Pergamon

*Tetrahedron* Vol. 51, No. 3, pp. 703-710, 1995

0040-4020/95 $9.50+0.00

0040-4020(94)00989-9

# Ligand Exchange Reaction of Sulfoxides in Organic Synthesis: A New Synthesis of α-Chloroketones from Carbonyl Compounds with One-Carbon Homologation

Tsuyoshi Satoh, Yasuhiro Mizu, Taku Kawashima, and Koji Yamakawa

Faculty of Pharmaceutical Sciences, Science University of Tokyo, Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162, Japan

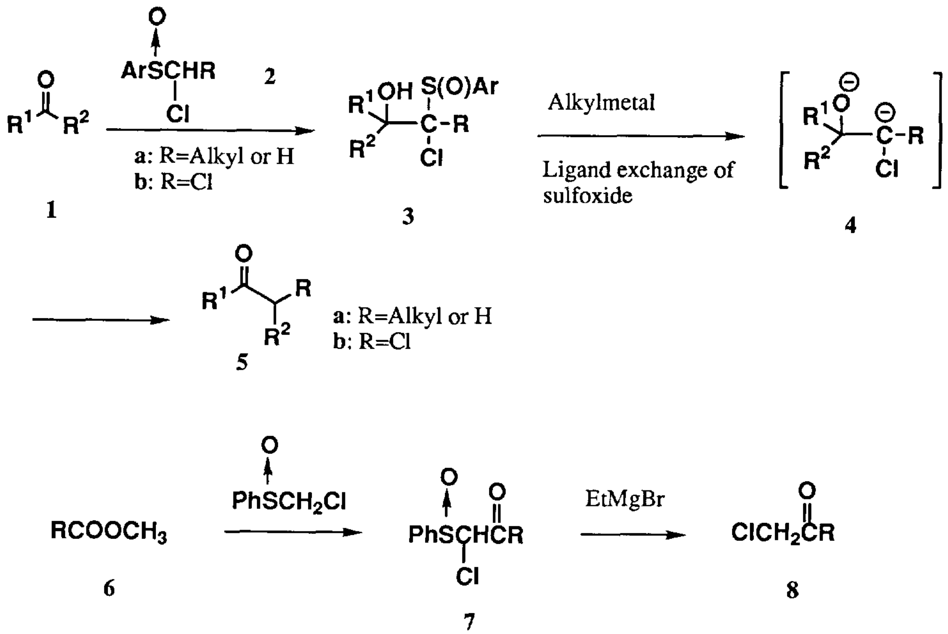
***Abstract:*** *A new procedure for one-carbon homologation of carbonyl compounds to α-chloroketones is described. Addition of the carbanion of dichloromethyl phenyl sulfoxide with ketones and aldehydes gave the adducts, chloro alcohols, in good yields. Treatment of the chloro alcohols with EtMgBr or lithium diisopropylamide gave one-carbon homologated α-chloroketones via β-oxido carbenoid rearrangement in moderate to good yields. One-carbon homologation of esters to α-chloroketones was realized via the ligand exchange reaction of the sulfinyl group of α-chloro α-sulfinyl ketones, which were synthesized from methyl esters and chloromethyl phenyl sulfoxide, with EtMgBr.*

α-Haloketones are quite important compounds in synthetic organic chemistry.[1] There is a number of direct halogenation methods for synthesizing α-haloketones from the corresponding ketones. However, procedures involving a carbon-carbon bond-forming reaction are limited.[2]

Recently, we have reported a new procedure for one-carbon homologation of carbonyl compounds **1** to carbonyl compounds having an α-alkyl substituent **5a** using aryl 1-chloroalkyl sulfoxide **2a** as the homologating agents[3] (Scheme 1). This procedure is based on the rearrangement of the β-oxido carbenoid[4] **4** which is generated from the chloro alcohol **3** with alkylmetal via the ligand exchange reaction of sulfoxide.[5,6] In the study, we anticipated that the reaction using dichloromethyl phenyl sulfoxide **2b** (Ar=Ph, R=Cl) may afford a new procedure for homologation of carbonyl compounds to α-chloroketones **5b** (R=Cl).

