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A facile sulfenylchlorination of alkenes with $Me_2SO/(COCl)_2$

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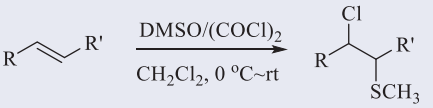
ABSTRACT

The sulfenylchlorination of a series of alkenes is investigated by using the combined reagent of dimethyl sulfoxide and oxalyl chloride. The corresponding β-chloro sulfides were obtained in mediate to good yields. Most of the terminal alkenes give the Markovnikov adducts mainly and the sulfenylchlorination of cyclic alkenes is stereospecific to produce the adducts with *trans* configuration. Methanesulfenyl chloride is supposed to be the real species for sulfenylchlorination.

GRAPHICAL ABSTRACT



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KEYWORDS
Sulfenylchlorination; alkenes; dimethyl sulfoxide; oxalyl chloride; methanesulfenyl chloride

Introduction

It is a very important process in organic synthesis that the electrophilic additions across carbon-carbon double bonds introduce two different vicinal functional groups simultaneously to alkene substrates.[1–6] The sulfenylchlorination of alkenes has been paid a lot of attention due to the great flexibility of β-chloroalkyl sulfides for structural elaboration. The most common approach for the sulfenylchlorination is by the addition of reagents containing an S-Cl bond to alkenes. Various organic sulfonyl chlorides add to alkenes catalyzed by copper(I) chloride[7] or ruthenium(II) complexes[8–11] affording β-chlorinated sulfones, and unsaturated sulfonyl chlorides undergo an intramolecular addition to give cyclized products.[12,13] Meanwhile, organic sulfenyl chlorides are also widely used for the sulfenylchlorination, such as bezenesulfenyl chloride, methanesulfenyl chloride,[14] and electron-poor trifluoromethanesulfenyl chloride.[15] The additions between chloro(pentafluoro)-λ^6-sulfane and various alkenes have been investigated for the products with the potential pharmacological activities.[16,17] In addition, several combined reagents have been developed to achieve this process, such as dimethyl sulfoxide activated by phenyl dichlorophosphate or phosphorus oxychloride,[18] trimethylchloro- or

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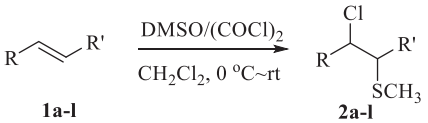


Scheme 1. Sulfenylchlorination of alkenes with DMSO-$(COCl)_2$.

trimethylbromosilane-dimethyl sulfoxide[19,20] and dimethyl sulfide/sulfuryl chloride/dimethyl sulfoxide.[21] A quite new combination for sulfenylchlorination of alkenes is dimethyl sulfoxide/HCl/DMPU (1,3-dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone) reported by Xu et. al.[22]

The combination of dimethyl sulfoxide and oxalyl chloride has been used widely in the oxidation of primary and secondary alcohols[23] since it was developed by Swern et al.[24] We have developed several applications of the combined reagents of R_2SO (R = Me or Ph) and $(COX)_2$ (X = Cl or Br) for other transformations, such as sulfenyllactonization[25] and chlorolactonization of alkenoic acids,[26] bromination of alkenes, alkynes and ketones,[27] preparation of α,β-unsaturated γ-lactones[28] and sulfenyletherification[29] in our recent work. For sulfenyllactonization, methanesulfenyl chloride was proposed as the real species for the reaction, which was generated at 0 °C via DMSO attack on the dimethylchlorosulfonium salt derived from the reaction of $(COCl)_2$ with DMSO.[25] It is conceivable that the combination of dimethyl sulfoxide and oxalyl chloride can also serve as a sulfenylchlorination reagent for alkenes. Herein, we report our results about the reactions of a series of alkenes with dimethyl sulfoxide and oxalyl chloride (Scheme 1).

