NaOH-Promoted Thiolysis of Oxiranes Using 2-[Bis(alkylthio)methylene]-3-oxo-*N*-*o*-tolylbutanamides as Odorless Thiol Equivalents

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Received 30 September 2006

Abstract: A convenient and efficient protocol for the thiolysis of oxiranes using 2-[bis(alkylthio)methylene]-3-oxo-*N*-*o*-tolylbutanamides as thiol equivalents has been developed. Promoted by sodium hydroxide (NaOH) in ethanol at room temperature, the cleavage commences and the generated thiolate anions undergo nucleophilic addition in situ. β-Hydroxy sulfides were obtained in high yields along with good β-regioselectivity, and *trans* β-hydroxy sulfides were also isolated. The thiolysis of one α,β-epoxyketone product with the thiol equivalents was accomplished to afford the corresponding α-carbonyl sulfides in excellent yields. In all the cases, 3-oxo-*N*-*o*-tolylbutanamide, the precursor of the thiol equivalents, could be recovered in the novel thiolysis process as a byproduct in good yield.

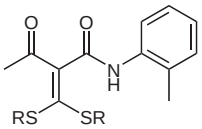
Key words: α-carbonyl sulfides, epoxides, β-hydroxy sulfides, α-oxo ketene-*S*,*S*-acetals, thiolysis

The β-hydroxy sulfide unit is a common structural component in a vast group of natural products along with useful biological and pharmaceutical activities,[1] and is a versatile moiety for the synthesis of allylic alcohols, benzoxathiepines, benzotiazepines, α-thioketones, α-substituted α,β-unsaturated enones, β-hydroxy sulfoxides and naturally occurring compounds such as leukotrienes LTC_4 and LTD_4.[2,3] A general and straightforward access to β-hydroxy sulfides is via the thiolysis of 1,2-epoxides with thiols in the presence of a base in a protic solvent.[4,5] Recently, other methods have been developed using promoters and/or catalysts, such as Lewis acids, Brønsted acids, and ionic liquids to perform these epoxide-ring-opening reactions.[6,7]

So far, extensive related work have focused on the investigation of various catalysts and reaction media that can result in mild reaction conditions, highly selectivity, and general tolerance to a wide range of functionalities.[4–7] To minimize the amount of harmful organic solvents used in the chemical processes, some research groups achieved the thiolysis of 1,2-epoxides in water,[7f,8] ionic liquid[7g] or in the absence of solvent (under solvent-free conditions).[6d,9] However, many of the thiolysis reactions still suffer from some disadvantages, such as drastic reaction conditions, poor regioselectivity, difficult recovery of expensive catalysts, unsatisfactory yields, or entailing undesirable side reactions. Additionally, the thiols, in particular those with low molecular weight, used in the thiolysis process are odorous, harmful, highly volatile and flammable, which can create serious environmental and safety problems. Indeed, some attempts to develop practically odorless and less volatile substitutes for the odorous thiols used in various organic reactions have been made. Accordingly, a range of odorless or faint-smelling thiols or their equivalents have been prepared by increasing the alkyl chain length of thiols,[10] making sulfides and thioesters,[11,12] introducing trialkylsilyl group onto the benzene ring of benzyl mercaptan and benzenethiol,[13] or incorporating propane-1,3-dithiol functions within linear or cross-linked co-polymeric reagents.[14] These reagents have been widely applied in Swern reaction, Corey–Kim reaction, thioacetalization, thia-Michael addition, and umpolung chemistry. To the best of our knowledge, there is only one report dealing with the use of odorless thiol equivalents in the thiolysis of 1,2-epoxides, in which aryl disulfides were employed.[7g]

In our search for the substitutes for the odorous thiols to contribute to the development of an environmentally-responsible chemistry, we have found that various types of ketene-*S*,*S*-acetals could be used in thioacetalization and thia-Michael additions as non-thiolic and odorless thiol equivalents under acidic conditions.[15] Our recent work has revealed that thia-Michael reactions of α,β-unsaturated carbonyl compounds could be achieved using 2-[bis(alkylthio)methylene]-3-oxo-*N*-*o*-tolylbutanamides **1** (Figure 1) as thiol equivalents in the presence of NaOH at room temperature.[16] In our ongoing research to expand the applications of these kinds of thiol equivalents in organic synthesis, we investigated the thiolysis of 1,2-epoxides **2** with compounds **1** under basic conditions. Herein, we wish to report our findings.

