4Cl. The organic layer was dried over $MgSO_4$ and the solvent was evaporated. The product was purified by silica gel column chromatography (hexane:AcOEt=2:1) to afford **10** (2.9g; 91%) as a colorless solid (about 3:11 diastereomeric mixture). IR (neat) 1085, 1055 (SO) cm^{-1}; ^{1}H NMR δ 1.4-2.3 (6H, m), 2.43 (3H, s), 2.62 (2H, m), 4.36 (11/14H, dd, *J*=10, 3 Hz), 4.49 (3/14H, dd, *J*=10, 4 Hz), 7.1-7.7 (9H, m).

1-Chloro-1-methyl-5-phenylpentyl *p*-tolyl sulfoxide (12a) and 1-Chloro-1-benzyl-5-phenylpentyl *p*-tolyl sulfoxide (12b). A solution of the sulfoxide **10** (802 mg; 2.5 mmol) in 1 ml of THF was added dropwise to a stirred solution of LDA (3 mmol) in 5 ml of THF at -65 °C. The solution was stirred at -65 °C for 10 min, then iodomethane (0.37 ml; 6 mmol) was added. The reaction mixture was stirred and gradually allowed to warm to -35 °C (2 h). The reaction was quenched by adding sat. NH_4Cl. The usual workup followed by column chromatography gave 840 mg (99%) of **12a** as colorless solid (about 2:1 diastereomeric mixture). IR (KBr) 1080, 1050, 1016 (SO) cm^{-1}; ^{1}H NMR δ 1.45 (3H, s), 1.5-2.2 (6H, m), 2.42 (3H, s), 2.60 (2/3H, t, *J*=7 Hz), 2.67 (4/3H, t, *J*=7 Hz), 7.1-7.7 (9H, m).

Compound **12b** was synthesized from **10** with benzyl bromide in a similar way described above in quantitative yield as a colorless oil (about 2:1 diastereomeric mixture). IR (neat) 1081, 1053 (SO) cm^{-1}; ^{1}H NMR δ 1.4-2.2 (6H, m), 2.41 (1H, s), 2.44 (2H, s), 2.5-2.6 (2H, m), 3.19 (2/3H, d, *J*=14 Hz), 3.38 (4/3H, d, *J*=14 Hz), 7.0-7.8 (14H, m).

(*E*)-6-Phenyl-2-hexene (13). To a solution of **12a** (150 mg; 0.45 mmol) in 2 ml of THF in a 30 ml flame-dried flask at -75 °C was added *t*-BuLi (1.35 mmol) dropwise with stirring. The reaction mixture was stirred for 5 min, then the reaction was quenched with sat. NH_4Cl. The whole was extracted with ether-hexane and the solution was dried over $MgSO_4$. The product was purified by column chromatography to afford 63 mg (88%) of **13** as a colorless oil. IR (neat) 1605, 1497, 1454, 966 cm^{-1}; ^1H NMR δ 1.5-1.8 (5H, m), 1.9-2.2 (2H, m), 2.60 (2H, t, *J*=8 Hz), 5.43 (2H, m), 7.1-7.3 (5H, m); ^{13}C NMR δ 17.95, 31.30, 32.17, 35.40, 125.19, 125.62, 128.25, 128.46, 131.09, 142.66. The geometry of the double bond was assigned to be *E* from the chemical shift of methyl carbon (δ 17.95).[8] MS *m/z* (%) 160 (M^+, 35), 133 (12), 117 (16), 104 (100). Calcd for $C_{12}H_{16}$: M, 160.1251. Found: *m/z* 160.1250.

Treatment of 12b with *t*-BuLi. In a similar way as described above, **12b** (205 mg; 0.5 mmol) in 2 ml of dry THF at -90 °C was treated with 1.5 mmol of *t*-BuLi for 5 min to afford a mixture of olefins **14** and **15** (76mg; 65%) and chloride **16** (48mg; 35%). Olefines (**14** and **15**): Colorless oil; IR (neat) 1603, 1495, 1452, 966 cm^{-1}; ^1H NMR δ 5.55 (m, olefine protons of **14**), 6.1-6.5 (olefine protons of **15**); MS *m/z* (%) 236 (M^+, 45), 145 (20), 131 (20), 117 (51), 104 (75), 91 (100). Calcd for $C_{18}H_{20}$: M, 236.1565. Found: *m/z* 236.1556. Chloride **16**: Colorless oil; IR (neat) 1603, 1497, 1454, 748, 698 cm^{-1}; ^1H NMR δ 1.4-1.9 (6H, m), 2.59 (2H, t, *J*=7 Hz), 3.02 (2H, m), 4.07 (1H, m), 7.1-7.4 (10H, m); ^{13}C NMR δ 26.11, 30.91, 35.76, 37.43, 45.05, 63.83, 125.71, 126.74, 128.28, 128.37, 129.34, 138.0, 142.37; MS *m/z* (%) 272 (M^+, 15), 145 (18), 91 (100). Calcd for $C_{18}H_{21}Cl$: M, 272.1332. Found: *m/z* 272.1331.

