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Tetrahedron 63 (2007) 3408–3414
Tetrahedron

Thermolysis of β-hydroxysulfides bearing several heteroaromatics

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Received 27 November 2006; revised 22 January 2007; accepted 23 January 2007
Available online 25 January 2007

Abstract—Thermolyses of β-hydroxysulfides **2**, bearing groups, such as 2-benzothiazolyl and 4-(4-methyl)-4*H*-1,2,4-triazolyl groups, were studied and found to afford the corresponding substituted styrenes **5** and hydroxy heteroaromatics in good yields, respectively. The product distribution change in the course of the thermolysis of **2a** was also studied. The olefin products **5a** were considered to be formed by the thermal desulfurization of the corresponding thiiranes **4a** initially formed via the five-membered spiro intermediate **6a**.

1. Introduction

Recently, we have reported that the thermolytic reaction of phenacyl sulfoxides bearing several heteroaromatics, such as 2-*N*-oxypyridyl, 2-benzothiazolyl, 5-(1-methyl)-1,2,3,4-tetrazolyl, and 5-(1-phenyl)-1,2,3,4-tetrazolyl groups afforded the corresponding thioaldehyde[1,2] or sulfines,[3] depending on the substituted heteroaryl groups. Thioaldehydes were considered to be formed by the elimination of hydroxy heteroaromatics via the sulfenate ester intermediate generated by rearrangement of the starting sulfoxide. In contrast to the other substituents, 5-(1-phenyl)-1,2,3,4-tetrazolyl derivatives revealed to afford sulfines via the elimination of tetrazole by the E2 type elimination mechanisms. In a continuing study of the thermolysis of β-ketosulfoxides in order to shed further light into their diverse field of synthetic organic chemistry[4–6] and also potent pharmaceutical derivatives,[7–9] we have prepared several heteroaryl substituted β-hydroxysulfide derivatives and studied their thermolysis behaviors.

Herein, we report the synthesis of β-hydroxysulfides bearing several heteroaromatics and their thermal behavior in mechanistic viewpoints. Their applications for several olefin syntheses are also described.

2. Results and discussion

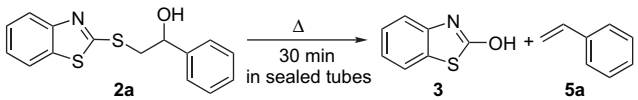
2.1. Thermolysis of 2-benzothiazolyl 2-hydroxyphenethyl sulfide (2a)

Among many synthetic methods for β-hydroxysulfides,[10] we have used the reduction of β-ketosulfides. β-Ketosulfides **1a–h** were prepared easily by reactions of α-haloketones with heterocyclic thiols in the presence of triethylamine in CH_2Cl_2 at rt. The heterocyclic sulfides containing tertiary hydroxy group **2i** were prepared by the Grignard reaction with corresponding β-ketosulfides.[11]

First, the thermolysis of **2a** without solvent was studied at several temperatures. The reaction proceeded smoothly with increasing the temperature above 150 °C to afford 2-hydroxybenzothiazole (**3**) in a quantitative yield. At 160 °C, formation of styrene (**5a**) became maximum and then, at higher temperature decreases gradually, probably due to the thermal polymerization of **5a** at higher temperature. The results are summarized in Table 1 and illustrated in Figure 1.

Next, thermolysis of 2-benzothiazolyl 2-hydroxy-2-(2-naphthyl)ethyl sulfide (**2c**) in *p*-xylene was found to afford **3** and 2-vinylnaphthalene (**5c**) in a quantitative and 82% yield, respectively.

Table 1. Thermolysis of 2-benzothiazolyl 2-hydroxyphenethyl sulfide (**2a**) under neat conditions



Entry	Temperature (°C)	Yield (%)[a]		
		3	**5a**	Recovery
1	130	8	5	92
2	140	23	14	77
3	150	66	39	34
4	160	98	44	4
5	170	100	30	0
6	180	100	16	0

[a] Determined by ^{1}H NMR.