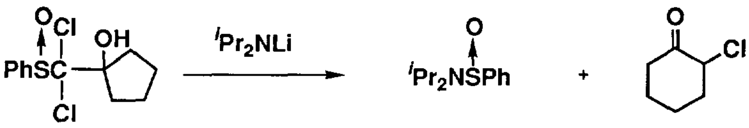
In this paper, we report, in detail, a new procedure for a synthesis of α-chloroketones **5b** from ketones and aldehydes with one-carbon homologation. We also report a new procedure for sythesizing α-chloroketones **8** from esters **6** and chloromethyl phenyl sulfoxide via the ligand exchange reaction of **7** with ethylmagnesium bromide (Scheme 1).

## One-Carbon Homologation of Ketones and Aldehydes to α-Chloroketones via β-Oxido Carbenoid Rearrangement.



Scheme 1

Dichloromethyl phenyl sulfoxide **2b**[7] was treated with lithium diisopropylamide (LDA) in THF at -60 °C followed by cyclopentanone to give the adduct **9** in 97% yield (see Table 1). First, in line with on our experience in the previous work,[3] the chloro alcohol **9** was treated with *t*-BuLi at -78 °C for 15 min; however, this reaction only gave a complex mixture with a trace of the desired 2-chloro-1-cyclohexanone **10** (Table 1; entry 1). Use of phenyllithium as the alkylmetal improved the yield of **10** to 43% (entry 2).



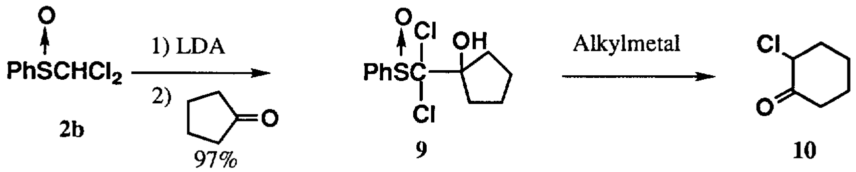
**9** **11** **10**

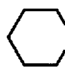
Meanwhile, we found that **9** reacted with LDA to afford sulfinamide **11** in quantitative yield. From this result it can be deduced that in this particular case even lithium amide having low nucleophilic property could be used for the ligand exchange reaction of the sulfoxide. Searching for the other part of **9**, the desired chloroketone **10** was obtained; however, the yield was only 30%. Other lithium amides gave the same results (Table 1; entries 4 and 5).

Next, we turned our attention to Grignard reagent as the alkylmetal for the ligand exchange reaction of the sulfoxides.[6f,k] Treatment of **9** with excess EtMgBr in THF at -70 to -40 °C for 1.5 h gave the desired **10** in 68% yield.

This reaction was applied to other ketones. As shown in Table 2, the carbanion of dichloromethyl phenyl soulfoxide reacted with cyclobutanone and cyclohexanone to give the adducts in high yields. Unfortunately, this carbanion did not react with cycloheptanone and other larger cycloalkanones, or with acyclic ketones. The chloro

Table 1. One-Carbon Homologation of Cyclopentanone to 2-Chloro-1-cyclohexanone




| Entry | Alkylmetal (equiv) | 10 Yield (%)[a)] |
|---|---|---|
| 1 | t-BuLi (4) | trace |
| 2 | PhLi (3) | 43 |
| 3 | LDA (3)[b)] | 30 [c)] |
| 4 | $Et_2NLi$ (3)[b)] | 30 [c)] |
| 5 |  NLi (3)[b)] | 30 [c)] |
| 6 | EtMgBr (5)[b)] | 68 |

a) Isolated yield. b) All the reactions were conducted at -70 to -40 °C for 1.5 h in THF.
c) Almost quantative yield of the corresponding sulfinamide was obtained.

alcohol obtained from cylcobutanone **12a** gave 2-chloro-1-cyclopentanone **13** in moderate yield (entry 1). The chloro alcohol **12b** gave β-naphthol **14** in 60% yield. Cyclohexanone gave the adduct **12c** in quantitative yield; however, the treatment of **12c** with EtMgBr gave only a complex mixture.

