Pergamon

Tetrahedron Vol. 50, No. 41, pp. 11839-11852, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)00743-8

New Method for Generation of β-Oxido Carbenoid via Ligand Exchange Reaction of Sulfoxides: A Versatile Procedure for One-Carbon Homologation of Carbonyl Compounds

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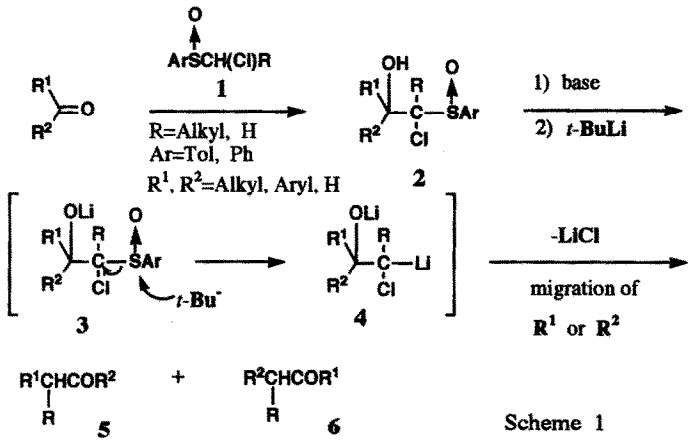
Abstract: *A new procedure for one-carbon homologation of carbonyl compounds is described. The method is based on the rearrangement of β-oxido carbenoid which is generated via the ligand exchange reaction of the sulfinyl group of α-chloro β-hydroxy sulfoxide with tert-butyllithium. Addition of the carbanion of aryl 1-chloroalkyl sulfoxides to carbonyl compounds gave the adducts in good yields. The β-oxido carbenoid rearrangement of the adducts gave one-carbon homologated carbonyl compounds having an α-alkyl substituent. A similar reaction of the adducts derived from carbonyl compounds with chloromethyl p-tolyl sulfoxide yielded a procedure for a methylene insertion. The stereochemistry of the β-oxido carbenoid rearrangement is also discussed.*

The rearrangement of β-oxido carbenoids is reported to be one of the most useful reactions for one-carbon homologation of carbonyl compounds[1] including one-carbon ring-expansion of cyclic ketones.[2] The method from Nozaki[3] and Villieras[4] is based on the rearrangement of the adduct of carbonyl compounds with dichloromethyllithium or dibromomethyllithium. Cohen reported a similar reaction using the adduct of cyclic ketones with bis(phenylthio)methyllithium.[5] These methods are quite versatile; however, in view of the importance of this kind of reaction in organic chemistry, new methods are still eagerly sought.

Recently, we have reported some new synthetic methods using aryl 1-haloalkyl sulfoxides.[6] Specifically, we have focused our attention on the chemistry of the ligand exchange reaction of sulfoxides,[7] and many new synthetic reactions have been developed.[8] In continuation of our studies on the ligand exchange reaction of sulfoxides in organic synthesis we report here, in detail, a new method for a synthesis of one-carbon homologated carbonyl compounds (**5** and **6**) from carbonyl compounds and aryl 1-chloroalkyl sulfoxides **1** via the β-oxido carbenoid rearrangement (Scheme 1).[9]

One-Carbon Homologation of Ketones to Ketones Having an α-Alkyl Substituent Using 1-Chloroalkyl *p*-Tolyl Sulfoxides as Homologating Agents.

Carbenes and carbenoids[10] have been known as highly reactive carbon species and are recognized as useful intermediates in organic synthesis.[11] Generation of carbenes and carbenoids has mainly been carried out in two



Scheme 1

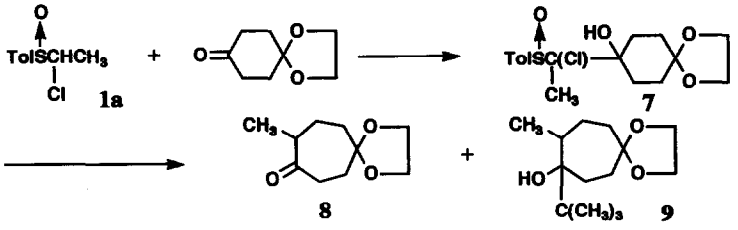
ways: photolysis, pyrolysis, and catalytic decomposition of diazo compounds, and base-induced α-elimination.[11b] In our studies on the ligand exchange reaction of sulfoxides, we anticipated that the easily prepared α-chloro β-hydroxy sulfoxides **2** would give β-oxido carbenoids **4** via the ligand exchange reaction of sulfoxides with alkyllithium as shown in Scheme 1. This expectation was soon confirmed.

Treatment of 1-chloroethyl *p*-tolyl sulfoxide **1a** with 1.2 equivalents of lithium diisopropylamide (LDA) in THF at -70 °C gave the carbanion, which was subjected to react with 1,4-cyclohexanedione mono-ethylene ketal to give the adduct **7** in 90% yield.[12] First, 5 equivalents of *t*-BuLi[13] was added dropwise to a solution of the adduct **7** in THF at -60 °C. After 5 min, the reaction was quenched with aqueous NH_4Cl. All the starting material disappeared and two products **8** and **9** were obtained in 49% and 36% yield, respectively (Scheme 2). Both were the ring-expanded products; however, in this procedure a fair amount of undesired **9** was obtained.

Formation of **8** and **9** can be assumed as follows (Scheme 3). Dropwise addition of *t*-BuLi to **7** gives, in part, the lithium alcoholate **10**. Then, ligand exchange reaction of the sulfinyl group of **10** gives β-oxido carbenoid **11**, which quickly rearranges to the enolate **12**. At this stage, **12** abstracts a proton from the remaining alcohol **7** to give the ketone **8** and the alcoholate **10**. The produced **8** reacts with *t*-BuLi to give the alcohol **9**. From this result, the rate of the ligand exchange reaction of the sulfinyl group with *t*-BuLi was thought to be as fast as the proton abstraction from the hydroxyl group.

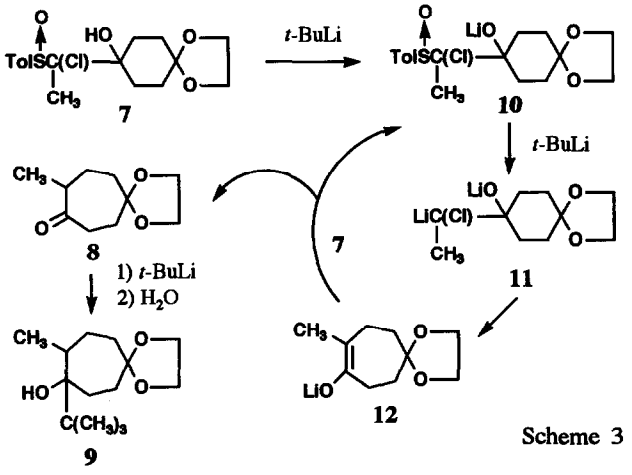
Next, based on this assumption, the alcohol **7** was first treated with 1.2 equivalents of LDA to afford lithium alcoholate **10**. Then 4 equivalents of *t*-BuLi was added at -70 °C. This procedure worked, and the desired ring-expanded ketone **8** was obtained in 69% yield without the byproduct **9** (Scheme 2).