The substrates **1** were easily prepared from 3-oxo-*N*-*o*-tolylbutanamide **3**, carbon disulfide and alkyl halides catalyzed by tetrabutylammonium bromide (TBAB) in the presence of potassium carbonate in water in excellent yields according to the reported procedure.[17]



1	R
1a	Bn
1b	*n*-Bu
1c	Et
1d	Me
1e	Allyl

Figure 1

SYNLETT 2007, No. 1, pp 0151–0155
Advanced online publication: 20.12.2006
DOI: 10.1055/s-2006-958438; Art ID: W20306ST

Our previous work has demonstrated that the cleavage of compounds **1** could be realized in the presence of NaOH in ethanol.[16] Thus, the reaction of 2-[bis(benzylthio)methylene]-3-oxo-*N*-*o*-tolylbutanamide (**1a**; 1.0 mmol) with 2-methyloxirane (**2a**; 2.0 mmol) in the presence of NaOH (2.0 mmol) in ethanol (5 mL) was first attempted in the present work (Table 1, entry 1). After the mixture was stirred at room temperature for 35 minutes, workup and column chromatography of the resulting mixture furnished a colorless liquid which was characterized as 1-(benzylthio)propan-2-ol (**4a**; 89% yield), an anti-Markovnikov-type adduct, on the basis of its elemental analyses and spectral data. It is widely known that the thiolysis process of 1,2-epoxides is strongly dependent on the experimental conditions.[6d,7e,8b] Under acidic conditions, the reaction favors the nucleophilic attack of thiol on the more-substituted α-carbon, depending on the substituents on the oxirane ring, while under basic conditions the less-substituted β-carbon is more favored. In the present work, the thiolysis was completely regioselective, as is usually observed under basic conditions to yield the terminal sulfide. Interestingly, compound **3** was obtained as a byproduct from the reaction system in 80% yield, which was easily isolated from the resulting mixture and reused for the preparation of compounds **1**. It is worth mentioning that only very faint thiol smell could be perceived during both the reaction and the workup processes, indicating that the generated thiolate anions quickly undergo the thiolysis of oxiranes in situ.

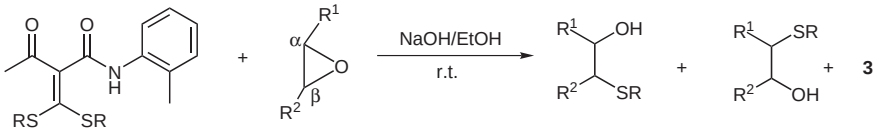
Table 1 Reactions between 2-[Bis(benzylthio)methylene]-3-oxo-*N*-*o*-tolylbutanamide (**1a**) and 2-Methyloxirane (**2a**)[a]

Entry	Base	Ratio[b]	Time (min)	Yield of **3**[c] (%)	Yield of **4a**[c] (%)
1	NaOH	2:1	35	80	89
2	NaOH	1:1	50	80	90
3	NaOH	1:2	360	76	88
4	NaOH	1:3	360	45	47 (44)
5	K_2CO_3	1:1	600	79	91

[a] Molar ratio of **2a**/**1a**: 2:1.
[b] Molar ratio of base/**1a**.
[c] Isolated yields, and the data in bracket represents the recovered **1a**.