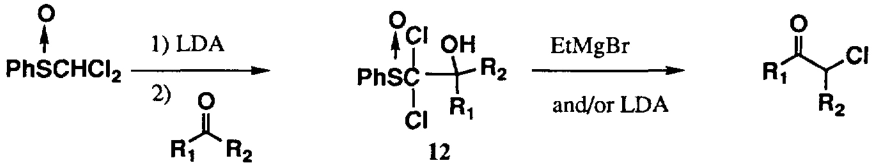
Entries 4-7 show the results with aldehydes. The carbanion of dichloromethyl phenyl sulfoxide reacted with various aldehydes to give good yields of the adducts. The ligand exchange reaction of the sulfinyl group and the rearrangement of the resulting β-oxido carbenoid was carried out with both EtMgBr and LDA. As shown in Table 2 (entries 4-7), this reaction gave moderate to good yields of the desired α-chloroketones. Usually, the yield was better when EtMgBr was used as the alkylmetal. In the β-oxido carbenoid rearrangement, migration of both hydrogen and the alkyl group (or aryl group) is possible. These results (products **15-18**) can be explained by the much higher migratory aptitude of hydrogen over the alkyl (or aryl) group in this type of rearrangement.[8]

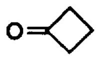
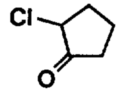
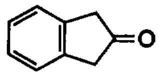
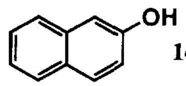
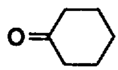
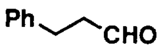
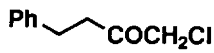
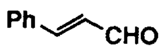
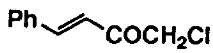
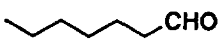
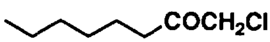
## One-Carbon Homologation of Esters to α-Chloroketone via Ligand Exchange Reaction of Sulfoxide.

In previous papers, we reported that the ligand exchange reaction of the sulfinyl group of α-halo α-sulfinylketones gave desulfinylated magnesium enolates.[6f] If this reaction can be applied to chloro(sulfinyl)methyl ketone **7** (Scheme 1), a new procedure for one-carbon homologation of esters to α-chloroketones would be realized.

First, lithium carbanion of chloromethyl phenyl sulfoxide[7a,9] was reacted with methyl benzoate to give the desired α-chloro α-sulfinylketone **19a** in 84% yield as a mixture of two diastereomers (Table 3; entry 1). Next,

Table 2. One-Carbon Homologation of Carbonyl Compound to α-Chloroketones via the Ligand Exchange Reaction of Sulfoxides

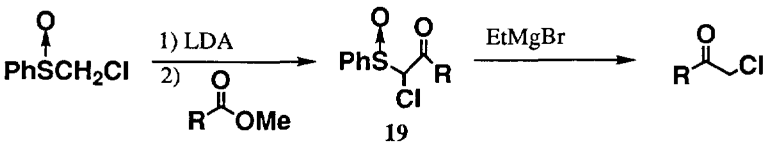



| Entry | Ketone or Aldehyde | Chloro alcohol Yield(%) | α-Chloroketone [a] Yield(%) |
|---|---|---|---|
| 1 |  | **12a** (90) |  **13** (63) |
| 2 |  | **12b** (85) |  **14** (60) |
| 3 |  | **12c** (99) | — |
| 4 | PhCHO | **12d** (97) | $PhCOCH_2Cl$ **15** (83, 30[b]) |
| 5 |  | **12e** (80) |  **16** (55, 55[b]) |
| 6 |  | **12f** (88) |  **17** (38, 41[b]) |
| 7 |  | **12g** (75) |  **18** (50, 27[b]) |

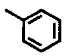
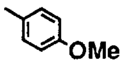
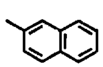
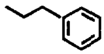
a) All reactions were carried out in THF with 3 equivalents of EtMgBr at -78 to -45 °C for 1.5 h.
b) The yield when this reaction was carried out with 3 equivalents of LDA in THF at -78 to -40 °C for 2 h.

ligand exchange reaction of the sulfinyl group of **19a** with alkylmetal was investigated. The optimal conditions are as follows. A solution of **19a** in THF was added to a solution of 4 equivalents of EtMgBr in THF at -70 °C and the reaction mixture was stirred for 2 h. This reaction gave chloromethyl phenyl ketone **15** in 65% yield with ethyl phenyl sulfoxide (85%). Representative examples are shown in Table 3. Though the yield of the ligand exchange reaction was moderate, this two-step homologation of esters to α-chloroketones offers a useful procedure for chloromethylation of esters.