Keywords: β-Hydroxysulfides; Benzothiazole; Thermolysis; Spiro compounds; Olefin syntheses.
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doi:10.1016/j.tet.2007.01.043

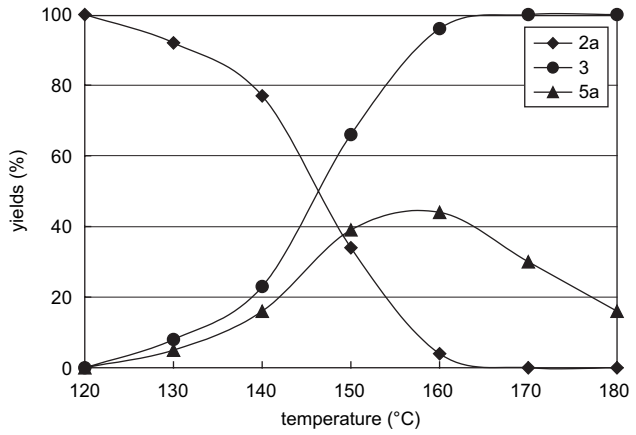


Figure 1. Thermolysis of 2-benzothiazolyl 2-hydroxyphenethyl sulfide (**2a**).

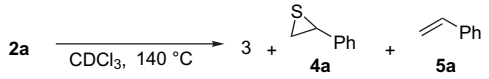
TLC monitoring in the progress of thermolysis of **2c** in *p*-xylene revealed the initial formation of the compound other than **3** and **5c**. In order to identify the intermediate product, the thermal reaction of **2a** in the presence of mesitylene as an internal standard was carried out every 30 min interval for 5.0 h at 140 °C in $CDCl_3$ in sealed tubes. The product identification and distribution measurements were directly carried out by ^{1}H NMR. The intermediate was revealed to be phenyl episulfide **4a** by comparison with an authentic sample prepared by the known method.[12] The results are summarized in Table 2.

The time dependence study revealed that the maximum yield of **3** approximately reached at around 1.5 h as illustrated in Figure 2. Consequently, the olefin **5a** was obviously formed by the desulfurization of **3** initially formed.

2.2. Thermolysis of β-hydroxysulfides bearing several heteroaromatics

We have extended the thermolysis of β-hydroxysulfides bearing heteroaromatics other than benzothiazole. The results are summarized in Table 3. In the case of **2c** and **2f** (entries 1 and 2), thermolysis proceeded smoothly to afford the corresponding hydroxy heteroaromatics and

Table 2. Thermal reaction of **2a** in $CDCl_3$[a]



Entry	Time (h)	Yield (%)[b]			
		3	**4a**	**5a**	Recovery
1	0.0	0	0	0	100
2	0.5	21	3	3	75
3	1.0	36	21	10	63
4	1.5	49	22	21	48
5	2.0	68	14	33	38
6	2.5	74	13	42	30
7	3.0	75	10	52	17
8	4.0	83	0	61	0
9	5.0	82	0	65	0

[a] In sealed tubes.
[b] Determined by ^{1}H NMR.

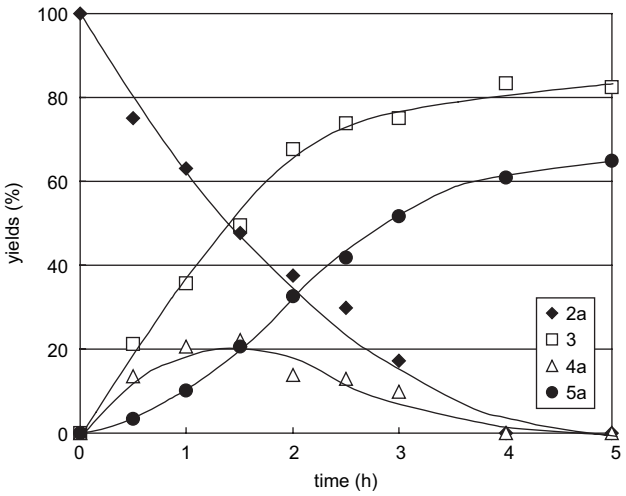
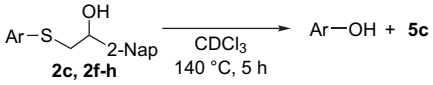


Figure 2. Time dependence study of thermolysis of **2a**.