Then a range of reactions of **1a** and **2a** was carried out in ethanol with varied molar ratio of NaOH/**1a** to optimize the conditions (Table 1, entries 2–4). When the molar ratio of NaOH/**1a** was decreased from 2:1 to 1:1, the reaction proceeded smoothly to give **4a** in a very high yield (Table 1, entry 2). Further decrease of the ratio, however, resulted in much lower reaction rate (Table 1, entries 3 and 4). It was observed that the reaction performed in the presence of a weak base such as potassium carbonate afforded **4a**, but required much prolonged reaction time for a complete conversion (Table 1, entry 5). These experiments demonstrate that the character and the feed amount of the base employed play important roles in the thiolysis. A 1:1 molar ratio of NaOH/**1a** was proven to be sufficient

Table 2 Reactions between 2-[Bis(alkylthio)methylene]-3-oxo-*N*-*o*-tolylbutanamides **1** and Oxiranes **2**



1 **2** **4** **5**

Entry	Substrates					Time	Product **4**	Yield of **4**	Product **5**	Yield of **5**	Yield of **3**
	1	R	**2**	R^1	R^2	(min)		(%)[a]		(%)[a]	(%)[a]
1	**1a**	Bn	**2a**	Me	H	50	**4a**	90	**5a**	0	80
2	**1b**	*n*-Bu	**2a**	Me	H	55	**4b**	87	**5b**	0	83
3	**1c**	Et	**2a**	Me	H	55	**4c**	90	**5c**	0	82
4	**1a**	Bn	**2b**	Ph	H	55	**4d**	71	**5d**	18	83
5	**1b**	*n*-Bu	**2b**	Ph	H	55	**4e**	75	**5e**	17	81
6	**1c**	Et	**2b**	Ph	H	50	**4f**	75	**5f**	15	84
7	**1d**	Me	**2b**	Ph	H	55	**4g**	73	**5g**	16	82
8	**1e**	Allyl	**2b**	Ph	H	50	**4h**	71	**5h**	16	85
9	**1a**	Bn	**2c**	$(CH_2)_4$		50	**4i**	91[b]	–		84
10	**1b**	*n*-Bu	**2c**	$(CH_2)_4$		45	**4j**	90[b]	–		83

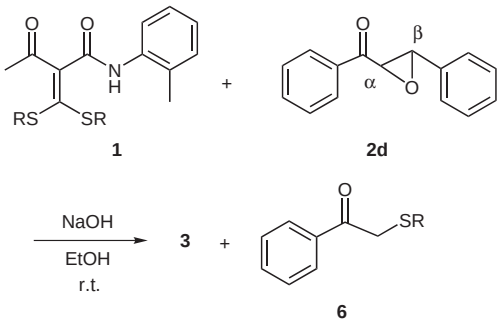
[a] The isolated yields
[b] *trans*-β-Hydroxy sulfide.

and effective for the cleavage of **1a** and the subsequent addition of the generated thiolate anions to **2a**, because while the thiolysis is proceeding, the ring opening of the 1,2-epoxide leads to the formation of an alkoxide ion which is responsible for further basification of the reaction medium.

Employing the identical conditions used for **4a** in Table 1 (entry 2), a range of reactions were performed on compounds **1a**–**e** with selected oxiranes **2a**–**c**, and some of the results are summarized in Table 2.[18] It is noted that the alkyl oxirane **2a** reacts with **1b** and **1c**, under basic conditions, also in a regioselective manner, affording exclusively the ring-opened products **4b** and **4c**, respectively (Table 2, entries 2 and 3). This regioselectivity is probably due to the steric hindrance faced by the nucleophile that attacks on the less-hindered carbon of the oxirane-ring. In the cases of aryl oxirane **2b**, a mixture of the two regioisomers (ca 4:1) was formed with the anti-Markovnikov-type adducts **4** as the major products (Table 2, entries 4–8). These results suggest that the steric hindrance effect should still be the predominant factor affecting the regioselectivity. The slightly lower regioselectivity in the thiolysis of **2b**, compared with that of **2a**, is attributed to the electronic effect from the substituted aryl groups. Cyclohexene oxide **2c**, as a representative of cycloalkyl epoxides, was investigated under the identical conditions. The ring opening of **2c** with **1a** and **1b** smoothly afforded the corresponding β-hydroxy sulfides **4i** and **4j** in 91% and 90% yields, respectively (Table 2, entries 9 and 10). The stereochemistry of the product **4i** was found to be *trans* from the coupling constants of the ring protons at δ = 2.41 (ddd, *J* = 4.0, 9.5, 11.5 Hz, 1 H) for SCH and at δ = 3.31 (ddd, *J* = 4.5, 9.5, 9.5 Hz, 1 H) for OCH in its ^{1}H NMR spectrum, and no *syn* adduct was observed. Compound **4j** showed similar splitting patterns at δ = 2.34 and δ = 3.26, respectively. The results reveal that the thiolysis of cycloalkyl epoxides with **1** is accomplished with high stereoselectivity.