Table 3. One-Carbon Homologation of Esters to α-Chloroketones via the Ligand Exchange Reaction of α-Sulfinylketones with EtMgBr




19

| Entry | R | α-Sulfinylketone Yield (%)[a] | α-Chloroketone Yield (%) |
|---|---|---|---|
| 1 |  | **19a** (84) | **15** (65) |
| 2 |  | **19b** (87) | **20** (60) |
| 3 |  | **19c** (77) | **21** (63) |
| 4 |  | **19d** (95) | **16** (50) |

a) Isolated yield. A mixture of two diastereomers.

## Experimental Section

All melting points are uncorrected. $^1$H NMR spectra were measured in a $CDCl_3$ solution with JEOL FX-100 or GX-270 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel BW-127 ZH (Fuji-Devison) 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 was dried over $CaH_2$ and distilled.

**1-[Dichloro(phenylsulfinyl)methyl]-1-cyclopentanol (9).** A solution of dichloromethyl phenyl sulfoxide (627 mg; 3 mmol) in 2 ml of dry THF was added to a solution of LDA (3.6 mmol) in 10 ml of dry THF at -65 °C under Ar atmosphere with stirring. The reaction mixture was stirred at -65 °C for 10 min. Cyclopentanone (0.3 ml; 3.3 mmol) was added to the reaction mixture and the solution was stirred for 30 min. The reaction was quenched with sat. aq. $NH_4Cl$ and the whole was extracted with ether-benzene. The extract was washed with sat. aq. $NH_4Cl$, dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by silica gel column chromatography (hexane:AcOEt=4:1) to afford **9** (853 mg; 97%) as colorless crystals; mp 94-95 °C (AcOEt-hexane). IR (KBr) 3280 (OH), 1060 (SO) $cm^{-1}$; $^1H$ NMR δ 1.4-2.7 (8H, m), 3.74 (1H, s, OH), 7.4-7.9 (5H, m); MS *m/z* (%) 293 ($[M+H]^+$, 0.2), 191 (1.6), 126 (100). Found: C, 49.22; H, 4.78; Cl, 23.83; S, 11.15%. Calcd for $C_{12}H_{14}Cl_2O_2S$: C, 49.16; H, 4.81; Cl, 24.18; S, 10.94%.