Results and discussion

A total of twelve alkenes are investigated, including 5 terminal alkenes, 3 cyclic alkenes, 3 allylic alcohols, and 1 allyl *trans*-2-butenoate. The obtained results are shown in Table 1. 1-Decene **1a** was sulfenylchlorinated with DMSO/$(COCl)_2$ to produce a Markovnikov adduct 1-methylthio-2-chlorodecane **2a** mainly in 87% yield, which contained about 7% of the anti-Markovnikov adduct 1-chloro-2-methylthiodecane (Entry 1). In the case of allylbenzene **1b**, 1-methylthio-2-chloro-3-phenylpropane **2b** was obtained in 90% yield also containing a certain amount of anti-Markovnikov adduct (11%) (Entry 2). 3,3-Dimethyl-1-butene **1c** was converted into a single Markovnikov adduct, 1-methylthio-2-chloro-3,3-dimethylbutane **2c** in 92% yield (Entry 3). Likewise, the sulfenylchlorination of 1-cyclohexylethene **1d** also afforded a single Markovnikov adduct, 1-chloro-1-cyclohexyl-2-methylhtioethane **2d** in 88% yield (Entry 4). In contrast, the reaction of styrene **1e** underwent with relatively poor regioselectivity (Entry 5). The crude product was a mixture of Markovnikov and anti-Markovnikov adducts **2e** with a ratio of 3/1 based on the ^{1}H NMR spectrum. After purification on silica gel column, the corresponding hydrolyzed product 1-hydroxy-1-phenyl-2-methylthioethane **3a** was obtained in 87% yield.

For cylcohexene **1f**, 1-chloro-2-methylthiocyclohexane **2f** was generated in 96% yield (Entry 6), which was determined to be *trans* configuration based on the multiplicities of the protons attached to the C-1 and C-2 positions in the ^{1}H NMR spectrum.

Table 1. The reaction results of alkenes with DMSO/$(COCl)_2$.

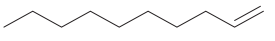
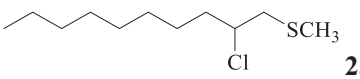
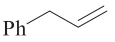
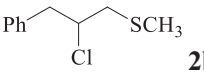
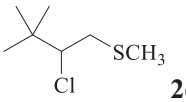
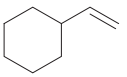
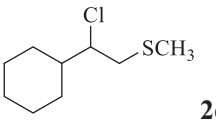
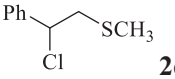
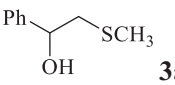
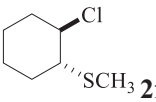
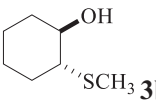
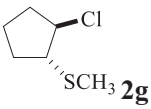
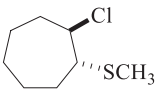
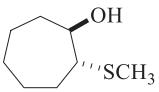
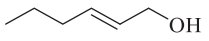
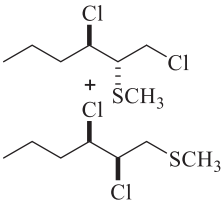
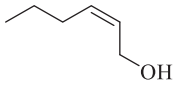
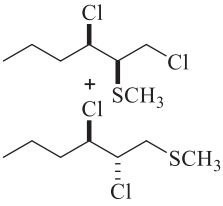
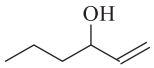
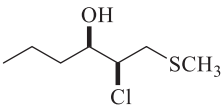
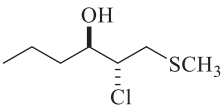
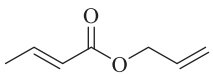
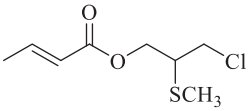
Entry	Substrate	Product	Reaction time[a]	Yield (%)
1	 **1a**	 **2a**	5 h	87[b]
2	 **1b**	 **2b**	5 h	90[b]
3	 **1c**	 **2c**	12 h	92
4	 **1d**	 **2d**	10 h	88
5	 **1e**	 **2e**	2 h	90[c]
		 **3a**		87[d]
6	 **1f**	 **2f**	1h	96[c]
		 **3b**		93[d]
7	 **1g**	 **2g**	3 h	91
8	 **1h**	 **2h**	2 h	86[c]
		 **3c**		81[d]

Table 1. Continued.