Table 3. Thermolysis of β-hydroxysulfides bearing several heteroaromatics[a]



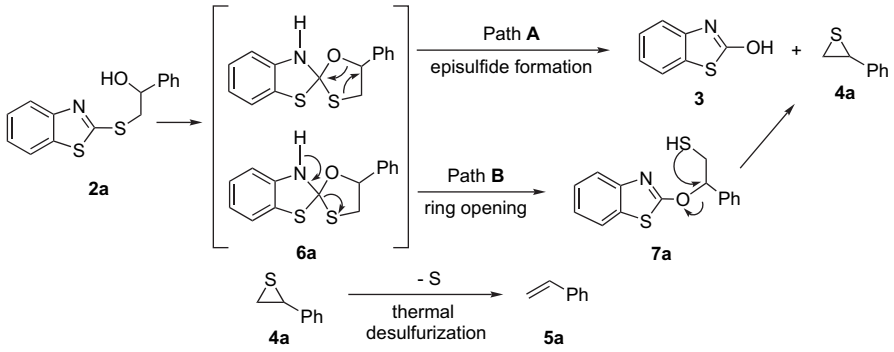
Entry	Ar	Yield (%)[b]		
		Ar–OH	**5c**	Recovery
1	**2c**	92	86	0
2	**2f**	95	90	0
3	**2g**	0	0	97
4	**2h**	0	0	82

[a] In sealed tubes.
[b] Determined by ^{1}H NMR.

2-vinylnaphthalene (**5c**) in excellent yields. However, in the case of β-hydroxysulfides bearing 5-(1-phenyl)-1,2,3,4-tetrazolyl group **2g** and 2-pyridyl group **2h**, the reaction did not proceed and starting materials were recovered quantitatively. Probably, in these cases the formation of spiro intermediates will be retarded greatly by both sterically and electronically.

2.3. Reaction mechanism of thermolysis of hydroxysulfides

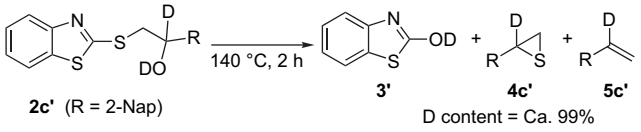
Almost quantitative formation of 2-hydroxybenzothiazole **3** suggested that the thermolyses of β-hydroxysulfides apparently involve oxygen–sulfur exchange. The plausible formation pathway of **3** and **5** is illustrated in Scheme 1. β-Hydroxysulfide (**2a**) leads to spiro intermediate **6a** by the internal *ipso*-addition of the hydroxy group at β-position. The possible decomposition route of this intermediate to **3** and **4a** will be either Path **A** or Path **B**, or both. Path **A** is the route for the thiirane **4a** formation, and Path **B** is the



Scheme 1. Probable mechanism of thermolysis of β-hydroxysulfide **2a**.

concerted ring-opening route, followed by the elimination of **7a** to form **4a**. In both cases, the good leaving ability of hydroxybenzothiazole group seems to operate the crucial role. The final product, olefin **5a** was formed by the thermal desulfurization from **4a**.

In order to obtain a clue to clarify the mechanism, trapping experiment of thiol **7a** in the presence of ethyl propiolate or *N*-phenylmaleimide was carried out. However, the resultant Michael addition product was not obtained. Further, deuterium labeled compound **2c′**, which was prepared by the reduction of **1b** with $NaBD_4$, demonstrated the thermolysis under the same conditions to reveal the formation of **5c′** with no loss of deuterium content (Scheme 2). These results also suggest the pathway via the spiro intermediate **7a** among other possible routes to olefin **5** in thermolysis of **2a**.