**Chloro Alcohols 12a-12g**. The chloro alcohols **12a-12g** in Table 2 were synthesized in a similar way as described for **9**. 1-[Dichloro(phenylsulfinyl)methyl]-1-cyclobutanol (**12a**). Colorless crystals; mp 152-154 °C (AcOEt-hexane); IR (KBr) 3355 (OH), 1080, 1047 (SO) $cm^{-1}$; $^1H$ NMR δ 1.8-2.0 (1H, m), 2.0-2.4 (3H, m), 2.7-2.9 (2H, m), 3.96 (1H, s, OH), 7.5-7.7 (3H, m), 7.8-8.0 (2H, m). Found: C, 47.00; H, 4.27; C, 25.03; S, 11.63%. Calcd for $C_{11}H_{12}Cl_2O_2S$: C, 47.32; H, 4.33; Cl, 25.40; S, 11.48%. 2-[Dichloro(phenylsulfinyl)-methyl]-2-indanol (**12b**). Colorless crystals; mp 169-170 °C (AcOEt-hexane); IR (KBr) 3390 (OH), 1080, 1040 (SO) $cm^{-1}$; $^1H$ NMR δ 3.28, 3.38, 3.83, 4.00 (each 1H, d, *J*=16 Hz), 7.1-7.4 (4H, m), 7.5-7.7 (3H, m), 7.9-8.0 (2H, m). Found: C, 56.13; H, 4.04; Cl, 20.71; S, 9.66%. Calcd for $C_{16}H_{14}Cl_2O_2S$: C, 56.31; H, 4.14; Cl, 20.78; S, 9.40%. **12c**. Lit. 7b and 7c; mp 135-136 °C (AcOEt-hexane); Found: C, 50.83; H, 5.17; Cl, 22.85; S, 10.64%. Calcd for $C_{13}H_{16}Cl_2O_2S$: C, 50.82; H, 5.25; Cl, 23.08; S, 10.44%. 2,2-Dichloro-1-phenyl-2-(phenylsulfinyl)-1-ethanol (**12d**). Colorless crystals (about 1:1 diastereomeric mixture); IR (KBr) 3300 (OH), 1080, 1050 (SO) $cm^{-1}$; $^1H$ NMR δ 5.44, 5.46 (each 0.5H, s), 7.2-7.9 (10H, m); MS *m/z* (%) 315 ($[M+H]^+$, trace), 126 (100). Found: *m/z* 315.0011. Calcd for $C_{14}H_{13}Cl_2O_2S$: M, 315.0011. 1,1-Dichloro-4-phenyl-1-(phenylsulfinyl)-2-butanol (**12e**). Colorless oil (about 1:1 diastereomeric mixture); IR (neat) 3400 (OH), 1080, 1050 (SO) $cm^{-1}$; $^1H$ NMR δ 2.0-2.4 (2H, m), 2.7-3.1 (2H, m), 4.23, 4.34 (each 0.5H, m), 7.1-7.4 (5H, m), 7.5-7.7 (3H, m), 7.8-7.9 (2H, m). Found: *m/z* 343.0320 (M+H). Calcd for $C_{16}H_{17}Cl_2O_2S$: M, 343.0324. (*E*)-1,1-Dichloro-4-phenyl-1-(phenylsulfinyl)-3-buten-2-ol (**12f**). Colorless oil (about 7:3 diastereomeric mixture); IR (neat) 3260 (OH), 1085, 1040 (SO) $cm^{-1}$; $^1H$ NMR δ 4.94 (0.3H, t, *J*=6 Hz), 5.09 (0.7H, t, *J*=6 Hz), 6.3-6.5 (1H, m), 6.8-7.0 (1H, m), 7.2-8.0 (10H, m); MS *m/z* (%) 340 ($M^+$, 0.5), 288 (0.5), 179 (30), 126 (100). Found: *m/z* 340.0105. Calcd for $C_{16}H_{14}Cl_2O_2S$: M, 340.0099. 1,1-Dichloro-1-(phenylsulfinyl)-2-octanol (**12g**). Colorless oil (about 1:1 diastereomeric mixture); IR (neat) 3400 (OH), 1080, 1060 (SO) $cm^{-1}$; $^1H$ NMR δ 0.88 (3H, t, *J*=7 Hz), 1.2-2.1 (10H, m), 4.14, 4.32 (each 0.5H, m), 7.5-7.9 (5H, m). Found: *m/z* 323.0644 (M+H). Calcd for $C_{14}H_{21}Cl_2O_2S$: M, 323.0638.

**2-Chloro-1-cyclohexanone (10)**. A solution of EtMgBr (2.5 mmol) in ether was added with stirring to a solution of the chloro alcohol **9** (147 mg; 0.5 mmol) in 5 ml of dry THF at -70 °C under Ar atmosphere. The reaction mixture was stirred at -70 to -45 °C for 2 h, then quenched with sat. aq. $NH_4Cl$. The whole was extracted with ether-benzene. The product was purified by silica gel column chromatography to afford 45 mg (68%) of **10** as a colorless oil.

A solution of **9** (147 mg; 0.5 mmol) in 2 ml of dry THF was added to a solution of LDA (1.5 mmol) in 5 ml of dry THF at -78 °C with stirring. The reaction mixture was stirred at -78 to -45 °C for 2 h, then the reaction was quenched with sat. aq. $NH_4Cl$. Similar workup as described above gave 112 mg (99%) of the sulfinamide **11** (Colorless crystals; IR (KBr) 1085, 1060 (SO) $cm^{-1}$; NMR δ 1.12, 1.42 (each 6H, d, *J*=7 Hz), 3.56 (2H, septet, *J*=7 Hz), 7.4-7.7 (5H, m)) and α-chloroketone **10** (30%).