9	 **1i**		**2i** **2i′**	5 h	65[e]
10	 **1j**		**2j** **2j′**	5 h	68[e]
11	 **1k**		**2k**	5 h	33
			**2k′**		41
12	 **1l**		**2l**	5 h	80

(a) The experiments of entries 1–8 were carried out in CH2Cl2 at 0 °C ∼ rt, and entries 9 ∼ 12 in CH3CN at 0–55 °C. (b) The contents of the anti-Markovnikov adducts based on the 1H NMR data were 7% (Entry 1), 11% (Entry 2), and 33% (Entry 5), respectively. (c) The yield based on GC analysis before purification by column chromatography. (d) The yield of the product obtained after purification by column chromatography. (e) The yield of the mixture.

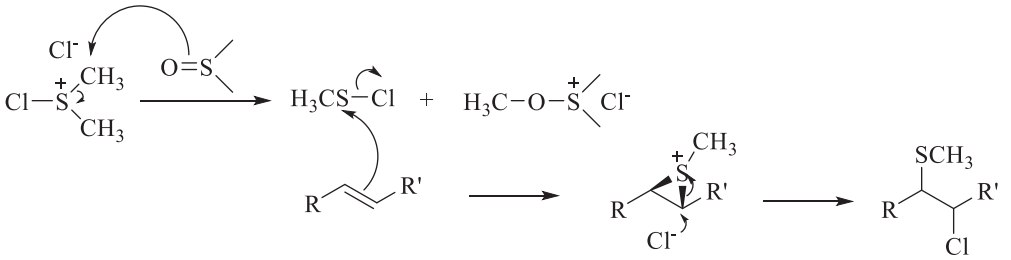
The stereoselectivity was confirmed further by comparison of the ^{1}H NMR data with those of *trans*-1-chloro-2-methylthiocyclohexane in literature.[20,21] Similar to the product **2e**, 1-chloro-2-methylthiocyclohexane **2f** also hydrolyzed to 1-hydroxy-2-methylthiocyclohexane **3b** when submitted on silica gel column for purification. The hydrolyzed product **3b** was *trans* configuration same as **2f**. Cylcopentene **1g** was transformed to the corresponding adduct **2g** in 91% yield without hydrolysis occurring on silica gel column (Entry 7). 1-Chloro-2-methylthiocycloheptane **2h** was also obtained as the crude prodcut when cylcoheptene **1h** was treated under the same conditions as above (Entry 8), which was converted to 1-hydroxy-2-methylthiocycloheptane **3c** after purification on silica gel column. The relative configuration of the products **2g**, **2h** and **3c** was determined by NOE experiments to be *trans*.

Three allyl alcohols were also investigated, including *trans*-2-hexen-1-ol **1i**, *cis*-2-hexen-1-ol **1j**, and 1-hexen-3-ol **1k**. No desired product was produced when *trans*-2-