Representative examples of the one-carbon ring-expansion of cyclic ketones to cyclic ketones having an alkyl substituent are summarized in Table 1. Addition of the carbanion of 1-chloroalkyl *p*-tolyl sulfoxide to cyclic ketones usually gave good yields except for cyclopentanone and cyclooctanone (entries 2, 3, and 7). The step for the β-oxido carbenoid rearrangement gave 60-80% yields except for one example (entry 7). These results indicated that this method is applicable to small- to large-ring ketones. In the case of the chloro alcohol having a long alkyl group, preformation of the lithium alcoholate was not necessary (entries 1 and 2). Addition of the



t-BuLi (5 equiv)	49%	36%
LDA (1.2 equiv) then *t*-BuLi (4 equiv)	69%	0%

Scheme 2



Scheme 3

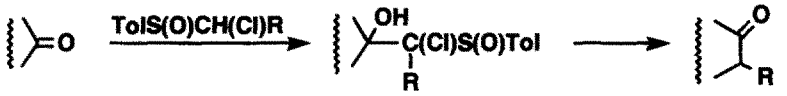
carbanion of **1a** with α-tetralone gave easily separable two diastereomers (**18L** and **18P**). Both were treated with *t*-BuLi to give different results (entry 6), which indicated that the intermediate of this reaction is not free carbene but carbenoid (the stereochemistry of this rearrangement is discussed later).

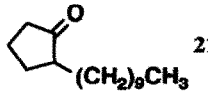
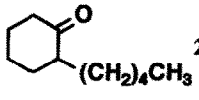
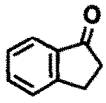
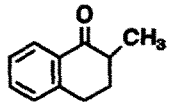
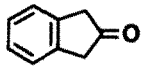
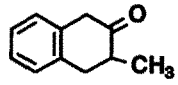
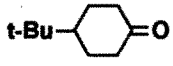
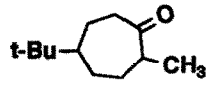
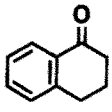
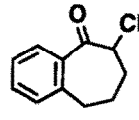
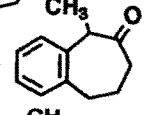
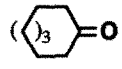
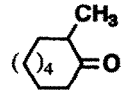
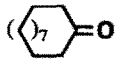
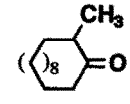
Next, this procedure was applied to acyclic ketones. The results are summarized in Table 2. The table shows that this procedure is also effective with acyclic ketones. In some cases, preformation of alcoholate was carried out both with LDA and KH; however, little difference was observed (entries 1 and 2). Entries 2-4 show the results with unsymmetrical ketones. The rearrangement of chloro alcohols **32** and **33** gave both aryl-migrated and methyl-migrated ketones and no significant selectivity was observed. One reason for this result is that the chloro alcohols are a diastereomeric mixture. The rearrangement of the chloro alcohol having cyclohexyl group **34** gave the ketone **42** in low yield (entry 5). As usually the aryl 1-chloroalkyl sulfoxides having a cyclohexyl or isopropyl group react with ketones in low to moderate yields, this procedure is effective with the aryl 1-chloroalkyl sulfoxides having a normal alkyl group.

One-Carbon Homologation of Aldehydes and Stereochemistry of the Rearrangement of the β-Oxido Carbenoid.

Carbanion of aryl 1-chlorobutyl sulfoxide reacted with aldehydes to afford the chloro alcohol **43** in nearly quantitative yields (Table 3). In these reactions, because the stereochemistry of the carbon bearing the chlorine atom is completely controlled by the chirality of the sulfinyl group,[8f] only two diastereomers were obtained as the

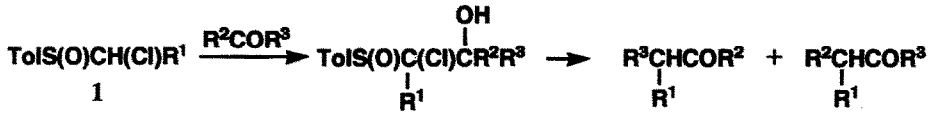
Table 1. One-Carbon Ring-Expansion of Cyclic Ketones to Cyclic Ketones Having an α-Alkyl Substituent



Entry	Ketone	Chloro alcohol R (Yield/%)		Conditions[a]	Product Yield (%)[b]	
1		$CH_3(CH_2)_9$	**13** (91)	A		**21** (60)
2		$CH_3(CH_2)_4$	**14** (29)	A		**22** (66)
3		CH_3	**15** (34)[c]	B		**23** (70)
4		CH_3	**16** (93)	B		**24** (73)
5		CH_3	**17** (90)	B		**25** (64)
6		CH_3	**18L** (57)[d]	B		**26** (82)
			18P (36)[d]	B	**26** (23) + 	**27** (42)
7		CH_3	**19** (37)	B		**28** (49)
8		CH_3	**20** (85)	B		**29** (76)

a) Conditions: All reactions were carried out in THF at about -70 °C. A, 5 eq. *t*-BuLi. B, 1.2 eq. LDA, 4 eq. *t*-BuLi. b) The yield from the chloro alcohol. Isolated yield. c) Single isomer. d) Two diastereomers of the adduct (less polar adduct (L) and more polar adduct (P)) were separated and they were treated separately with *t*-BuLi.

Table 2. One-Carbon Homologation of Acyclic Ketones to Ketones Having an α-Alkyl Substituent

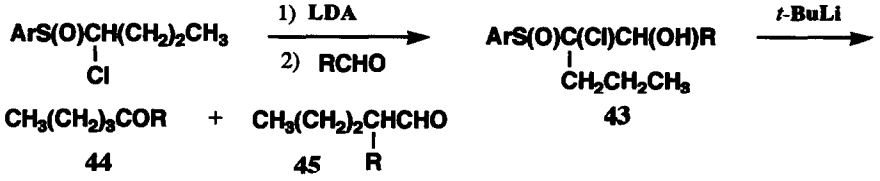


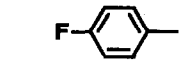
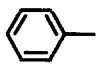
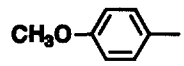
Entry	1 R¹	Acyclic Ketone R²	Acyclic Ketone R³	Chloro alcohol (Yield/%)[a]	Conditions[b]	Product (Yield/%)[a]
1	CH_3	$CH_3(CH_2)_4$	$CH_3(CH_2)_4$	**30** (89)	C	$CH_3(CH_2)_4CH(CH_3)CO(CH_2)_4CH_3$ **35** (77)
2	CH_3	CH_3	$PhCH_2CH_2$	**31** (66)[c]	C	$PhCH_2CH_2CH(CH_3)COCH_3$ **36** (35); $PhCH_2CH_2COCH(CH_3)CH_3$ **37** (41)
3	CH_3	CH_3	CH_3O-Ph	**32** (99)[c]	D	CH_3O-Ph-$CH(CH_3)COCH_3$ **38** (33); CH_3O-Ph-$COCH(CH_3)_2$ **39** (26)
4	CH_3	CH_3	F-Ph	**33** (79)[c]	D	F-Ph-$CH(CH_3)COCH_3$ **40** (40); F-Ph-$COCH(CH_3)_2$ **41** (26)
5	c-Hex	CH_3	CH_3	**34** (71)	E	$CH_3CH(c\text{-}Hex)COCH_3$ **42** (39)

a) Isolated yield. b) Conditions: All reactions were carried out in THF at about -70 °C. C, 1.5 eq. KH, 3 eq. *t*-BuLi. D, 1.2 eq. LDA, 3 eq. *t*-BuLi. E, 1.2 eq. LDA, 4 eq. *t*-BuLi. c) A mixture of two inseparable diastereomers.

adducts **43**. These diastereomers were easily separated by silica gel column chromatography. The rearrangement of the isolated diastereomers was carried out separately and the results are summarized in Table 3. In these reactions, it was found that the preformation of lithium alcoholate was not necessary.