**Chloroketones 15-18** (Table 2). These chloroketones were synthesized from **12d-12g**, respectively, in a similar way as described for **10** with 3 equivalents of EtMgBr or LDA. 2-Chloro-1-phenyl-1-ethanone (**15**). Colorless oil; IR (neat) 1695 (CO) $cm^{-1}$; $^1H$ NMR δ 4.72 (2H, s), 7.4-7.7 (3H, m), 7.95-8.0 (2H, m); MS *m/z*

(%) 154 ($M^+$, 2.5), 105 (100). Found: *m/z* 154.0183. Calcd for $C_8H_7ClO$: M, 154.0184. 1-Chloro-4-phenyl-2-butanone (**16**). Colorless oil; IR (neat) 1735 (CO) $cm^{-1}$; $^1H$ NMR δ 2.93 (4H, m), 4.02 (2H, s), 7.1-7.4 (5H, m); MS *m/z* (%) 182 ($M^+$, 45), 133 (50), 105 (100). Found: *m/z* 182.0488. Calcd for $C_{10}H_{11}ClO$: M, 182.0497. (*E*)-1-Chloro-4-phenyl-3-buten-2-one (**17**). Colorless oil; IR (neat) 1690 (CO), 1610 (C=C) $cm^{-1}$; $^1H$ NMR δ 4.30 (2H, s), 6.98 (1H, d, *J*=16 Hz), 7.35-7.50 (3H, m), 7.55-7.65 (2H, m), 7.71 (1H, d, *J*=16 Hz); MS *m/z* (%) 180 ($M^+$, 20), 131 (100). Found: *m/z* 180.0329. Calcd for $C_{10}H_9ClO$: M, 180.0341. 1-Chloro-2-octanone (**18**). Colorless oil; IR (neat) 1730, 1720 (CO) $cm^{-1}$; $^1H$ NMR δ 0.89 (3H, t, *J*=7 Hz), 1.29 (4H, m), 1.61 (2H, m), 2.59 (2H, t, *J*=7 Hz), 4.08 (2H, s); MS *m/z* (%) 162 ($M^+$, 0.3), 113 (96), 43 (100). Found: *m/z* 162.0809. Calcd for $C_8H_{15}ClO$: M, 162.0809.

**2-Chloro-2-(phenylsulfinyl)-1-phenyl-1-ethanone (19a).** A solution of chloromethyl phenyl sulfoxide (353 mg; 2 mmol) in 2 ml of dry THF was added dropwise with stirring to a solution of LDA (4 mmol) in 10 ml of dry THF at -65 °C. The mixture was stirred at -65 °C for 10 min. Methyl benzoate (0.25 ml; 2.2 mmol) was added to the reaction mixture with stirring and the stirring was continued for 30 min at -65 °C. The reaction was quenched with sat. aq. $NH_4Cl$ and the whole was extracted with ether-benzene. The product was purified by silica gel column chromatography (hexane:AcOEt=4:1-2:1) to give 468 mg (84%) of **19a** as pale yellow crystals (about 1:1 diastereomeric mixture). IR (KBr) 1680 (CO), 1080, 1050 (SO) $cm^{-1}$; $^1H$ NMR δ 5.81, 5.86 (each 0.5H, s), 7.3-8.1 (10H, m); MS *m/z* (%) 278 ($M^+$, 6), 125 (100). Found: *m/z* 278.0152. Calcd for $C_{14}H_{11}ClO_2S$: M, 278.0167.