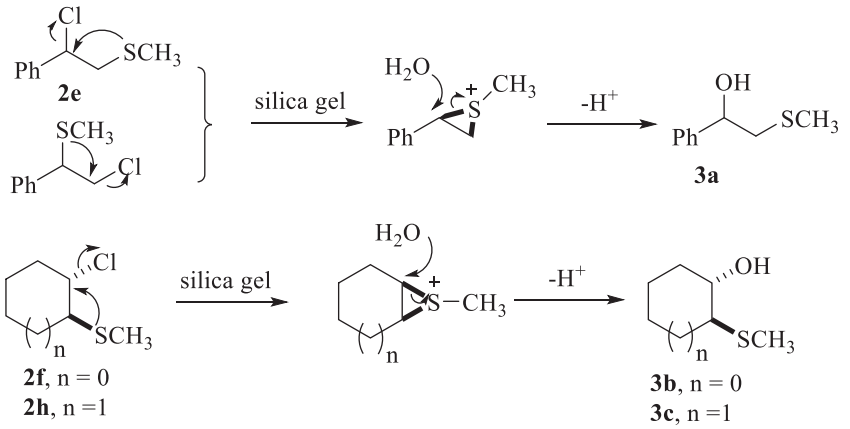
hexen-1-ol **1i** was treated with DMSO/$(COCl)_2$ under the above conditions. When the reaction was carried out in CH_3CN instead of CH_2Cl_2 and the reaction temperature was raised to about 55 °C from 0 °C after the addition of **1i**, a mixture of *anti*-1,3-dichloro-2-methylthiohexane **2i** and *syn*-1-methylthio-2,3-dichlorohexane **2i′** with a ratio of about 1/1 was obtained in about 65% yield (Entry 9). Under the same conditions, *cis*-2-hexen-1-ol **1j** was converted to a mixture of *syn*-1,3-dichloro-2-methylthiohexane **2j** and *anti*-1-methylthio-2,3-dichlorohexane **2j′** in 68% yield with a ratio of about 1/4 (Entry 10). It failed to separate two isomers on silica column for these two reactions. However, the ^{1}H NMR signals in the lower field were apart from each other enough to be identified with the aid of H–H cosy, C–H cosy, and HMBC. When 1-hexen-3-ol **1k** was treated with DMSO/$(COCl)_2$ under the same conditions, *syn*- and *anti*-1-methylthio-2-chloro-3-hexenol (**2k** and **2k′**) were obtained in 33% and 41% yields respectively (Entry 11). Allyl *trans*-2-butenoate **1l** reacted with DMSO/$(COCl)_2$ to give 2′-methylthio-3′-chloropropyl *trans*-2-butenoate **2l** in 80% yield (Entry 12).

Among the five terminal alkenes under investigation, two substrates **1c** and **1d** gave single Markovnikov adducts, whereas the sulfenylchlorination of the other three substrates **1a**, **1b**, and **1e** afforded mixtures of Markovnikov and anti-Markovnikov adducts. The Markovnikov adducts predominated in all cases. The additions to the substrates **1a** and **1b** presented similar regioselectivities with ratios of 13/1 and 8/1, respectively, whereas the substrate **1e** showed the poorest regioselectivity with a ratio of 3/1. It was reported that anti-Markovnikov products were kinectically favored at low temperature for steric reasons when the sulfenyl chlorides were used as sulfenylchlorination reagents directly.[14] Whereas, the anti-Markovnikov products were susceptible to isomerize to the thermodynamically more stable Markovnikov products at ambient temperature. However, styrene reacted with methanesulfenyl chloride to give the Markovnikov product preferentially with a ratio of 49/1, which was interpreted due to some carbonium ion character in the transition state.[14] In contrast, the reaction of styrene **1e** in our work didn't show the same preference for the Markovnikov product as literature,[14] which indicated that the carbonium ion character of the episulfonium ion intermediate in the transition state was not very significant in our reaction system. This regioselectivity for the Markovnikov product is consistent with that of the combined reagents, trimethylchloro- or trimethylbromosilane-dimethyl sulfoxide[20] and dimethyl sulfide/sulfuryl chloride/dimethyl sulfoxide[21] developed by Bellesia et. al. However, styrene was not examined in these two literatures.[20,21] Another combined reagent, dimethyl sulfoxide activated by phenyl dichlorophosphate or phosphorus oxychloride was reported to convert styrene into 1,2-dimethylthio-1-phenylethane abnormally instead of the sulfenylchlorination product.[18]

These results can be interpreted by the involvement of methanesulfenyl chloride, which is generated via DMSO attack on the chlorosulfonium intermediate as proposed in our previous work.[25] The electrophilic addition of methanesulfenyl chloride to the C = C bond of alkene produces an episulfonium ion intermediate, which is then attacked by a chloride ion to afford the corresponding sulfenylchlorination product (Scheme 2). The intervention of the episulfonium ion intermediate can also be speculated from the facts that the sulfenylchlorination of cyclic alkenes **1f–h** is stereospecific to afford the products with *trans* configuration.