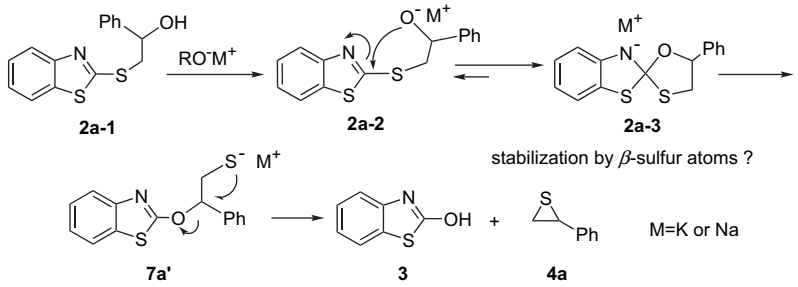


Scheme 2. Thermolysis of deuterium introduced β-hydroxysulfide **2c′**.

The thermolysis in the presence of bases is also interesting, since all the reaction steps in Scheme 1, i.e., those of **2a** to **6a** and Path **A** or Path **B**, are considered to be catalyzed by base. Therefore, the thermolysis of **2a** and **2b** in the presence of DMAP was carried out, expecting the reaction acceleration. However, the addition of base revealed to result in retardation of the reaction, and 83% of starting material was recovered after 5.0 h in $CDCl_3$ at 140 °C. When DBU was used as a stronger amine base, the result was the same and almost all the starting material was recovered. In both cases, more than 18 h was needed to proceed the reaction completely. In these cases, probably the step **2a** to **6a** would be accelerated by the increase of nucleophilic addition of hydroxy group to NC double bond. Therefore, the reason why the reaction was retarded contrary to the expectation would be due to the following steps, i.e., *ipso*-ring opening and/or episulfide formation steps. However, the more plausible reason is not clear at present.

The reaction of **2a** in the presence of stronger bases in protic solvent, such as potassium *tert*-butoxide or sodium methoxide, revealed that the reaction proceed rapidly to form **3** and **5a**. The discrepancy between amine base and alkoxide bases may be accounted for by the strong coordination between metal cation and the nitrogen anion, and probably by the participation of β-sulfur atoms, resulted in the formation of **2a**-**3** predominately as depicted in Scheme 3. Further, in the case of alkoxide base, the formation of thiolate anion of **7a′** will be the driving force to accelerate the reaction, Path **B** in Scheme 1, to produce **3** and **4a** by internal SN reaction. Similar results have been reported in the reaction of thiazole derivatives in the presence of sodium methoxide[13] and oxazoline derivatives in the presence of butyllithium.[14]

Additionally, in view of the retardation effect of amine, thermolysis was suggested to proceed by the homolytic processes. The thermolysis of **2a** in the presence of radical scavenger (2,6-di-*tert*-butylphenol) or initiator (2,2′-azobis(2-methylpropionitrile)) was carried out, however, the reaction acceleration or retardation was not observed. Therefore, the involvement of homolytic process will be excluded. All these results seem to suggest that the thermal reaction proceed via intramolecular addition of hydroxy group at β-position to NC double bond forming spiro intermediate **6a**, probably via Path **A** and successively via the concerted episulfide formation in Scheme 1.

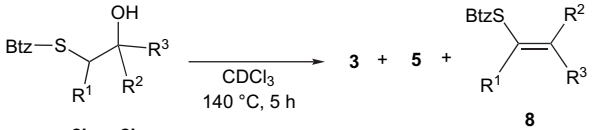


Scheme 3.