**α-Sulfinyl Ketones 19b-19d** (Table 3). These ketones were synthesized from the corresponding methyl esters in a similar way as described for **19a**. 2-Chloro-1-(4-methoxyphenyl)-2-(phenylsulfinyl)-1-ethanone (**19b**). Colorless oil (about 1:1 diastereomeric mixture); IR (neat) 1670 (CO), 1080, 1050 (SO) $cm^{-1}$; $^1H$ NMR δ 3.83, 3.89 (each 1.5H, s), 5.76, 5.80 (each 0.5H, s), 7.8-8.0 (9H, m); MS *m/z* (%) 308 ($M^+$, 7), 218 (4), 155 (64), 135 (100). Found: *m/z* 308.0272. Calcd for $C_{15}H_{13}ClO_3S$: M, 308.0272. 2-Chloro-1-(2-naphthyl)-2-(phenylsulfinyl)-1-ethanone (**19c**). Pale yellow crystals (about 1:1 diastereomeric mixture); IR (KBr) 1685 (CO), 1085, 1055 (SO) $cm^{-1}$; $^1H$ NMR δ 5.98, 6.01 (each 0.5H, s), 7.3-8.5 (12H, m); MS *m/z* (%) 328 ($M^+$, s), 250 (2), 218 (22), 155 (100). Found: 328.0324. Calcd for $C_{18}H_{13}ClO_2S$: M, 328.0324. 1-Chloro-4-phenyl-1-(phenylsulfinyl)-2-butanone (**19d**). Colorless oil (about 1:1 diastereomeric mixture); IR (neat) 1720 (CO), 1085, 1050 (SO) $cm^{-1}$; $^1H$ NMR δ 2.5-3.2 (4H, m), 4.99, 5.03 (each 0.5H, s), 7.0-7.7 (10H, m); MS *m/z* (%) 306 ($M^+$, 1.5), 250 (0.6), 181 (23), 125 (100). Found: *m/z* 306.0463. Calcd for $C_{16}H_{15}ClO_2S$: M, 306.0479.

**2-Chloro-1-(4-methoxyphenyl)-1-ethanone (20).** A solution of **19b** (154 mg; 0.5 mmol) in 1 ml of dry THF was added dropwise to a solution of EtMgBr (2 mmol) in 5 ml of dry THF at -70 °C with stirring. The reaction mixture was stirred at -70 to -40 °C for 2 h. The reaction was quenched with sat. aq. $NH_4Cl$ and the whole was extracted with ether-benzene. The product was purified by silica gel column chromatography to give 110 mg (60%) of **20** as a colorless oil. IR (neat) 1693 (CO) $cm^{-1}$; $^1H$ NMR δ 3.88 (3H, s), 4.65 (2H, s), 6.95 (2H, m), 7.95 (2H, m); MS *m/z* (%) 184 ($M^+$, 11), 165 (4), 135 (100). Found: *m/z* 184.0290. Calcd for $C_9H_9ClO_2$: M, 184.0290.

α-Chloroketones **15**, **16** and **21** (Table 3) were synthesized in a similar way as described for **20**. 2-Chloro-1-(2-naphthyl)-1-ethanone (**21**). Colorless crystals; IR (KBr) 1690 (CO) $cm^{-1}$; $^1H$ NMR δ 4.84 (2H, s), 7.25-8.0 (6H, m), 8.47 (1H, s); MS *m/z* (%) 204 ($M^+$, 25), 155 (100), 127 (55). Found: *m/z* 204.0350. Calcd for $C_{12}H_9ClO$:M, 204.0342.

**Acknowledgements:** We are grateful to Noriko Sawabe and Fukiko Hasegawa of this laboratory for NMR and MS measurements. This work was supported by a Grant-in-Aid for Scientific Research No 05671771 from the Ministry of Education, Science and Culture, and the SUT Grant for Research Promotion 1994 (T. S.) from Science University of Tokyo, which are gratefully acknowledged.

## References and Notes


1. N. D. Kimpe and R. Verhe, "The Chemistry of α-Haloketones, α-Haloaldehydes and α-Haloimines", S. Patai and Z. Rappoport Ed., John Wiley and Sons, Chichester (1988).

2. H. Taguchi, H. Yamamoto, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **50**, 1592 (1977); V. Reutrakul, A. Tiensripojamarn, K. Kusamran, and S. Nimgirawath, *Tetrahedron Lett.*, **1977**, 209; V. Reutrakul and W. Kanghae, *Tetrahedron Lett.*, **1977**, 1225; J. Villieras and M. Rambaud, *Synthesis*, **1980**, 644; J. Villieras, M. Rambaud, R. Tarhouni, and B. Kirschleger, *Synthesis*, **1981**, 68; V. Reutrakul and K. Herunsalee, *Tetrahedron Lett.*, **24**, 527 (1983); V. Reutrakul and V. Rukachaisirikul, *Tetrahedron Lett.*, **24**, 725 (1983).