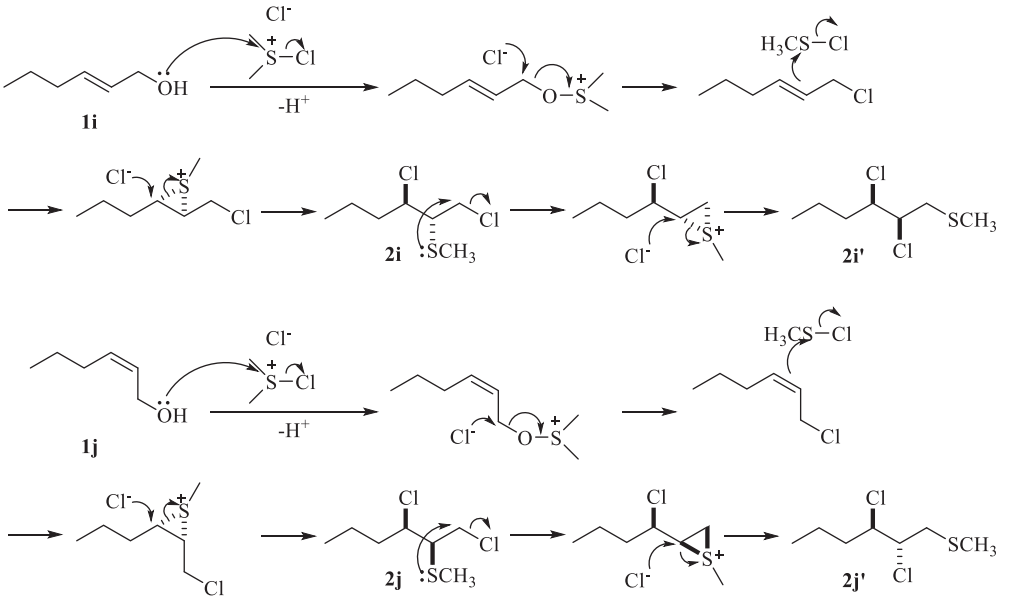


Scheme 2. Proposed mechanism of sulfenylchlorination of alkenes with DMSO/$(COCl)_2$.



Scheme 3. The hydrolysis of β-chloro sulfides on silica gel column.

Three sulfenylchlorination products **2e**, **2f**, and **2h** were observed labile to hydrolyze on silica gel column. As mentioned above, the product **2e** is a mixture of Markovnikov and anti-Markovnikov adducts. Both adducts were converted to one single product 1-hydroxy-1-phenyl-2-methylthioethane **3a** (Entry 5), which should be due to the neighboring group effect of methylthio group (Scheme 3). Likewise, *trans*-1-chloro-2-methylthiocyclohexane **2f** and *trans*-1-chloro-2-methylthiocycloheptane **2h** were transformed to *trans*-1-hydroxy-2-methylthiocyclohexane **3b** and *trans*-1-hydroxy-2-methylthiocycloheptane **3c** on silica gel column respectively (Entries 6 and 8). In order to confirm the hydrolyzed product, **3b** was acylated with Ac_2O in pyridine and 1-acetoxy-2-methylthiocyclohexane **4** was obtained successfully. Both **3b** and **4** were supposed to be *trans* configuration according to the multiplicities of the protons attached to the C-1 and C-2 positions in the ^{1}H NMR spectra. Moreover, the NMR data of **3b** and **4** were in consistent with those with *trans* configuration in the literatures.[30,31] These results were also consistent with the involvement of the neighboring group effect of methylthio group (Scheme 3). In Xu's work,[22] the sulfenylchlorinated product was also reported to be labile to hydrolyze during work up when styrene was treated with DMSO/HCl/DMPU. However, the sulfenylchlorinated products **2e**, **2f**, and **2h** were observed to be stable during work up and even could stand in atmosphere for several days without any hydrolysis occurring in our present work. The hydrolysis of these products should be



Scheme 4. The possible mechanism of sulfenylchlorination of *trans*- and *cis*-2-hexen-1-ol.