2.4. Synthetic application for several olefin syntheses

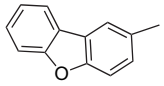
In order to study the scope and limitations, we prepared several β-hydroxysulfides **2** with several substituents at α- or β-position and studied their thermolysis under the same conditions. The results are summarized in Table 4. All reactions are found to afford the corresponding olefins **5** in good to excellent yields. In the case of **2i** (entry 5), the dehydration product **8** was also formed in a low yield.

Table 4. Thermal reactions of 2-benzothiazolyl sulfides having several substituents at α- and β-position[a]



2b-e, 2i

Btz = 2-benzothiazolyl

Entry	R^1	R^2	R^3		Yield (%)[b]		
					3	**5**	**8**
1	H	1-Nap	H	**2b**	Quant.[c]	Quant.[c]	0
2	H	2-Nap	H	**2c**	92	86	0
3	Ph	Ph	H	**2d**[d]	95	88	0
4	H		H	**2e**	96	91	0
5	Ph	Ph	Ph	**2i**	77	82	5

[a] In sealed tubes.
[b] Isolated yield.
[c] Determined by ^{1}H NMR.
[d] Diastereomeric mixture (6:1).

3. Conclusion

Thermolysis of β-hydroxysulfides bearing benzothiazoles **2a–f** afforded **3** and the corresponding olefins **5a–f**, **i** in good to excellent yields, respectively. The reactions are considered to proceed via five-membered spiro intermediate **6** by the *ipso*-addition of hydroxy group at β-position to NC double bond of benzothiazole, followed by the formation of 2-hydroxybenzothiazole (**3**) and olefin **5** generated by thermal desulfurization of thiirane **4a**. Thermal reactions of β-hydroxysulfides are useful in olefin synthesis, and in addition, further purification of olefins is very easy by silica flash column chromatography. Additionally, this methodology does not require any strong acid, unstable toxic metallic reagents, or other expensive reagents.

4. Experimental

4.1. General

All the melting points were uncorrected using micro melting point apparatus. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ using TMS as an internal standard. The elemental analyses were performed at Microanalytical Laboratory of the Department of Material Systems Engineering and Life Science, University of Toyama. All the reactions were monitored with TLC and the products were separated by column chromatography using silica gel 60 and also by preparative layer chromatography using silica gel 60 PF_{254} with UV detection. All the reagents were of highest quality and further purified by distillation or recrystallization. The solvents were further purified by general method.

4.2. General procedure for the preparation of β-ketosulfides 1a–h

To a mixture of heterocyclic mercaptan (1 mmol) and α-haloketones (1 mmol) in dichloromethane (10 ml) was added dry triethylamine (0.5 ml) with stirring at rt under N_2. After the starting materials were consumed, the solvent and excess triethylamine were evaporated off, and the residue was dissolved in dichloromethane. The organic layer was washed with 10 ml of brine and dried over anhydrous $MgSO_4$. Then, the solvent was removed to afford crude β-ketosulfides **1a–h**, which were purified by flash column chromatography.

4.2.1. 2-Benzothiazolyl phenacyl sulfide (1a). Yield 93%; mp 109–111 °C (colorless needles from CH_2Cl_2–diethylether–hexane); ^{1}H NMR ($CDCl_3$): δ 4.98 (s, 2H), 7.28 (t, J=7.6 Hz, 1H), 7.40 (t, J=7.6 Hz, 1H), 7.52 (t, J=8.0 Hz, 2H), 7.61–7.65 (m, 1H), 7.75 (d, J=8.0 Hz, 1H), 7.81 (d, J=8.0 Hz, 1H), 8.08–8.10 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 41.0, 121.1, 121.5, 124.4, 126.0, 128.6, 128.8, 133.8, 135.4, 135.5, 152.8, 165.2, 192.9; IR (KBr): ν=1660 cm^{-1}. Anal. Calcd for $C_{15}H_{11}NOS_2$: C, 63.13; H, 3.89; N, 4.91. Found: C, 63.20; H, 3.93; N, 4.95.