3. T. Satoh, N. Itoh, K. Gengyo, and K. Yamakawa, *Tetrahedron Lett.*, **33**, 7543 (1992); T. Satoh, N. Itoh, K. Gengyo, S. Takada, N. Asakawa, Y. Yamani, *Tetrahedron*, in press.

4. H. Taguchi, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **96**, 6510 (1974); H. Taguchi, H. Yamamoto, and H. Nozaki, *Tetrahedron Lett*, **1976**, 2617; J. Villieras, P. Perriot, and J. F. Normant, *Synthesis*, **1979,** 968; W. D. Abraham, M. Bhupathy, and T. Cohen, *Tetrahedron Lett.*, **28**, 2203 (1987); H. D. Ward, D. S. Teager, and R. K. Murray, Jr., *J. Org. Chem.*, **57**, 1926 (1992);

5. A review for ligand exchange reaction of sulfoxides: S. Oae, "Reviews on Heteroatom Chemistry" ed. by S. Oae, MYU, Tokyo, **4**, 195 (1991).

6. Some of our recent publications for the ligand exchange reaction of sulfoxides in organic synthesis: a) T. Satoh, Y. Kaneko, and K. Yamakawa, *Bull. Chem. Soc. Jpn.*, **59**, 2463 (1986); b) T. Satoh, T. Oohara, Y. Ueda, and K. Yamakawa, *Tetrahedron Lett.*, **29**, 313 (1988); c) T. Satoh, T. Oohara, and K. Yamakawa, *Tetrahedron Lett.*, **29**, 4093 (1988); d) T. Satoh, T. Oohara, Y. Ueda, and K. Yamakawa, *J. Org. Chem.*, **54**, 3130 (1989); e) T. Satoh, T. Sato, T. Oohara, and K. Yamakawa, *J. Org. Chem.*, **54**, 3973 (1989); f) T. Satoh, N. Itoh, K. Onda, Y. Kitoh, and K. Yamakawa, *Bull. Chem. Soc. Jpn.*, **65**, 2800 (1992); g) T. Satoh, Y. Kitoh, K. Onda, and K. Yamakawa, *Tetrahedron Lett.*, **34**, 2331 (1993); h) T. Satoh, Y. Hayashi, and K. Yamakawa, *Bull. Chem. Soc. Jpn.*, **66**, 1866 (1993); i) T. Satoh, Y. Mizu, Y. Hayashi, and K. Yamakawa, *Tetrahedron Lett.*, **35**, 133 (1994); j) T. Satoh, N. Itoh, S. Watanabe, H. Matsuno, and K. Yamakawa, *Chem. Lett.*, **1994**, 567; k) T. Satoh, Y. Kitoh, K. Onda, K. Takano, and K. Yamakawa, *Tetrahedron*, **50**, 4957 (1994).

7. a) K. C. Tin and T. Durst, *Tetrahedron Lett.*, **1970**, 4643; b) V. Reutrakul and K. Herunsalee, *Tetrahdron Lett.*, **24**, 527 (1983); c) V. Reutrakul and P. Poochaivatananon, *Tetrahedron Lett.*, **24**, 531 (1983); d) C. Mahidol, V. Reutrakul, C. Panyachotipun, G. Turongsomboon, V. Prapansiri, and B. M. R. Bandara, *Chem. Lett.*, **1989**, 163.

8. B. P. Philip and J. Keating, *Tetrahedron Lett.*, **1961**, 523; B. P. Philip, M. K. Lowery, and J. Havel, *Tetrahedron Lett.*, **1967**, 5049.

9. G. Tsuchihashi, K. Ogura, S. Iriuchijima, *Synthesis*, **1971**, 89; T. Satoh and K. Yamakawa, *Synlett*, **1992**, 455.


(*Received in Japan* 16 *September* 1994; *accepted* 4 *November* 1994)