due to the participation of silica gel. This kind of decomposition of *β*-chloro sulfide promoted by silica gel has been reported before for *β*,*β*′-dichloro sulfides.[32]

It is interesting that both *trans*-2-hexen-1-ol **1i** and *cis*-2-hexen-1-ol **1j** produced a mixture of 1,3-dichloro-2-methylthiohexane and 1-methylthio-2,3-dichlorohexane but with opposite configuration and different ratios (Entries 9 and 10). The possible mechanism for the formation of 1,3-dichloro-2-methylthiohexane and 1-methylthio-2,3-dichlorohexane was proposed as shown in Scheme 4. 2-Hexen-1-ols were first converted to 2-hexenyl chlorides by the chlorodimethylsulfonium salt. Although the hydroxy group was not replaced by chloride in our previous work of sulfenyletherification of unsaturated alcohols,[29] the allyl alcohols were reported to be transformed to the corresponding allyl halides with chloro- or bromodimethylsulfonium salt.[33] The obtained 2-hexenyl chlorides then reacted with methanesulfenyl chloride via an episulfonium ion intermediate to give *anti*- or *syn*-1,3-dichloro-2-methylthiohexane (**2i** or **2j**), of which methylthio group and the chloro on the carbon 1 swapped via an episulfonium ion to generate *syn*- or *anti*-1-methylthio-2,3-dichlorohexanes (**2i**′ or **2j**′). The addition of MeSCl to the double bond and the following swap between methylthio group and chloro on the carbon 1 are stereospecific due to the intervention of episulfonium ions. Therefore, *trans*-2-hexen-1-ol **1i** afforded a mixture of *anti*-1,3-dichloro-2-methylthiohexane **2i** and *syn*-1-methylthio-2,3-dichlorohexane **2i**′ with a ratio of about 1/1. In contrast, *cis*-2-hexen-1-ol **1j** produced a mixture of *syn*-1,3-dichloro-2-methylthiohexane **2j** and *anti*-1-methylthio-2,3-dichlorohexane **2j**′ with a ratio of about 1/4. The higher ratio of *anti*-1-methylthio-2,3-dichlorohexane **2j**′ might be due to the repulsion between the *syn* substituents of *syn*-1,3-dichloro-2-methylthiohexane **2j**, which is more favorable for the occurrence of intramolecular nucleophilic substitution. *trans*-2-Hexen-1-ol was reported to be converted to 1,3-dichloro-2-methylthiohexane with excess DMSO/

TMSCl, but without mention of the relative configuration of the product.[20] The characteristic ^{1}H NMR signals in the lower field of **2i** we obtained from *trans*-2-hexen-1-ol **1i** were consistent with the reference data. In contrast, another allyl alcohol **1k** produced two stereoisomers *syn*- and *anti*-1-methylthio-2-chloro-3-hexanol **2k** and **2k′** with hydroxy group intact (Entry 11). It is unclear why the hydroxy group was not replaced by chloride in this case. More allyl alcohols will be investigated for chemoselectivity and regioselectivity in our further work.

Ally *trans*-2-butenoate **1l** only produced single isomer product 2′-methylthio-3′-chloropropyl *trans*-2-butenoate **2l** (Entry 12). It is unexpected that the anti-Markovnikov adduct was obtained in this case. The double bond conjugate with carbonyl group did not participate the reaction, which indicates that electron-poor double bond is unreactive toward the electrophilic species CH_3SCl in this reaction.

Conclusion

In summary, sulfenylchlorination of the alkenes is carried out with DMSO/$(COCl)_2$ to afford β-chloro sulfides with preference of Markovnikov adducts in mediate to high yields. The real species for sulfenylchlorination is supposed to be methanesulfenyl chloride and the products are generated via episulfonium ion intermediates. The reactions of allyl alcohols are kind of complicated and the further research is still ongoing in our lab. This method offers another good alternative for the sulfenylchlorination of alkenes due to the easy availability of reagents and simple operation.