4.2.2. 2-Benzothiazolyl 1-naphthonyl sulfide (1b). Yield 85%; mp 122–123 °C (white crystal from CH_2Cl_2–diethylether–hexane); ^{1}H NMR ($CDCl_3$): δ 4.96 (s, 2H), 7.26–7.30 (m, 1H), 7.35–7.39 (m, 1H), 7.52–7.60 (m, 3H), 7.74 (t, J=8.0 Hz, 2H), 7.88–7.90 (m, 1H), 8.03 (d, J=8.4 Hz, 1H), 8.11 (d, J=7.2 Hz, 1H), 8.61 (d, J=7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 43.3, 121.1, 121.5, 124.3, 124.4, 125.9, 126.0, 126.7, 128.1, 128.2, 128.4, 130.3, 133.4, 134.0, 134.4, 135.6, 152.9, 165.1, 196.2; IR (KBr) ν=1661 cm^{-1}. Anal. Calcd for $C_{19}H_{13}NOS_2$: C, 68.03; H, 3.91; N, 4.18. Found: C, 67.93; H, 4.01; N, 4.28.

4.2.3. 2-Benzothiazolyl 2-naphthonyl sulfide (1c). Yield 84%; mp 146–147 °C (white solid from CH_2Cl_2–diethylether–hexane); ^{1}H NMR ($CDCl_3$): δ 5.09 (s, 2H), 7.29 (t, J=7.8 Hz, 1H), 7.40 (t, J=7.6 Hz, 1H), 7.55–7.65 (m, 2H), 7.74 (d, J=8.0 Hz, 1H), 7.82–7.99 (m, 4H), 8.09 (dd, J=8.8, 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 40.9, 121.1, 121.5, 123.9, 124.4, 126.1, 127.0, 127.8, 128.7, 128.9, 129.7, 130.6, 132.4, 132.8, 135.5, 135.9, 152.9, 165.3, 193.0; IR (KBr): ν=1688 cm^{-1}. Anal. Calcd for $C_{19}H_{13}NOS_2$: C, 68.03; H, 3.91; N, 4.18. Found: C, 67.73; H, 4.09; N, 4.03.

4.2.4. 2-Benzothiazolyl α-phenylphenacyl sulfide (1d). Yield 85%; mp 116–118 °C (white crystal from CH_2Cl_2–diethylether–hexane); ^{1}H NMR ($CDCl_3$): δ 6.95 (s, 1H), 7.24–7.38 (m, 5H), 7.44 (t, J=7.6 Hz, 2H), 7.55 (t, J=8.2 Hz, 3H), 7.71 (d, J=8.0 Hz, 2H), 8.07 (d, J=6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 58.2, 121.1, 121.5, 124.3, 125.9, 128.6, 128.7, 129.0, 129.1, 129.2, 133.4, 134.6, 135.6, 152.8, 164.9, 194.3; IR (KBr): ν=1683 cm^{-1}. Anal. Calcd for $C_{21}H_{15}NOS_2$: C, 69.78; H, 4.18; N, 3.87. Found: C, 69.70; H, 4.22; N, 3.85.

4.2.5. 2-Benzothiazolyl 2-dibenzofuranoyl sulfide (1e). Yield 80%; mp 157–158 °C (white solid from CH_2Cl_2–diethylether–hexane); ^{1}H NMR ($CDCl_3$): δ 5.09 (s, 1H), 7.28–7.32 (m, 1H), 7.38–7.43 (m, 2H), 7.50–7.54 (m, 1H), 7.61 (d, J=8.0 Hz, 3H), 7.64 (d, J=8.8 Hz, 1H), 7.75 (d, J=8.4 Hz, 1H), 7.85 (d, J=8.4 Hz, 1H), 7.97–8.00 (m, 1H), 8.23 (dd, J=8.8, 2.0 Hz, 1H), 8.72 (d, J=1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 41.0, 111.9, 112.0, 121.0, 121.4, 122.1, 123.5 (2C), 124.5, 124.8, 126.1, 128.15, 128.2, 130.6, 135.5, 152.7, 156.9, 159.3, 165.5, 192.2; IR (KBr): ν=1674 cm^{-1}. Anal. Calcd for $C_{21}H_{15}NO_2S_2$: C, 67.18; H, 3.49; N, 3.73. Found: C, 67.08; H, 3.60; N, 3.73.