We next examined the thiolysis of chalcone oxide **2d** with compounds **1** under the above optimized conditions. In these cases, as shown in Table 3, α-carbonyl sulfides **6a**–**e** instead of the desired adducts, β-hydroxy sulfides **4**, were isolated in excellent yields. Meanwhile, both compound **3** and benzaldehyde were obtained as byproducts in good yields. The results reveal that **2d** shows a peculiar behavior in the thiolysis process in comparison to the oxiranes **2a**–**c**. A similar phenomenon had been observed in Fringuelli's recent work on NaOH-catalyzed thiolysis of α,β-epoxyketones in water.[8a] Silverman has pointed out that two β-hydroxy sulfide isomers are interconvertible under basic conditions, and the interconversion has been shown to involve a retroaldol–aldol condensation process.[19] Thus, the thiolysis of **2d** involves the nucleophilic addition of the thiolate ions, generated from the cleavage of compounds **1** under basic conditions, to the α-position of chalcone oxide **2d** with complete regioselectivity, and the subsequent retroaldol reaction of the Markovnikov-type adducts to afford α-carbonyl sulfides **6**.

Table 3 The Thiolysis of Chalcone Oxide **2d** with Compounds **1**[a]



Entry	Substrate	R	Time (min)	Product **6**	Yield of **6**[b] (%)	Yield of **3**[b] (%)
1	**1a**	Bn	55	**6a**	94	85
2	**1b**	*n*-Bu	50	**6b**	95	81
3	**1c**	Et	55	**6c**	97	84
4	**1d**	Me	55	**6d**	96	80
5	**1e**	Allyl	50	**6e**	95	82

[a] Molar ratio of **2d**/**1** was 2:1, molar ratio of NaOH/**1** was 1:1.
[b] Isolated yields.

In summary, we have described a novel and odorless thiolysis of oxiranes **2** using 2-[bis(alkylthio)methylene]-3-oxo-*N*-*o*-tolylbutanamides **1** as thiol equivalents. Promoted by NaOH in ethanol at room temperature, the cleavage of **1** commences and the generated thiolate anions undergo nucleophilic addition to **2** in situ. In the cases of alkyl and aryl 1,2-epoxides **2a** and **2b**, β-hydroxy sulfides **4a**–**h** were obtained in high yields along with good β-regioselectivity, while in the case of cyclohexene oxide **2c**, *trans* β-hydroxy sulfides **4i** and **4j** were isolated as a mixture of two diastereoisomers. In contrast, the thiolysis of α,β-epoxyketone **2d** with compounds **1** was accomplished with complete α-regioselectivity, which was followed by a retroaldol reaction to afford the corresponding α-carbonyl sulfides **6a**–**e** in excellent yields. The simple procedure, mild conditions, and high yields provide a convenient, efficient and odorless thiolysis of oxiranes.

Acknowledgment

Financial support of this research by the National Natural Science Foundation of China (20572013), the Ministry of Education of China (105061 and 10412) and the Department of Science and Technology of Jilin Province (20050392) is greatly acknowledged.

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(18) **Thiolysis of 2 with 1** (**4a as Example); Typical Procedure**: To a 25 mL flask containing NaOH (1.0 mmol) in EtOH (5 mL) were added **1a** (1.0 mmol) and **2a** (2.0 mmol) under stirring. The mixture was stirred at r.t. for about 50 min, after which time the reaction was complete as indicated by TLC. The resulting mixture was neutralized with aq HCl (0.1 N, 10 mL), and extracted with Et_2O (3 × 15 mL). The combined organic extracts were washed with H_2O (3 × 15 mL), dried over $MgSO_4$, filtered and concentrated in vacuo. Separation was carried out by silica gel chromatography using PE–Et_2O (10:1) as eluent to afford product **4a** in 90% yield.