Table 3. Homologation of Aldehydes to Aldehydes and Ketones via β-Oxido Carbenoid Using Aryl 1-Chlorobutyl Sulfoxide as a Homologating Agent



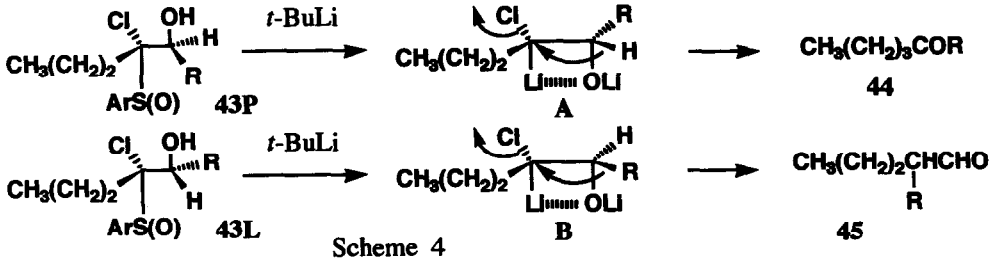
Entry	Ar	Aldehyde (R)	Chloro alcohol Yield (%)[a]	Product Yield (%)[c]	Product 44/45[d]
1	Ph	$PhCH_2CH_2$	**43a-P**[b] (54)	(89)	96/4
2			**43a-L**[b] (42)	(89)	77/23
3	Tol		**43b-P** (51)	(97)	94/6
4			**43b-L** (43)	(40)	1/99
5	Tol		**43c-P** (44)	(82)	94/6
6			**43c-L** (38)	(71)	21/79
7	Tol		**43d-P** (63)	(80)	99/1
8			**43d-L** (35)	(76)	1/99

a) Isolated yield. b) See Table 1. c) The rearrangement was carried out in THF at -70 °C with 4 equivalents of t-BuLi without preformation of lithium alcoholate. d) The ratio of the products was determined by ^1H NMR.

As shown in the table, the rearrangement gave good yields of the products except for one example (entry 4). The ratio of the produced ketones and aldehydes is particularly interesting. Both the adduct **43a-P** and **43a-L** (prepared from **aliphatic** aldehyde) gave hydrogen-migrated ketone **44a** as the main product (entries 1 and 2). This result can be explained by the much higher migratory aptitude of hydrogen over the alkyl group in this type of rearrangement.[14]

In contrast to this result, the rearrangement of the chloro alcohols derived from **aromatic** aldehydes (**43b-43d**) showed significant stereospecificity. Namely, the **P**-isomer gave hydrogen-migrated ketones (**44b-44d**) and **L**-isomers gave aryl-migrated aldehydes (**45b-45d**), respectively, as the main products. This specificity is explained as follows (Scheme 4). As already reported,[15] the stereochemistry of the diastereomers **P** and **L** was determined to be as shown in Scheme 4. The ligand exchange reaction of the alcoholate of **43P** and **43L** gave the β-oxide carbenoids, whose conformations were fixed as **A** and **B** by formation of the chelate ring. The rearrangement must take place through this conformation and **44** was formed from **A**, **45** from **B**, respectively.

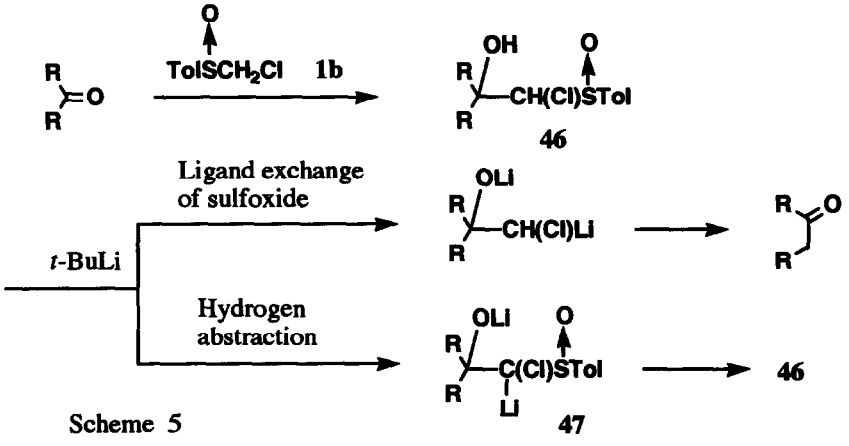
Needless to say, this expectation is valid when the migratory aptitude of the aromatic ring is nearly equal to that of the hydrogen.



Scheme 4

One-Carbon Homologation of Ketones and Aldehydes to Ketones Using Chloromethyl *p*-Tolyl Sulfoxide as the Homologating Agent.

When chloromethyl *p*-tolyl sulfoxide **1b** is used in the above-mentioned method, a methylene insertion procedure must be realized (Scheme 5). However, one problem is that the chloro alcohol **46** has a highly acidic hydrogen on the carbon bearing the sulfinyl group. If the hydrogen is abstracted faster than the ligand exchange of sulfoxide, carbanion **47** is generated, which must give the starting material by quenching the reaction.[16]



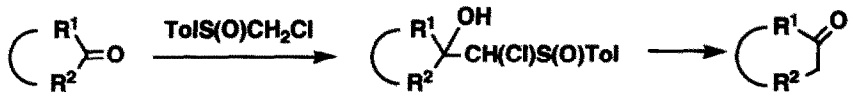
Scheme 5

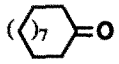
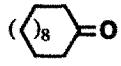
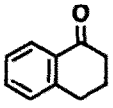
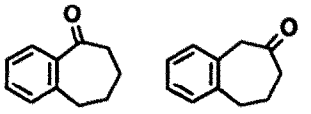
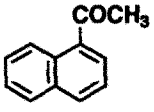
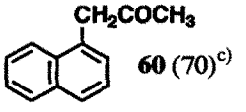
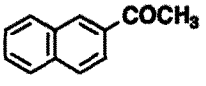
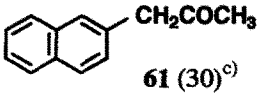
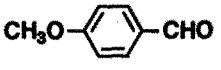
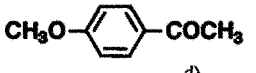
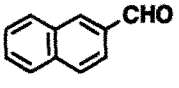
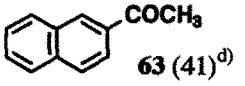
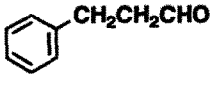
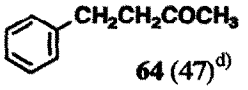
At any rate, the carbanion of chloromethyl *p*-tolyl sulfoxide **1b** was reacted with 6-undecanone to give the chloro alcohol **48** in 93% yield (Table 4). The chloro alcohol was treated with 1.2 equivalents of LDA in THF at -70 °C followed by 5 equivalents of *t*-BuLi for 5 min. Fortunately, this reaction gave the desired 6-dodecanone **56** in 63% yield without the starting material. This result indicated that the ligand exchange reaction of the sulfoxide is much faster than the hydrogen abstraction. The reaction using various ketones is summarized in Table 4 (entries 1-5).

Both acyclic and cyclic ketones gave one-carbon homologated ketones in moderate to good yields; however, the yields are dependent on the ketones used (entries 4 and 5). In the cases of alkyl aryl ketones, all the main products are aryl-migrated ones (entries 3-5).

Entries 6-8 show the results with aromatic- and aliphatic aldehydes. The rearrangement of **53-55** gave hydrogen-migrated ketones **62-64** in 40-50% yields. No aryl- or alkyl-migrated aldehyde was observed.