2-Chloro-1,3-diphenyl-2-(*p*-tolylsulfinyl)propane (17). A solution of 1-chloro-2-phenyl-1-(*p*-tolylsulfinyl)ethane[9] (980 mg; 3.5 mmol) in 5 ml of THF was added with stirring to a solution of LDA (4.2 mmol) at -70 °C. After 10 min, HMPA (4.2 mmol) followed by benzyl bromide (5.3 mmol) were added and the temperature of the reaction mixture was allowed to warm to -30 °C for 4 h. The reaction was quenched by adding sat. NH_4Cl and the whole was extracted with ether-benzene. The product was purified by silica gel column chromatography to give 1.18 g (91%) of **17** as colorless amorphous. IR (KBr) 1078, 1049 (SO) cm^{-1}; ^1H NMR δ 2.42 (3H, s), 2.56, 2.72 (each 1H, d, *J*=14 Hz), 3.50, 3.56 (each 1H, d, *J*=9 Hz), 7.2-7.7 (14H, m); MS *m/z* (%) 368 (M^+, trace), 228 (40), 193 (52), 140 (100).

1,3-Diphenyl-1-propene (19). A solution of *t*-BuLi in pentane (1.62 mmol) was added to a solution of **17** (270 mg; 0.73 mmol) in 5.5 ml of dry THF at -100 °C under Ar atmosphere. After 5 min stirring the reaction was quenched with sat. NH_4Cl. The whole was extracted with ether-hexane and the product was purified by silica gel column chromatography to give **19** as a colorless oil. IR (neat) 1600, 1470, 1452, 964 cm^{-1}; ^1H NMR δ 3.54, 3.68 (each d, *J*=7 Hz; total 2H, intensity 13:1), 5.8-5.9 (1/14H, m), 6.3-6.6 (13/14H, m), 7.1-7.4 (10H, m); MS *m/z* (%) 194 (M^+, 100), 179 (40), 115 (79). Calcd for $C_{15}H_{14}$: M, 194.1094. Found: *m/z* 194.1089.

2-Chloro-1,3-diphenylpropane (20). Table 1, entry 3: A solution of EtMgBr (0.9 mmol) in ether was added dropwise with stirring to a solution of **17** (220 mg; 0.6 mmol) in 5 ml of THF at -78 °C. The reaction mixture was stirred for 5 min, then quenched by sat. NH_4Cl. The usual workup described above gave the chloride **20** (100 mg; 73%) as a colorless oil. IR (neat) 1601, 1497, 1454 cm^{-1}; ^1H NMR δ 3.0-3.2 (4H, m), 4.30 (1H, m), 7.2-7.4 (10H, m); MS *m/z* (%) 230 (M^+, 36), 194 (52), 91 (100). Calcd for $C_{15}H_{15}Cl$: M, 230.0862. Found: *m/z* 230.0876. This reaction was quenched with 0.2 ml of CD_3OD (Table 1, entry 10) to give deuterated **20** (R=D) in 88% yield. MS *m/z* 231 (M^+, 20), 195 (32), 91 (100). Calcd for $C_{15}H_{14}DCl$: M, 231.0925. Found: m/z 231.0918.

Treatment of 17 with Alkylmetal in the Presence of Internal Proton (Deuterium) Source. A representative example (Table 2, entry 8) is reported. A solution of *t*-BuLi in pentane (0.97 mmol) was added to a solution of **17** (89 mg; 0.24 mmol) and DMSO-d_6 (43 μl; 0.6 mmol) in 12 ml of THF at -78 °C under Ar atmosphere. The reaction mixture was stirred at -78 °C for 10 min and quenched by sat. NH_4Cl. The usual workup described above gave the deuterated chloride **20** (R=D; 54 mg; 96%; D content 88%). ^{1}H NMR δ 2.99, 3.10 (each 2H, d, *J*=14 Hz, benzyl-H).