Selected Data for Compounds 4–6:

Compounds **4a**, **4d**, **4i** and **5d** are known, and were identified by ^{1}H NMR, IR spectroscopy and elemental analyses, the data for these compounds are in good agreement with those in literature (refs. 6e–g).

1-(Butylthio)propan-2-ol (4b): colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83–0.86 (m, 3 H), 1.17–1.20 (m, 3 H), 1.31–1.37 (m, 2 H), 1.48–1.51 (m, 2 H), 2.36–2.42 (m, 1 H), 2.45–2.49 (m, 2 H), 2.61–2.65 (m, 1 H), 2.91 (br, 1 H), 3.77 (br, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.5, 21.8 (2 × C), 31.7, 31.8, 41.5, 65.3. IR (KBr, neat): 3340, 2925, 1734, 1539, 1459, 1284 cm^{-1}. Anal. Calcd for $C_7H_{16}OS$: C, 56.71; H, 10.88. Found: C, 56.82; H, 10.96.

1-(Ethylthio)propan-2-ol (4c): colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.80–0.86 (m, 3 H), 1.25–1.28 (m, 3 H), 2.41–2.46 (m, 1 H), 2.54–2.58 (m, 2 H), 2.63 (br, 1 H), 2.73–2.76 (m, 1 H), 3.83–3.85 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.8, 21.7, 31.6, 41.2, 65.4. IR (KBr, neat): 2955, 2869, 1458, 1247, 1200 cm^{-1}. Anal. Calcd for $C_5H_{12}OS$: C, 49.96; H, 10.06. Found: C, 49.81; H, 10.14.

2-(Butylthio)-1-phenylethanol (4e): colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91–0.94 (m, 3 H), 1.38–1.45 (m, 2 H), 1.56–1.62 (m, 2 H), 2.53–2.56 (m, 2 H), 2.70–2.74 (m, 1 H), 2.91–2.94 (m, 1 H), 3.10 (br, 1 H), 4.72–4.74 (m, 1 H), 7.28–7.31 (m, 1 H), 7.31–7.39 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9, 22.2, 31.9, 32.0, 42.3, 71.8, 126.1 (2 × C), 128.1, 128.8 (2 × C), 142.8. IR (KBr, neat): 3426, 3029, 2926, 1740, 1456, 1274 cm^{-1}. Anal. Calcd for $C_{12}H_{18}OS$: C, 68.52; H, 8.63. Found: C, 68.64; H, 8.72.

2-(Butylthio)-2-phenylethanol (5e): colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.87 (m, 3 H), 1.31–1.39 (m, 2 H), 1.48–1.54 (m, 2 H), 2.09 (br, 1 H), 2.42–2.45 (m, 2 H), 3.83–3.87 (m, 2 H), 3.94–3.97 (m, 1 H), 7.26–7.28 (m, 1 H), 7.29–7.38 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9, 22.2, 31.1, 31.8, 53.2, 65.8, 127.9, 128.2 (2 × C), 129.0 (2 × C), 139.1. IR (KBr, neat): 3386, 3028, 2927, 1713, 1538, 1456, 1276 cm^{-1}. Anal. Calcd for $C_{12}H_{18}OS$: C, 68.52; H, 8.63. Found: C, 68.67; H, 8.58.

2-(Ethylthio)-1-phenylethanol (4f): colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.25–1.30 (m, 3 H), 2.53–2.58 (m, 2 H), 2.70–2.75 (m, 1 H), 2.90–2.94 (m, 1 H), 4.71–4.73 (m, 1 H), 7.26–7.30 (m, 1 H), 7.31–7.38 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.1, 26.3, 41.8, 71.9, 126.1 (2 × C), 128.1, 128.8 (2 × C), 142.7. IR (KBr, neat): 3424, 3029, 2921, 1720, 1540, 1451, 1265 cm^{-1}. Anal. Calcd for $C_{10}H_{14}OS$: C, 65.89; H, 7.74. Found: C, 65.73; H, 7.62.