Table 4. One-Carbon Homologation of Carbonyl Compounds to Ketones Using Chloromethyl *p*-Tolyl Sulfoxide as the Homologating Agent



Entry	Carbonyl compound	Chloro alcohol Yield (%)[a]	Conditions[b]	Ketone Yield (%)[a]
1	$[CH_3(CH_2)_4]_2CO$	**48** (93)	F	$CH_3(CH_2)_5CO(CH_2)_4CH_3$ **56** (63)
2		**49** (79)	G	 **57** (63)
3		**50P** (55)	F	 **58** (5) **59** (66)
		50L (45)	F	**58** (13) **59** (36)
4		**51** (99)	H	 **60** (70)[c]
5		**52** (93)	H	 **61** (30)[c]
6		**53** (99)	I	 **62** (50)[d]
7		**54** (99)	J	 **63** (41)[d]
8		**55** (93)	H	 **64** (47)[d]

a) Isolated yield. b) Conditions: Unless otherwise specified, the reaction was carried out at about -70 °C. F, 1.2 eq. LDA, 5 eq. *t*-BuLi. G, 1.5 eq. KH, 4 eq. *t*-BuLi. H, 1.2 eq. LDA, 3 eq. *t*-BuLi. I, 1.2 eq. LDA, 3 eq. *t*-BuLi, at -80 °C. J, 1.2 eq. LDA, 3 eq. *t*-BuLi, at -90 °C. c) No methyl-migrated product was obtained. d) No aryl- or alkyl-migrated product was obtained.

Experimental Section

All melting points are uncorrected. ^{1}H NMR spectra were measured in a $CDCl_3$ solution with a JEOL FX-100 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. Potassium hydride (KH; Aldrich): In a flame-dried flask, mineral oil was washed three times with dry hexane and the remaining hexane was distilled under vacuum.

1-[1-Chloro-1-(*p*-tolylsulfinyl)undecyl]-1-cyclobutanol (13). A representative example for a synthesis of the chloro alcohol is as follows. In a flame-dried flask under Ar atmosphere at 0 °C, 6 ml of dry THF was placed and diisopropylamine (3.2 mmol) and *n*-BuLi (3.2 mmol) were successively added. The solution was stirred at 0 °C for 5 min, then cooled to -65 °C. A solution of 1-chloroundecyl *p*-tolyl sulfoxide (988 mg; 3 mmol) in 4 ml of THF was added dropwise to the solution and stirred at -65 °C for 15 min. To the reaction mixture, cyclobutanone (3.3 mmol) was added and the stirring was continued for 10 min. The reaction was quenched by adding sat. aqueous NH_4Cl. The whole was extracted with CH_2Cl_2. The organic layer was washed once with sat. aqueous NH_4Cl, dried over $MgSO_4$ and the solvent was evaporated. The product was purified by silica gel column chromatography to give **13** (1.09 g; 91%) as a colorless oil. IR (neat) 3400 (OH), 1080, 1035 (SO) cm^{-1}; ^{1}H NMR δ 0.89 (3H, t, *J*=7 Hz), 1.1-2.8 (25H, m), 2.42 (3H, S), 7.2-7.8 (4H, m); MS *m/z* (%) 398 (M^+, trace), 381 (0.2), 140 (100). Found: *m/z* 398.2082. Calcd for $C_{22}H_{35}ClO_2S$: M, 398.2044.

Chloro Alcohols 14-20. Other chloro alcohols in Table 1 were synthesized in a similar way as described above. 1-[1-Chloro-1-(*p*-tolylsulfinyl)hexyl]-1-cyclopentanol (**14**): Colorless crystals; mp 89-91 °C (AcOEt-hexane); IR (KBr) 3380 (OH), 1080, 1040 (SO) cm^{-1}; ^{1}H NMR δ 0.87 (3H, t, *J*=7 Hz), 1.1-2.3 (17H, m), 2.43 (3H, s), 7.38, 7.66 (each 2H, d, *J*=8 Hz); MS *m/z* (%) 342 (M^+, trace), 241 (1.2), 140 (100). Found: C, 63.23; H, 7.99; Cl, 10.29; S, 9.30%. Calcd for $C_{18}H_{27}ClO_2S$: C, 63.23; H, 7.94; Cl, 10.34; S, 9.35%. 1-[1-Chloro-1-(*p*-tolylsulfinyl)ethyl]-1-indanol (**15**): Colorless crystals; mp 91-95 °C (AcOEt-hexae); IR (KBr) 3375 (OH), 1050, 1020, 1010 (SO) cm^{-1}; ^{1}H NMR δ 1.25 (3H, s), 2.44 (3H, s), 2.5-3.3 (4H, m), 7.1-7.8 (4H, m). Found: C, 64.26; H, 5.57; Cl, 10.38; S, 9.36%. Calcd for $C_{18}H_{19}ClO_2S$: C, 64.56; H, 5.72; Cl, 10.59; S, 9.57%. **16**: see lit. 12. 1-[1-Chloro-1-(*p*-tolylsulfinyl)ethyl]-4-*tert*-butyl-1-cyclohexanol (**17**): Colorless crystals; mp 184-186 °C ($CHCl_3$-hexane); IR (KBr) 3390 (OH), 1040, 1025 (SO) cm^{-1}; ^{1}H NMR δ 0.88 (9H, s), 1.44 (3H, s), 1.45-2.40 (8H, m), 2.43 (3H, s), 7.2-7.7 (4H, m). Found: C, 63.81; H, 8.19; Cl, 9.83; S, 8.96%. Calcd for $C_{19}H_{29}ClO_2S$: C, 63.93; H, 8.19; Cl, 9.93; S, 8.89%. 1-[1-Chloro-1-(*p*-tolylsulfinyl)ethyl]-1-tetralol (**18**): **18L**: Colorless crystals; mp 122-124 °C (AcOEt-hexane); IR (KBr) 3420 (OH), 1090, 1050 (SO) cm^{-1}; ^{1}H NMR δ 1.18 (3H, s), 1.6-2.2 (2H, m), 2.43 (3H, s), 2.6-2.9 (4H, m), 7.0-7.6 (7H, m), 7.9-8.1 (1H, m). Found: C, 65.34; H, 6.08; Cl, 10.32; S, 9.35%. Calcd for $C_{19}H_{21}ClO_2S$: C, 65.41; H, 6.07; Cl, 10.16; S, 9.19%. **18P**: Colorless amorphous; IR (KBr) 3360 (OH), 1040 (SO) cm^{-1}; ^{1}H NMR δ 1.20 (3H, s), 1.4-2.8 (6H, m), 2.40 (3H, s), 7.0-7.6 (7H, m), 8.0-8.2 (1H, m); MS *m/z* (%) 349 ([M+H]$^+$, 0.05), 147 (100). Found: *m/z* 349.1009. Calcd for $C_{19}H_{22}ClO_2S$: M, 349.1027. 1-[1-Chloro-1-(*p*-tolylsufinyl)ethyl]-1-cyclooctanol (**19**): Colorless crystals; mp 110-112 °C (AcOEt-hexane); IR (KBr) 3440 (OH), 1055, 1035 (SO) cm^{-1}; ^{1}H NMR δ 1.3-2.3 (14H, m), 1.46 (3H, s), 2.43 (3H, s), 4.03 (1H, s, OH), 7.2-7.7 (4H, m). Found: C, 62.13; H, 7.72; Cl, 10.80; S, 9.71%. Calcd for $C_{17}H_{25}ClO_2S$: C, 62.08; H, 7.66; Cl, 10.78; S, 9.75%. 1-[1-Chloro-1-(*p*-tolylsulfinyl)ethyl]-1-cyclododecanol (**20**): Colorless crystals; mp 134-136 °C ($CHCl_3$-hexane); IR (KBr) 3490 (OH), 1040, 1020 (SO) cm^{-1}; ^{1}H NMR δ 1.1-2.3 (22H, m), 1.46 (3H, s), 2.43 (3H, s), 7.2-7.7 (4H, m). Found: C, 65.70; H, 8.68; Cl, 9.20; S, 8.37%. Calcd for $C_{21}H_{33}ClO_2S$: C, 65.51; H, 8.64; Cl, 9.21; S, 8.33%.