α-Haloalkyl aryl sulfoxides in Table 3. The sulfoxides in Table 3 were synthesized by alkylation of 1-haloalkyl aryl sulfoxides with alkyl halides.[9] 1-Chloro-1,2-diphenylethyl phenyl sulfoxide (entries 1-3): Colorless amorphous: IR (KBr) 1095, 1061(SO) cm^{-1}; ^{1}H NMR δ 3.82, 4.06 (each 1H, d, *J*=14 Hz), 6.9-7.5 (15H, m); MS *m/z* (%) 304 ([M-HCl]$^+$, 3), 215 (82), 179 (100). 1-Benzyl-1-fluoro-2-phenylethyl *p*-tolyl sulfoxide (entries 5-7): Colorless amorphous; IR (KBr) 1082, 1041 (SO) cm^{-1}; ^{1}H NMR δ 2.42 (3H, s), 2.5-3.4 (4H, m), 7.1-7.6 (14H, m); MS *m/z* (%) 352 (M$^+$, 0.2), 212 (100). Calcd for $C_{22}H_{21}FOS$: M, 352.1298. Found: *m/z* 352.1295. 1-Fluoro-1,2-diphenylethyl phenyl sulfoxide (entries 8-10): Colorless amorphous (about 1:1 diastereomeric mixture); IR (KBr) 1082, 1051 (SO) cm^{-1}; ^{1}H NMR δ 3.64 (1H, dd, *J*=39, 14.5 Hz), 3.88 (1H, dd, *J*=14.5, 11Hz), 6.9-7.5 (15H, m); MS *m/z* (%) 324 (M$^+$, trace), 304 ([M-HF]$^+$, 0.5), 199 (100). 1-Fluoro-1-(4-phenylbutyl)undecyl phenyl sulfoxide (entries 11, 12): Light yellow oil (about 1:1 diastereomeric mixture); IR (neat) 1086, 1049 (SO) cm^{-1}; ^{1}H NMR δ 0.88 (3H, CH_3), 1.1-2.2 (24H, m), 2.55 (1H, t, *J*=7.4 Hz), 2.69 (1H, t, *J*=7 Hz), 7.0-7.7 (10H, m); MS *m/z* (%) 304 ([M-PhSOH]$^+$, 69), 117 (59), 91 (100). 1-Benzyl-1-bromo-2-phenylethyl phenyl sulfoxide (entry 13): Colorless amorphous; IR (KBr) 1084, 1072, 1043 (SO) cm^{-1}; ^{1}H NMR δ 2.72, 2.92 (each 1H, d, *J*=14 Hz), 3.65, 3.71 (each 1H, d, *J*=15 Hz), 7.2-7.9 (15H, m); MS *m/z* (%) 399, 401 (M$^+$, 20), 193 (78), 91 (100). Calcd for $C_{21}H_{20}BrOS$: M, 401.0397. Found: *m/z* 401.0407. 1-Benzyl-1-bromo-5-phenylpentyl phenyl sulfoxide (entry 14): Colorless oil (about 2:1 diastereomeric mixture): IR (neat) 1080, 1049 (SO) cm^{-1}; ^{1}H NMR δ 1.4-2.4 (6H, m), 2.4-2.7 (2H, m), 2.72 (2/3H, d, *J*=14.2 Hz), 3.27 (1/3H, d, *J*=14.5 Hz), 3.54 (2/3H, d, *J*=14.2 Hz), 3.50 (1/3H, d, *J*=14.5 Hz), 7.0-7.9 (15H, m); MS *m/z* (%) 316, 314 ([M-PhSOH]$^+$, 1.2), 91 (100). 1-Bromo-1-(4-phenylbutyl)undecyl phenyl sulfoxide (entry 15): Light yellow oil (about 1:1 diastereomeric mixrure); IR (neat) 1082, 1051 (SO) cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, *J*=7 Hz), 1.1-2.3 (24H, m), 2.57 (1H, t, *J*=7.3 Hz), 2.66 (1H, t, *J*=7 Hz), 7.0-7.8 (10H, m); MS *m/z* (%) 366, 364 ([M-PhSOH]$^+$, 4), 91 (100).