2-(Ethylthio)-2-phenylethanol (5f): colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.19–1.22 (m, 3 H), 2.04–2.07 (m, 1 H), 2.42–2.49 (m, 2 H), 3.84–3.89 (m, 2 H), 3.97–4.00 (m, 1 H), 7.26–7.28 (m, 1 H), 7.28–7.35 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.0, 25.4, 52.8, 65.8, 127.9, 128.3 (2 × C), 129.0 (2 × C), 140.0. IR (KBr, neat): 3334, 3028, 2924, 1712, 1540, 1453, 1265 cm^{-1}. Anal. Calcd for $C_{10}H_{14}OS$: C, 65.89; H, 7.74. Found: C, 65.77; H, 7.81.

2-(Methylthio)-1-phenylethanol (4g): colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.13 (s, 3 H), 2.71–2.76 (m, 1 H), 2.86–2.89 (m, 1 H), 3.02 (br, 1 H), 4.76–4.78 (m, 1 H), 7.29–7.31 (m, 1 H), 7.32–7.38 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.4, 44.0, 71.1, 125.7 (2 × C), 127.8, 128.4 (2 × C), 142.4. IR (KBr, neat): 3421, 3029, 2915, 1721, 1540, 1449, 1235 cm^{-1}. Anal. Calcd for $C_9H_{12}OS$: C, 64.25; H, 7.19. Found: C, 64.13; H, 7.24.

2-(Methylthio)-2-phenylethanol (5g): colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.99 (s, 3 H), 2.06 (br, 1 H), 3.87–3.90 (m, 3 H), 7.26–7.29 (m, 1 H), 7.30–7.37 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.7, 54.0, 64.8, 127.6, 127.9 (2 × C), 128.6 (2 × C), 139.0. IR (KBr, neat): 3358, 3027, 2923, 1722, 1597, 1458, 1269 cm^{-1}. Anal. Calcd for $C_9H_{12}OS$: C, 64.25; H, 7.19. Found: C, 64.36; H, 7.15.

2-(Allylthio)-1-phenylethanol (4h): colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.66–2.71 (m, 1 H), 2.86–2.90 (m, 1 H), 2.94 (br, 1 H), 3.10–3.19 (m, 2 H), 4.72–4.74 (m, 1 H), 5.10–5.15 (m, 2 H), 5.75–5.83 (m, 1 H), 7.28–7.31 (m, 1 H), 7.32–7.37 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 34.9, 40.2, 72.0, 118.0, 126.1 (2 × C), 128.1, 128.8 (2 × C), 134.3, 142.9. IR (KBr, neat): 3425, 3030, 2914, 1715, 1540, 1452, 1228 cm^{-1}. Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26. Found: C, 68.21; H, 7.21.

2-(Allylthio)-2-phenylethanol (5h): colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.94–1.96 (m, 1 H), 2.98–3.02 (m, 1 H), 3.11–3.15 (m, 1 H), 3.85–3.88 (m, 2 H), 3.94–3.97 (m, 1 H), 5.05–5.12 (m, 2 H), 5.75–5.81 (m, 1 H), 7.27–7.29 (m, 1 H), 7.30–7.37 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 34.3, 51.6, 65.9, 117.8, 127.9, 128.5 (2 × C), 129.0 (2 × C), 134.4, 139.7. IR (KBr, neat): 3388, 3028, 2919, 1711, 1538, 1454, 1230 cm^{-1}. Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26. Found: C, 68.12; H, 7.19.