5,5-Ethylenedioxy-2-methylcycloheptanone (8) and Alcohol (9). Conditions A: To a solution of **7** (108 mg; 0.3 mmol) in 3 ml of dry THF in a flame-dried flask under Ar at -60 °C was added *t*-BuLi (1.57 M in pentane; 0.96 ml; 1.5 mmol) dropwise with stirring. The reaction mixture was stirred at -60 °C for 5 min, then the reaction was quenched by adding sat. aqueous NH_4Cl. The whole was extracted with ether-benzene. The organic layer was washed once with sat. aqueous NH_4Cl and dried over $MgSO_4$. The products were separated by silica gel column chromatography to afford **8** (24 mg; 49%) and **9** (26 mg; 36%). **8**: Colorless oil; IR (neat)

1710 (CO) cm^{-1}; ^1H NMR δ 1.09 (3H, d, *J*=7 Hz), 1.5-2.0 (6H, m), 2.2-2.9 (3H, m), 3.93 (4H, s); MS *m/z* (%) 184 (M^+, 12), 156 (30), 127 (12), 99 (100). Found: *m/z* 184.1104. Calcd for $C_{10}H_{16}O_3$: M, 184.1099. **9**: Colorless crystals (about 1:4 diastereomeric mixture); mp 72-75 °C (hexane); IR (KBr) 3570 (OH) cm^{-1}; ^1H NMR δ 0.92 (7H, s),1.01 (2H, s), 1.05 (2.4H, d, *J*=7 Hz), 1.17 (0.6H, d, *J*=7 Hz), 1.3-2.5 (9H, m), 3.92 (4H, s); MS *m/z* (%) 242 (M^+, 0.8), 185 (94), 99 (100). Found: *m/z* 242.1884. Calcd for $C_{14}H_{26}O_3$: M, 242.1880.

Synthesis of 8 from 7 via Preformation of the Lithium Alcoholate. To a solution of LDA (0.36 mmol) in 3 ml of THF at -60°C was added a solution of **7** (108 mg; 0.3 mmol) in 1.5 ml of THF. The reaction mixture was stirred at -60 °C for 5 min, then *t*-BuLi (1.2 mmol) was added dropwise to the solution. After 10 min, the reaction was quenched by sat. aqueous NH_4Cl. A similar workup as described above gave 38 mg (69%) of **8** without the byproduct **9**.

Ketones 21-29. (Table 1) 2-Decylcyclopentanone (**21**): Colorless oil; IR (neat) 1740 (CO) cm^{-1}; ^1H NMR δ 0.87 (3H, t, *J*=7 Hz), 1.0-2.3 (25H, m); MS *m/z* (%) 224 (M^+, 5), 97 (12), 84 (100). Found: *m/z* 224.2143. Calcd for $C_{15}H_{28}O$: M, 224.2138. 2-Pentylcyclohexanone (**22**): Colorless oil; IR (neat) 1705 cm^{-1}; ^1H NMR δ 0.87 (3H, t, *J*=7 Hz), 1.0-2.5 (17H, m), MS *m/z* (%) 168 (M^+, 4), 98 (100). Found: *m/z* 168.1508. Calcd for $C_{11}H_{20}O$: M, 168.1513. 2-Methyl-1-tetralone (**23**): Colorless oil; IR (neat) 1685 (CO) cm^{-1}; ^1H NMR δ 1.27 (3H, d, *J*=7 Hz), 1.6-2.3 (2H, m), 2.4-2.8 (1H, m), 2.9-3.1 (2H, m), 7.1-7.6 (3H, m), 7.0-8.1 (1H, m); MS *m/z* (%) 160 (M^+, 56), 145 (22), 131 (18), 118 (100). Found: *m/z* 160.0875. Calcd for $C_{11}H_{12}O$: M, 160.0887. 3-Methyl-2-tetralone (**24**): Colorless oil; IR (neat) 1760, 1720 (CO) cm^{-1}; ^1H NMR δ 1.19 (3H, d, *J*=7 Hz), 2.3-3.2 (3H, m), 3.58 (2H, s), 7.16 (4H, m); MS *m/z* (%) 160 (M^+, 67), 117 (71), 104 (100). Found: *m/z* 160.0883. Calcd for $C_{11}H_{12}O$: M, 160.0887. 5-*tert*-Butyl-4-methylcycloheptanone (**25**): Colorless oil (about 1:1 diastereomeric mixture); IR (neat) 1710 (CO) cm^{-1}; ^1H NMR δ 0.85 (4H, s), 0.86 (5H, s), 1.05, 1.08 (each 1.5H, d, *J*=7 Hz), 1.1-2.6 (10H, m); MS *m/z* (%) 182 (M^+, 16), 167 (5), 154 (7), 126 (64), 57 (100). Found: *m/z* 182.1670. Calcd for $C_{12}H_{22}O$: M, 182.1670. 2-Methyl-1-benzosuberone (**26**): Colorless oil; IR (neat) 1680 (CO) cm^{-1}; ^1H NMR δ 1.21 (3H, d, *J*=7 Hz), 1.4-2.2 (4H, m), 2.6-3.1 (3H, m), 7.1-7.7 (4H, m); MS *m/z* (%) 174 (M^+, 86), 145 (38), 131 (100). Found: *m/z* 174.1046. Calcd for $C_{12}H_{14}O$: M, 174.1044. 1-Methyl-2-benzosuberone (**27**): Colorless oil; IR (neat) 1715 (CO) cm^{-1}; ^1H NMR δ 1.44 (3H, d, *J*=7 Hz), 1.6-3.0 (6H, m), 3.86 (1H, q, *J*=7 Hz), 7.16 (4H, m); MS *m/z* (%) 174 (M^+, 80), 145 (19), 131 (100). Found: *m/z* 174.1047. Calcd for $C_{12}H_{14}O$: M, 174.1044. 2-Methylcyclononanone (**28**): Colorless oil; IR (neat) 1700 (CO) cm^{-1}; ^1H NMR δ 1.04 (3H, d, *J*=7 Hz), 1.2-2.0 (12H, m), 2.3-2.9 (3H, m); MS *m/z* (%) 154 (M^+, 27), 125 (10), 98 (85), 41 (100). Found: *m/z* 154.1363. Calcd for $C_{10}H_{18}O$; M, 154.1357. 2-Methylcyclotridecanone (**29**): Colorless oil: IR (neat) 1705 (CO) cm^{-1}; ^1H NMR δ 1.04 (3H, d, *J*=7 Hz), 1.1-1.9 (20H, m), 2.2-2.8 (3H, m); MS *m/z* (%) 210 (M^+, 50), 181 (19), 55 (100). Found: *m/z* 210.2002. Calcd for $C_{14}H_{26}O$: M, 210.1983.