4.2.6. 5-(4-Methyl)-4*H*-1,2,4-triazolyl 2-naphthonyl sulfide (1f). Yield 96%; mp 163–165 °C (white solid from CH_2Cl_2–diethylether–hexane); ^{1}H NMR ($CDCl_3$): δ 3.65 (s, 3H), 5.01 (s, 2H), 7.56–7.65 (m, 2H), 7.89 (dd, J=11.6, 8.4 Hz, 2H), 7.98 (d, J=8.4 Hz, 1H), 8.04 (dd, J=8.6, 1.8 Hz, 1H), 8.17 (s, 1H), 8.54 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 31.0, 42.1, 123.6, 127.1, 127.7, 128.7, 129.0, 129.7, 130.7, 132.2, 132.3, 135.8, 145.2, 150.2, 192.9; IR (KBr): ν=1685 cm^{-1}. Anal. Calcd for $C_{15}H_{13}N_3OS$: C, 63.58; H, 4.62; N, 14.83. Found: C, 63.58; H, 4.57; N, 14.82.

4.2.7. 5-(1-Phenyl)-1*H*-1,2,3,4-tetrazolyl 2-naphthonyl sulfide (1g). Yield 99%; mp 122–123 °C (white solid from CH_2Cl_2–diethylether–hexane); ^{1}H NMR ($CDCl_3$): δ 5.24 (s, 2H), 7.54–7.67 (m, 7H), 7.90 (d, J=8.0 Hz, 1H), 7.93 (d, J=8.4 Hz, 1H), 8.01 (d, J=8.0 Hz, 1H), 8.06 (dd, J= 1.6, 8.4 Hz, 1H), 8.61 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 42.8, 123.5, 123.8, 127.2, 127.8, 129.2, 129.9, 130.3, 130.8, 132.1, 132.4, 133.5, 136.0, 153.6, 192.1; IR (KBr): ν=1673 cm^{-1}. Anal. Calcd for $C_{19}H_{14}N_4OS$: C, 65.88; H, 4.07; N, 16.17. Found: C, 65.66; H, 4.21; N, 16.12.

4.2.8. 2-Pyridyl 2-naphthonyl sulfide (1h). Yield 74%; mp 89–90 °C (yellow crystal from CH_2CH_2–hexane); ^{1}H NMR ($CDCl_3$): δ 4.83 (s, 2H), 6.98 (ddd, J=8.4, 5.2, 1.2 Hz, 1H), 7.25–7.27 (m, 1H), 7.45–7.50 (m, 1H), 7.52–7.62 (m, 2H), 7.88 (t, J=4.8 Hz, 2H), 8.08 (dd, J=4.8, 1.6 Hz, 1H), 8.36–8.38 (m, 1H), 8.62 (s, 3H); ^{13}C NMR: δ 37.0, 119.8, 122.2, 124.2, 126.7, 127.7, 128.4, 128.4, 129.6, 130.4, 132.4, 133.3, 135.6, 136.0, 149.2, 156.9, 194.5; IR (KBr): ν= 1680 cm^{-1}. Anal. Calcd for $C_{17}H_{13}NOS$: C, 73.09; H, 4.69; N, 5.01. Found: C, 73.13; H, 4.77; N, 4.92.