2-(Butylthio)cyclohexanol (4j): colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.5 Hz, 3 H), 1.22–1.29 (m, 3 H), 1.36–1.44 (m, 3 H), 1.51–1.57 (m, 2 H), 1.68–1.73 (m, 2 H), 2.04–2.10 (m, 2 H), 2.31–2.37 (ddd, *J* = 4.0, 9.5, 12.5 Hz, 1 H), 2.53 (m, 2 H), 3.03 (br, 1 H), 3.25–3.27 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.6, 22.0, 24.4, 26.2, 29.4, 32.3, 32.9, 33.7, 53.4, 72.0. IR (KBr, neat): 3450, 2930, 1449, 1227 cm^{-1}. Anal. Calcd for $C_{10}H_{20}OS$: C, 63.77; H, 10.70. Found: C, 63.89; H, 10.62.

2-(Benzylthio)-1-phenylethanone (6a): colorless crystal; mp 68–70 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.68 (s, 2 H), 3.76 (s, 2 H), 7.25–7.27 (m, 2 H), 7.32–7.48 (m, 3 H), 7.47–7.49 (m, 2 H), 7.51–7.53 (m, 1 H), 7.93–7.95 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 35.6, 35.8, 127.0, 128.3 (2 × C), 128.4 (2 × C), 128.5 (2 × C), 129.0 (2 × C), 133.0, 135.1, 137.0, 194.2. IR (KBr, neat): 3058, 2923, 1672, 1545, 1450, 1200 cm^{-1}. Anal. Calcd for $C_{15}H_{14}OS$: C, 74.34; H, 5.82. Found: C, 74.48; H, 5.77.

2-(Butylthio)-1-phenylethanone (6b): colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.82–0.92 (m, 3 H), 1.34–1.42 (m, 2 H), 1.54–1.60 (m, 2 H), 2.54–2.57 (m, 2 H), 3.78 (s, 2 H), 7.45–7.48 (m, 2 H), 7.55–7.58 (m, 1 H), 7.95–7.98 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.7, 20.9, 30.0, 31.0, 36.1, 127.6 (2 × C), 127.8 (2 × C), 132.3, 134.2, 193.5. IR (KBr, neat): 3021, 2950, 1739, 1687, 1511, 1461, 1274 cm^{-1}. Anal. Calcd for $C_{12}H_{16}OS$: C, 69.19; H, 7.74. Found: C, 69.38; H, 7.67.

2-(Ethylthio)-1-phenylethanone (6c): colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.5 Hz, 3 H), 2.59 (q, *J* = 7.5 Hz, 2 H), 3.80 (s, 2 H), 7.46–7.49 (m, 2 H), 7.56–7.59 (m, 1 H), 7.98 (d, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.1, 25.3, 35.7, 127.3, 127.7 (2 × C), 127.8 (2 × C), 132.3, 193.5. IR (KBr, neat): 3061, 2967, 1675, 1450, 1276 cm^{-1}. Anal. Calcd for $C_{10}H_{12}OS$: C, 66.63; H, 6.71. Found: C, 66.51; H, 6.65.

2-(Methylthio)-1-phenylethanone (6d): colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.13 (s, 3 H), 3.76 (s, 2 H), 7.45–7.48 (m, 2 H), 7.56–7.59 (m, 1 H), 7.95–7.98 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.9, 38.0, 127.7, 127.8, 127.9 (2 × C), 132.4, 134.1, 193.0. IR (KBr, neat): 3060, 2918, 1672, 1579, 1447, 1278 cm^{-1}. Anal. Calcd for $C_9H_{10}OS$: C, 65.02; H, 6.06. Found: C, 65.20; H, 6.12.

2-(Allylthio)-1-phenylethanone (6e): colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.18 (d, *J* = 7.5 Hz, 2 H), 3.76 (s, 2 H), 5.15–5.21 (m, 2 H), 5.74–5.80 (m, 1 H), 7.45–7.48 (m, 2 H), 7.55–7.58 (m, 1 H), 7.96 (d, *J* = 7.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 34.9, 35.7, 118.8, 128.9, 129.0, 129.1, 129.2, 133.2, 133.6, 134.2, 194.7. IR (KBr, neat): 3061, 2917, 1676, 1540, 1449, 1275 cm^{-1}. Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 68.58; H, 6.37.

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