Chloro Alcohols 30-34. (Table 2) 6-[1-Chloro-1-(*p*-tolylsulfinyl)ethyl]-6-undecanol (**30**): Colorless crystals; mp 141-144 °C ($CHCl_3$-hexane); IR (KBr) 3350 (OH), 1085, 1045 (SO) cm^{-1}; ^1H NMR δ 0.89, 0.93 (each 3H, t, *J*=7 Hz), 1.1-2.2 (16H, m), 1.46 (3H, s), 2.43 (3H, s), 7.2-7.7 (4H, m). Found: C, 64.56; H, 8.90%. Calcd for $C_{20}H_{33}ClO_2S$: C, 64.49; H, 8.93%. 2-[1-Chloro-1-(*p*-tolylsulfinyl)ethyl]-4-phenyl-2-butanol (**31**): Colorless oil (about 1:1 diastereomeric mixture); IR (neat) 3270 (OH), 1090, 1035 (SO) cm^{-1}; ^1H NMR δ 1.44, 1.46 (each 1.5H, s), 1.49, 1.79 (each 1.5H, s), 2.43 (3H, s). 1-[1-Chloro-1-(*p*-tolylsulfinyl)-ethyl-1-(4-methoxyphenyl)-1-ethanol (**32**): Colorless oil (about 2:3 diastereomeric mixture); IR (neat) 3330, 3260 (OH), 1080, 1025 (SO) cm^{-1}; ^1H NMR δ 1.31 (1.8H, s), 1.44 (1.2H, s), 1.79 (1.2H, s), 2.13 (1.8H, s), 2.41 (3H, s), 3.79 (1.8H, s), 3.83 (1.2H, s). 1-[1-Chloro-1-(*p*-tolylsulfinyl)ethyl]-1-(4-fluorophenyl)-1-ethanol (**33**): Colorless oil (about 1:1 diastereomeric mixture); IR (neat) 3350, 3250 (OH), 1080, 1025 (SO) cm^{-1}; ^1H NMR δ 1.33, 1.43 (each 1.5H, s), 1.79, 2.22 (each 1.5H, s), 2.41 (3H, s). 1-Chloro-1-cyclohexyl-1-(*p*-tolylsulfinyl)-2-methyl-2-propanol (**34**): Colorless crystals; mp 131-133 °C (AcOEt-hexane); IR (KBr) 3305 (OH), 1080, 1040 (SO) cm^{-1}; ^1H NMR δ 1.44, 1.78, 2.45 (each 3H, s). Found: C, 62.16; H, 7.40%. Calcd for $C_{17}H_{25}ClO_2S$: C, 62.08; H, 7.66%.

7-Methyl-6-dodecanone (35). A solution of **30** (112 mg; 0.3 mmol) in 2 ml of THF was added dropwise to a suspension of KH (18 mg; 0.45 mmol) in 5 ml of dry THF at 0 °C under Ar atmosphere. The reaction mixture was stirred at 0 °C for 20 min, then cooled to -70 °C. To the reaction mixture, *t*-BuLi (0.9 mmol) was added and after 10 min, the reaction was quenched by sat. aqueous NH_4Cl. The whole was extracted with ether-benzene and the product was purified by silica gel column chromatography to afford **35** (46 mg; 77%) as a colorless oil. IR (neat) 1715 (CO) cm^{-1}; ^1H NMR δ 0.7-1.0 (6H, m), 1.05 (3H, d, J=7 Hz), 1.1-1.8 (14H, m), 2.3-2.6 (1H, m), 2.41 (2H, t, *J*=7 Hz); MS *m/z* (%) 198 (M^+, 10), 155 (14), 128 (52), 99 (100). Found: *m/z* 198.1979. Calcd for $C_{13}H_{26}O$: M, 198.1982.

Ketones 36-42. (Table 2) 3-Methyl-5-phenyl-2-pentanone (**36**): Colorless oil; IR (neat) 1710 (CO) cm^{-1}; ^1H NMR δ 1.13 (3H, d, *J*=7 Hz), 1.4-2.0 (2H, m), 2.12 (3H, s), 2.4-2.7 (3H, m), 7.0-7.4 (5H, m); MS *m/z* (%) 176 (M^+, 20), 117 (10), 91 (62), 72 (100). Found: *m/z* 176.1202. Calcd for $C_{12}H_{16}O$: M, 176.1200. 4-Methyl-1-phenyl-3-pentanone (**37**): Colorless oil; IR (neat) 1710 (CO) cm^{-1}; ^1H NMR δ 1.07 (6H, d, *J*=7 Hz), 2.4-3.0 (5H, m), 7.0-7.4 (5H, m); MS *m/z* (%) 176 (M^+, 47), 133 (51), 103 (100). Found: *m/z* 176.1197. Calcd for $C_{12}H_{16}O$: M, 176.1200. 3-(4-Methoxyphenyl)-2-butanone (**38**): Colorless oil; IR (neat) 1710 (CO) cm^{-1}; ^1H NMR δ 1.34 (3H, d, *J*=7 Hz), 2.02 (3H, s), 3.66 (1H, q, *J*=7 Hz), 3.77 (3H s), 6.7-7.3 (4H, m); MS *m/z* (%) 178 (M^+, 11), 135 (100). Found: *m/z* 178.1001. Calcd for $C_{11}H_{14}O_2$: M, 178.0993. 1-(4-Methoxyphenyl)-2-methyl-1-propanone (**39**): Colorless oil; IR (neat) 1665 (CO) cm^{-1}; ^1H NMR δ 1.20 (6H, d, *J*=7 Hz), 3.51 (1H, septet, *J*=7 Hz), 3.85 (3H, s), 6.8-7.0 (2H, m), 7.8-8.0 (2H, m); MS *m/z* (%) 178 (M^+, 7), 135 (100). Found: *m/z* 178.0995. Calcd for $C_{11}H_{14}O_2$: M, 178.0993. 3-(4-Fluorophenyl)-2-butanone (**40**): Colorless oil; IR (neat) 1715 (CO) cm^{-1}; ^1H NMR δ 1.37 (3H, d, *J*=7 Hz), 2.04 (3H, s), 3.72 (1H, q, *J*=7 Hz), 6.9-7.3 (4H, m); MS *m/z* (%) 166 (M^+, 9), 123 (100). Found: *m/z* 166.0793. Calcd for $C_{10}H_{11}FO$: M, 166.0793. 1-(4-Fluorophenyl)-2-methyl-1-propanone (**41**): Colorless oil; IR (neat) 1675 (CO) cm^{-1}; ^1H NMR δ 1.22 (6H, d, *J*=7 Hz), 3.51 (1H, septet, *J*=7 Hz), 6.9-7.4 (2H, m), 7.8-8.1 (2H, m); MS *m/z* (%) 166 (M^+, 13), 123 (100). Found: *m/z* 166.0794. Calcd for $C_{10}H_{11}FO$: M, 166.0793. 3-Cyclohexyl-2-butanone (**42**): Colorless oil; IR (neat) 1710 (CO) cm^{-1}; ^1H NMR δ 0.8-1.4 (5H, m), 1.02 (3H, d, *J*=7 Hz), 1.5-1.8 (6H, m), 2.12 (3H, s), 2.33 (1H, quintet, *J*=7 Hz); MS *m/z* (%) 154 (M^+, 2.6), 139 (1.6), 111 (7), 72 (100). Found: *m/z* 154.1376. Calcd for $C_{10}H_{18}O$: M, 154.1358.