Alkyl halides in Table 3. 1-Chloro-1,2-diphenylethane (**24**): Colorless oil; IR (neat) 1601, 1495, 1446 cm^{-1}; ^{1}H NMR δ 3.25-3.45 (2H, m), 5.03 (1H, t, *J*=7.4 Hz), 7.0-7.5 (10H, m); MS *m/z* (%) 216 (M$^+$, 40), 178 (47), 125 (100). Calcd for $C_{14}H_{13}Cl$: M, 216.0705. Found: *m/z* 216.0702. 1-Chloro-1-deuterio-1,2-diphenylethane (**25**): Colorless oil; IR (neat) 1601, 1495, 1454 cm^{-1}; MS *m/z* (%) 217 (M$^+$, 29), 181 (31), 126 (77), 91 (100). Calcd for $C_{14}H_{12}DCl$: M, 217.0767. Found: *m/z* 217.0777. 2-Chloro-2-deuterio-6-phenylhexane (**26**): Colorless oil; IR (neat) 1605, 1470, 1454 cm^{-1}; ^{1}H NMR δ 1.4-1.8 (6H, m), 1.49 (3H, s), 2.62 (2H, t, *J*=7.4 Hz), 7.1-7.4 (5H, m); MS *m/z* (%) 197 (M$^+$, 25), 104 (33), 91 (100). Calcd for $C_{12}H_{16}DCl$: M, 197.1081. Found: *m/z* 197.1098. 2-Fluoro-1,3-diphenylpropane (**27**): Colorless oil; IR (neat) 1603, 1497, 1454 cm^{-1}; ^{1}H NMR δ 2.8-3.1 (4H, m), 4.90 (1H, ddd, *J*=48, 7, 5 Hz), 7.1-7.4 (5H, m); MS *m/z* (%) 214 (M$^+$, 77), 194 (12), 123 (28), 91 (100). Calcd for $C_{15}H_{15}F$: M, 214.1157. Found: *m/z* 214.1163. 2-Deuterio-2-fluoro-1,3-diphenylpropane (**28**): Colorless oil; IR (neat) 1605, 1497, 1454 cm^{-1}; MS *m/z* (%) 215 (M$^+$, 57), 195 (10), 124 (23), 91 (100). Calcd for $C_{15}H_{14}DF$: M, 215.1219. Found: *m/z* 215.1230. 1-Fluoro-1,2-diphenylethane (**29**): Colorless oil; IR (neat) 1601, 1497, 1454 cm^{-1}; ^{1}H NMR δ 2.9-3.4 (2H, m), 5.60 (1H, ddd, *J*=47.5, 8, 5 Hz), 7.1-7.4 (10H, m); MS *m/z* (%) 200 (M$^+$, 40), 180 (78), 109 (100). Calcd for $C_{14}H_{13}F$: M, 200.1001. Found: *m/z* 200.1025. 1-Deuterio-1-fluoro-1,2-diphenylethane (**30**): Colorless oil; IR (neat) 1605, 1497, 1454 cm^{-1}; ^{1}H NMR δ 3.09 (1H, dd, *J*=28, 14.5 Hz), 3.26 (1H, dd *J*=18, 14.5 Hz), 7.1-7.4 (10H, m); MS *m/z* (%) 201 (M$^+$, 33), 181 (13), 110 (100). Calcd for $C_{14}H_{12}DF$: M, 201.1064. Found: *m/z* 201.1070. 5-Deuterio-5-fluoro-1-phenylpentadecane (**31**): Colorless oil; IR (neat) 1605, 1497, 1464, 1454 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, *J*=7 Hz), 1.2-1.8 (24H, m), 2.62 (2H, t, *J*=8 Hz), 7.1-7.3 (5H, m); MS *m/z* 307 (M$^+$, 0.6), 287 (10), 117 (13), 104 (100). Calcd for $C_{21}H_{34}DF$:M, 307.2785. Found: *m/z* 307.2788. 2-Bromo-2-deuterio-1,3-diphenylpropane (**32**): Colorless oil; IR (neat) 1603, 1496, 1454 cm^{-1}; ^{1}H NMR δ 3.13 (2H, d, *J*=14.5 Hz), 3.32 (2H, d, *J*=14.2 Hz), 7.1-7.4 (10H, m); MS *m/z* (%) 277, 275 (M$^+$, 7), 195 (17), 118 (37), 91 (100).

Calcd for $C_{15}H_{14}DBr$: M, 277.0399. Found: *m/z* 277.0406. 2-Bromo-2-deuterio-1,6-diphenylhexane (**33**): Colorless oil; IR (neat) 1603, 1470, 1454 cm^{-1}; ^{1}H NMR δ 1.4-2.0 (6H, m), 2.60 (2H, t, *J*=7.3 Hz), 3.12 (1H, d, *J*=14 Hz), 3.17 (1H, d, *J*=14 Hz), 7.1-7.4 (10H, m); MS *m/z* (%) 319, 317 (M$^+$, 2), 238 (19), 91 (100). Calcd for $C_{18}H_{20}DBr$: M, 317.0889. Found: *m/z* 317.0890. 5-Bromo-5-deuterio-1-phenylpentadecane (**34**): Colorless oil; IR (neat) 1605, 1497, 1464, 1454 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, *J*=7 Hz), 1.1-1.9 (24H, m), 2.62 (2H, t, *J*=7.6 Hz), 7.1-7.3 (5H, m); MS *m/z* (%) 369, 367 (M$^+$, 3), 287 (16), 91 (100). Calcd for $C_{21}H_{34}DBr$: M, 367.1985. Found: *m/z* 367.1994.

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