Experimental

All the alkenes and reagents were purchased from Beijing Bailingwei Science and Technology Company (Beijing, China). NMR spectra were obtained on a Bruker AV300 or 600 MHz NMR (^{1}H NMR at 300 or 600 MHz, ^{13}C NMR at 75 or 150 MHz) in $CDCl_3$ using TMS as internal standard. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz.

General reaction procedure of alkenes with dimethyl sulfoxide-oxalyl chloride

To a 50 mL three necked round bottom flask, fitted with a condenser and adapted with a $CaCl_2$ valve, dimethylsulfoxide (DMSO 1.7 mL, 24 mmol, 2.4 equivalents) and CH_2Cl_2 (10 mL) were poured. The stirred solution was cooled to 0 °C and then a solution of oxalyl chloride (1.0 mL, 12 mmol, 1.2 equivalents) in CH_2Cl_2 (10 mL) was added dropwise from a dropping funnel. After 10 min, a solution of the alkene (10 mmol, 1.0 equivalent) in CH_2Cl_2 (10 mL) was added. The reaction mixture was then allowed to warm to room temperature and stirred until TLC showed the reaction completed. Triethylamine (7.0 mL, 50 mmol, 5.0 equivalents) was added in one portion. After stirring for 10 min, the mixture was successively washed with a saturated aqueous solution of NH_4Cl (30 mL) and brine (2 × 30 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product was purified by chromatography on silica gel.

1-Methylthio-2-chlorodecane **2a**: colorless oil; 1.94 g, 87% yield. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.2 Hz, 3H, H-C-10), 1.22–1.46 (m, 11H, H-C-4–9), 1.55 (m, 1H, H′-C-4), 1.68 (m, 1H, H-C-3), 1.97 (m, 1H, H′-C-3), 2.17 (s, 3H, SCH_3), 2.81 (dd, J = 13.8, 7.8 Hz, 1H, H-C-1), 2.90 (dd, J = 13.8, 6.0 Hz, 1H, H′-C-1), 4.01 (m, 1H, H-C-2); ^{13}C NMR ($CDCl_3$) δ 14.2 (C-10), 16.6 (SCH_3), 22.7 (C-9), 26.3 (C-4), 29.2 (C-5), 29.3 (C-7), 29.5 (C-6), 31.9 (C-8), 36.8 (C-3), 42.6 (C-1), 62.0 (C-2). The ^{1}H NMR data were matched with those reported in lit.[21]

1-Chloro-2-methylthiocyclohexane **2f**: light yellow oil; 1.58 g, 96% yield. ^{1}H NMR ($CDCl_3$) δ 1.30–1.85 (m, 6H, H-C-3–6), 2.17 (s, 3H, SCH_3), 2.20–2.35 (m, 2H, H′-C-3 and H′-C-6), 2.75 (td, J = 7.8, 4.2 Hz, 1H, H-C-2), 4.01 (td, J = 7.8, 3.9 Hz, 1H, H-C-1); ^{13}C NMR ($CDCl_3$) δ 15.0 (SCH_3), 23.6 (C-5), 23.9 (C-4), 30.7 (C-3), 34.4 (C-6), 52.0 (C-2), 63.5 (C-1). The ^{1}H NMR data were matched with those reported in lit.[21]

1-Hydroxy-2-methylthiocyclohexane **3b**: colorless oil; 1.36 g, 93% yield. ^{1}H NMR ($CDCl_3$) δ 1.20–1.58 (m, 4H, H-C-4 and H-C-5), 1.65–1.82 (m, 2H, H-C-3 and H-C-6), 2.00–2.22 (m, 2H, H′-C-3 and H′-C-6), 2.07 (s, 3H, SCH_3), 2.34 (ddd, J = 12.0, 9.9, 3.9 Hz, 1H, H-C-2), 2.98 (br, 1H, OH), 3.34 (td, J = 9.9, 4.5 Hz, 1H, H-C-1); ^{13}C NMR ($CDCl_3$) δ 11.3 (SCH_3), 24.5 (C-5), 26.2 (C-4), 31.5 (C-3), 33.8 (C-6), 53.2 (C-2), 71.0 (C-1). The ^{1}H NMR data were matched with those reported in lit.[31]

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