Chloro Alcohols 43a-43d. (Table 3) 4-Chloro-4-(phenylsulfinyl)-3-heptanol (**43a**): **43a-P**; Colorless oil; IR (neat) 3370 (OH), 1075, 1030 (SO) cm^{-1}; ^1H NMR δ 0.93 (3H, t, *J*=7 Hz), 1.3-3.1 (9H, m), 3.73 (1H, dd, *J*=9, 2 Hz), 7.0-7.8 (10H, m); MS *m/z* (%) 351 ($[M+H]^+$, trace), 298 (0.7), 126 (75), 91 (100). Found: *m/z* 351.1175. Calcd for $C_{19}H_{24}ClO_2S$: M, 351.1183. **43a-L**; Colorless crystal; mp 120-124 °C (AcOEt-hexane); IR (KBr) 3390 (OH), 1075, 1030 (SO) cm^{-1}; ^1H NMR δ 1.05 (3H, t, *J*=7 Hz), 1.6-3.0 (8H, m), 3.83 (1H, dd, *J*=5, 6 Hz), 7.0-7.8 (10H, m); MS *m/z* (%) 351 ($[M+H]^+$, trace), 281 (trace), 126 (70), 91 (100). Found: *m/z* 351.1174. Calcd for $C_{19}H_{24}ClO_2S$: M, 351.1183. 2-Chloro-1-(4-fluorophenyl)-2-(*p*-tolylsulfinyl)-1-pentanol (**43b**): **43b-P**; Colorless crystals; mp 137-139 °C (AcOEt-hexane); IR (KBr) 3360 (OH), 1075, 1045 (SO) cm^{-1}; ^1H NMR δ 0.75 (3H, t, *J*=7 Hz), 1.1-1.8 (4H, m), 2.43 (3H, s), 5.35 (1H, s), 6.9-7.7 (8H, m). Found: C, 61.05; H, 5.66; Cl, 9.88; F, 5.25; S, 8.92%. Calcd for $C_{18}H_{20}ClFO_2S$: C, 60.92; H, 5.68; Cl, 9.99; F, 5.35; S, 9.03%. **43b-L**; Colorless crystals; mp 126-128 °C (AcOEt-hexane); IR (KBr) 3280 (OH), 1080, 1050 (SO) cm^{-1}; ^1H NMR δ 1.02 (3H, t, *J*=7 Hz), 1.5-2.1 (4H, m), 2.49 (3H, s), 4.93 (1H, s), 6.8-7.9 (8H, m). Found: C, 61.03; H, 5.66; Cl, 9.88; F, 5.25; S, 8.92%. Calcd for $C_{18}H_{20}ClFO_2S$: C, 60.92; H, 5.68; Cl, 9.99; F, 5.35; S, 9.03%. 2-Chloro-1-phenyl-2-(*p*-tolylsulfinyl)-1-pentanol (**43c**): **43c-P**; Colorless crystals; mp 124-126 °C (AcOEt-hexane); IR (KBr) 3360 (OH), 1075, 1040 (SO) cm^{-1}; ^1H NMR δ 0.73 (3H, t, *J*=7 Hz), 1.1-1.9 (4H, m), 2.44 (3H, s), 5.32 (1H, s), 7.2-7.8 (9H, m); MS *m/z* (%) 337 ($[M+H]^+$, trace), 284 (0.4), 179 (7), 140 (100). Found: *m/z* 337.1045. Calcd for $C_{18}H_{22}ClO_2S$: M, 337.1028. **43c-L**; Colorless crystals; mp 139-140 °C (AcOEt-hexane); IR (KBr) 3360 (OH), 1080, 1040 (SO) cm^{-1}; ^1H NMR δ 1.01 (3H, t, *J*=7 Hz), 1.4-2.0 (4H, m), 2.49 (3H, s), 4.95 (1H, s), 7.2-7.9 (9H, m); MS *m/z* (%) 337 ($[M+H]^+$, trace), 284 (0.3), 179 (15), 140 (100). Found: *m/z* 337.1018. Calcd for $C_{18}H_{22}ClO_2S$: M, 337.1028. 2-Chloro-1-(4-methoxyphenyl)-2-(*p*-tolylsulfinyl)-1-pentanol (**43d**): **43d-P**; Colorless crystals; mp 112-115 °C (AcOEt-hexane); IR (KBr) 3350

(OH), 1080, 1045 (SO) cm^{-1}; ^1H NMR δ 0.74 (3H, t, *J*=7 Hz), 1.1-1.8 (4H, m), 2.43 (3H, s), 3.79 (3H, s), 5.27 (1H, s), 6.7-7.7 (8H, m). Found: C, 62.03; H, 6.38; Cl, 9.61; S, 8.71%. Calcd for $C_{19}H_{23}ClO_3S$: C, 62.20; H, 6.32; Cl, 9.66; S, 8.74%. **43d-L**; Colorless crystals; mp 127-129 °C (AcOEt-hexane); IR (KBr) 3300 (OH), 1060, 1040 (SO) cm^{-1}; ^1H NMR δ 1.01 (3H, t, *J*=7 Hz), 1.5-2.0 (4H, m), 2.47 (3H, s), 3.75 (3H, s), 4.90 (1H, s), 6.7-7.9 (8H, m). Found: C, 62.36; H, 6.37; Cl, 9.51; S, 8.49%. Calcd for $C_{19}H_{23}ClO_3S$: C, 62.20; H, 6.32; Cl, 9.66; S, 8.74%.

Ketones 44 and Aldehydes 45. (Table 3) 1-Phenyl-3-heptanone (**44a**): Colorless oil; IR (neat) 1715 (CO) cm^{-1}; ^1H NMR δ 0.87 (3H, t, *J*=7 Hz), 1.1-2.0 (4H, m), 2.38 (2H, t, *J*=7 Hz), 2.5-3.0 (4H, m), 7.0-7.4 (5H, m); MS *m/z* (%) 190 (M^+, 37), 148 (17), 133 (35), 91 (100). Found: *m/z* 190.1356. Calcd for $C_{13}H_{18}O$: M, 190.1356. Aldehyde (**45a**): ^1H NMR δ 9.55 (d, *J*=3 Hz, CHO). 1-(4-Fluorophenyl)-1-pentanone (**44b**): Colorless oil; IR (neat) 1680 (CO) cm^{-1}; ^1H NMR δ 0.95 (3H, t, *J*=7 Hz), 1.1-1.9 (4H, m), 2.94 (2H, t, *J*=7 Hz), 6.8-7.4 (3H, m), 7.8-8.1 (2H, m); MS *m/z* (%) 180 (M^+, 5), 151 (23), 138 (28), 123 (48), 109 (100). Found: *m/z* 180.0954. Calcd for $C_{11}H_{13}FO$: M, 180.0949. 2-(4-Fluorophenyl)pentanal (**45b**): Colorless oil; IR (neat) 1725 (CO) cm^{-1}; ^1H NMR δ 0.91 (3H, t, *J*=7 Hz), 1.0-2.3 (6H, m), 3.48 (1H, m), 6.8-7.3 (4H, m), 9.59 (1H, d, *J*=2 Hz); MS *m/z* (%) 180 (M^+, 5), 151 (20), 109 (100). Found: *m/z* 180.0953. Calcd for $C_{11}H_{13}FO$: M, 180.0949. 1-Phenyl-1-pentanone (**44c**): Colorless oil; IR (neat) 1690 (CO) cm^{-1}; ^1H NMR δ 0.95 (3H, t, *J*=7 Hz), 1.1-1.9 (4H, m), 2.96 (2H, t, *J*=7 Hz), 7.1-8.0 (5H, m); MS *m/z* (%) 162 (M^+, 11), 120 (36), 105 (100). Found: *m/z* 162.1051. Calcd for $C_{11}H_{14}O$: M, 162.1044. 2-Phenylpentanal (**45c**): Colorless oil; IR (neat) 1735 (CO) cm^{-1}; ^1H NMR δ 0.91 (3H, t, *J*=7 Hz), 1.0-2.3 (4H, m), 3.49 (1H, m), 7.0-7.5 (5H, m), 9.61 (1H, d, *J*=2 Hz); MS *m/z* (%) 162 (M^+, 6), 133 (21), 91 (100). Found: *m/z* 162.1043. Calcd for $C_{11}H_{14}O$: M, 162.1044. 1-(4-Methoxyphenyl)-1-pentanone (**44d**): Colorless oil; IR (neat) 1675 (CO) cm^{-1}; ^1H NMR d 0.94 (3H, t, *J*=7 Hz), 1.1-1.9 (4H, m), 2.91 (2H, t, *J*=7 Hz), 3.84 (3H, s), 6.8-7.0 (2H, m), 7.8-8.0 (2H, m); MS *m/z* (%) 192 (M^+, 7), 150 (48), 135 (100). Found: *m/z* 192.1151. Calcd for $C_{12}H_{16}O_2$: M, 192.1150. 2-(4-Methoxyphenyl)pentanal (**45d**): Colorless oil; IR (neat) 1730 (CO) cm^{-1}; ^1H NMR d 0.92 (3H, t, *J*=7 Hz), 1.1-2.2 (4H, m), 3.44 (1H, m), 3.78 (3H, s), 6.7-7.2 (4H, m), 9.58 (1H, d, *J*=2 Hz); MS *m/z* (%) 192 (M^+, 9), 163 (36), 121 (100). Found: *m/z* 192.1147. Calcd for $C_{12}H_{16}O_2$: M, 192.1149.

Chloro Alcohols 48-55. (Table 4) 6-[Chloro(*p*-tolylsulfinyl)methyl]-6-undecanol (**48**): Colorless crystals; mp 81-84 °C (AcOEt-hexane); IR (KBr) 3380 (OH), 1080, 1040 (SO) cm^{-1}; ^1H NMR δ 0.7-1.0 (6H, m), 1.1-2.2 (16H, m), 2.42 (3H, s), 4.34 (1H, s), 7.2-7.5 (4H, m); MS *m/z* (%) 358 (M^+, trace), 341 (0.8), 219 (3), 140 (100); Found: *m/z* 358.1725. Calcd for $C_{19}H_{31}ClO_2S$: M, 358.1731. 1-{Chloro(*p*-tolylsulfinyl)methyl]-1-cyclododecanol (**49**): Colorless crystals; mp 145-147 °C (AcOEt-hexane); IR (KBr) 3330 (OH), 1080, 1040 (SO) cm^{-1}; ^1H NMR δ 1.1-2.4 (22H, m), 2.43 (3H, s), 4.28 (1H, s), 7.4-7.6 (4H, m). Found: C, 64.87; H, 8.48; Cl, 9.53; S, 8.76%. Calcd for $C_{20}H_{31}ClO_2S$: C, 64.75; H, 8.42; Cl, 9.58; S, 8.64%. 1-[1-Chloro(*p*-tolylsulfinyl)methyl]-1-tetralol (**50**): **50P**; Colorless crystals; mp 126-128 °C (AcOEt-hexane); IR (KBr) 3390 (OH), 1085, 1040 (SO) cm^{-1}; ^1H NMR δ 1.7-2.6 (4H, m), 2.40 (3H, s), 2.80 (2H, t, *J*=6 Hz), 4.68 (1H, s), 7.0-7.6 (8H, m). Found: C, 64.52; H, 5.74; Cl, 10.53; S, 9.52%. Calcd for $C_{18}H_{19}ClO_2S$: C, 64.56; H, 5.72; Cl, 10.59; S, 9.58%. **50L**; Colorless crystals; mp 86-88 °C (AcOEt-hexane); IR (KBr) 3430, 3340 (OH), 1080, 1055, 1035 (SO) cm^{-1}; ^1H NMR δ 1.6-2.6 (4H, m), 2.38 (3H, s), 2.7-3.0 (2H, m), 4.93 (1H, s), 7.1-7.5 (8H, m). Found: C, 64.34; H, 5.75; Cl, 10.83; S, 9.49%. Calcd for $C_{18}H_{19}ClO_2S$: C, 64.56; H, 5.72; Cl, 10.59; S, 9.58%. 1-Chloro-2-(1-naphthyl)-1-(*p*-tolylsulfinyl)-2-propanol (**51**): Colorless crystals (about 4:1 diastereomeric mixture); IR (KBr) 3370 (OH), 1085, 1050 (SO) cm^{-1}; ^1H NMR δ 2.05 (3H, s), 2.35 (3H, s), 5.41 (0.2H, s), 5.45 (0.8H, s), 7.0-8.2 (7H, m). 1-Chloro-2-(2-naphthyl)-1-(*p*-tolylsulfinyl)-2-propanol (**52**): Colorless crystals (about 3:2 diastereomeric mixture); IR (KBr) 3300 (OH), 1085, 1050 (SO) cm^{-1}; ^1H NMR δ 1.82 (1.8H, s), 2.12 (1.2H, s), 2.38 (3H, s), 4.71 (0.4H, s), 4.77 (0.6H, s), 7.2-8.2 (9H, m). 2-Chloro-1-(4-methoxyphenyl)-2-(*p*-tolylsulfinyl)-1-ethanol (**53**): Colorless amorphous (about 3:2 diastereomeric mixture); IR (KBr) 3340 (OH), 1030 (SO) cm^{-1}; ^1H NMR δ 2.41 (1.8H, s), 2.43 (1.2H, s), 3.79 (1.2H, s), 3.81 (1.8H, s), 4.5-4.7 (1H, m), 5.00 (0.4H, m), 5.28 (0.6H, m), 6.8-7.6 (8H, m). 2-Chloro-1-(2-naphthyl)-2-(*p*-tolylsulfinyl)-1-ethanol (**54**): Colorless amorphous (about 1:1 diastereomeric mixture); IR (KBr) 3330 (OH), 1040 (SO) cm^{-1}; ^1H NMR δ 2.39, 2.42 (each 1.5H, s), 4.5-4.9 (1H, m), 5.1-5.3 (0.5H, m), 5.45-5.60 (0.5H, m), 7.2-8.0 (11H, m). 1-Chloro-4-phenyl-1-(*p*-tolylsulfinyl)-2-butanol (**55**): Colorless amorphous (about 1:1

diastereomeric mixture); IR (KBr) 3360 (OH), 1090, 1040 (SO) cm^{-1}; ^1H NMR δ 1.8-2.4 (2H, m), 2.42 (3H, s), 2.6-2.9 (2H, m), 4.10 (0.5H, m), 4.20 (0.5H, m), 4.40 (1H, m), 7.1-7.6 (9H, m).

2-Benzosuberone (59). Colorless oil; IR (neat) 1705 (CO) cm^{-1}; ^1H NMR δ 1.8-2.2 (2H, m), 2.57 (2H, t, *J*=7 Hz), 2.95 (2H, t, *J*=7 Hz), 3.71 (2H, s), 7.15 (4H, m); MS *m/z* (%) 160 (M^+, 100), 145 (8), 132 (11), 117 (21), 105 (61). Found: *m/z* 160.0885. Calcd for $C_{11}H_{12}O$: M, 160.0886.

3-(1-Naphthyl)-2-propanone (60). Colorless oil; IR (neat) 1710 (CO) cm^{-1}; ^1H NMR δ 2.07 (3H, s), 4.06 (2H, s), 7.3-7.9 (9H, m); MS *m/z* (%) 184 (M^+, 40), 141 (100). Found: *m/z* 184.0881. Calcd for $C_{13}H_{12}O$: M, 184.0887.

3-(2-Naphthyl)-2-propanone (61). Colorless oil; IR (neat) 1713 (CO) cm^{-1}; ^1H NMR δ 2.17 (3H, s), 3.84 (2H, s), 7.1-7.9 (9H, m); MS *m/z* (%) 184 (M^+, 35), 141 (100). Found: *m/z* 184.0893. Calcd for $C_{13}H_{12}O$: M, 184.0887.

Products **56-58**, and **62-64** are known compounds.

Acknowledgments: We are grateful to Dr. Norio Takamura, Tanabe Seiyaku Co., Ltd., for elemental analysis, to Noriko Sawabe and Fukiko Hasegawa of this laboratory for NMR and MS measurements, to Kenji Matsuda for technical assistance. This study was supported by a Grant-in-Aid for Scientific Research No 05671771 from the Ministry of Education, Scienc and Culture, and a bounty to a young scientist (T. S.) from Science University of Tokyo, which are gratefully acknowledged.

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(*Received in Japan* 1 *July* 1994; *accepted* 24 *August* 1994)