4.3. General procedure for the preparation of β-hydroxysulfides 2a–h

To a solution of sodium borohydride (1 mmol) in THF–methanol (1:1) was added sulfides **1a–h** (1 mmol) in THF with stirring at rt under N_2, and the reaction mixture was stirred until the starting β-ketosulfides disappeared. To the reaction mixture was added AcOEt and washed with brine. The aqueous layer was extracted with AcOEt. The combined organic layer was dried over anhydrous $MgSO_4$. Then, the solvent was removed to afford crude product. Purification by flash column chromatography on silica gel or recrystallization yielded pure β-hydroxysulfides **2a–h**.

4.3.1. 2-Benzothiazolyl 2-hydroxyphenethyl sulfide (2a). Yield 84%; mp 82–83 °C (white solid from CH_2Cl_2–hexane); ^{1}H NMR ($CDCl_3$): δ 3.53–3.74 (m, 2H), 5.03 (s, 1H), 5.20 (dd, J=8.0, 2.8 Hz, 1H), 7.29–7.48 (m, 7H), 7.75 (d, J=8.0 Hz, 1H), 7.90 (d, J=8.4 Hz); ^{13}C NMR ($CDCl_3$): δ 42.7, 73.7, 121.1, 121.3, 124.6, 125.8, 126.3, 127.8, 128.5, 135.5, 142.8, 152.4, 167.8; IR (KBr): ν=3233 cm^{-1}. Anal. Calcd for $C_{15}H_{11}NOS_2$: C, 62.69; H, 4.56; N, 4.87. Found: C, 62.77; H, 4.56; N, 4.87.

4.3.2. 2-Benzothiazolyl 2-hydroxy-2-(1-naphthyl)ethyl sulfide (2b). Yield 92%; mp 89–91 °C (colorless needles from CH_2Cl_2–hexane); ^{1}H NMR ($CDCl_3$): δ 3.53 (dd, J=14.8, 8.0 Hz, 1H), 3.98 (dd, J=14.4, 2.0 Hz, 1H), 6.01 (dd, J=14.0, 2.0 Hz, 1H), 7.35 (td, J=8.0, 1.2 Hz, 1H), 7.45–7.54 (m, 3H), 7.60 (td, J=8.0, 1.2 Hz, 1H), 7.78 (d, J=8.0 Hz, 1H), 7.81 (d, J=8.0 Hz, 1H), 7.87–7.91 (m, 2H), 7.97 (d, J=8.4 Hz, 1H), 8.31 (d, J=8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$.): δ 42.2, 70.4, 121.2, 121.3, 123.0, 123.3, 124.7, 125.5, 125.6, 126.26, 126.35, 128.3, 129.0, 130.1, 133.8, 135.4, 138.3, 152.4, 167.7; IR (KBr): ν=3316, 3248 cm^{-1}. Anal. Calcd for $C_{19}H_{15}NOS_2$: C, 67.62; H, 4.48; N, 4.15. Found: C, 67.79; H, 4.55; N, 4.14.

4.3.3. 2-Benzothiazolyl 2-hydroxy-2-(2-naphthyl)ethyl sulfide (2c). Yield 95%; mp 80–81 °C (pale yellow solid from CH_2Cl_2–diethylether–hexane); ^{1}H NMR ($CDCl_3$): δ 3.51–3.71 (m, 2H), 5.26 (dd, J=7.8, 2.6 Hz, 1H), 7.23 (t, J=7.4 Hz, 1H), 7.33–7.41 (m, 3H), 7.46 (dd, J=8.4, 1.6 Hz, 1H), 7.65 (d, J=8.0 Hz, 1H), 7.74 (t, J=7.6 Hz, 3H), 7.83 (d, J=11.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 42.7, 73.8, 121.0, 121.3, 123.8, 124.6, 124.7, 125.9, 126.1, 126.3, 127.7, 128.0, 128.3, 133.0, 133.2, 135.4, 140.2, 152.3, 167.9; IR (KBr): ν=3430, 3051 cm^{-1}. Anal. Calcd for $C_{19}H_{15}NOS_2$: C, 67.62; H, 4.48; N, 4.15. Found: C, 67.63; H, 4.57; N, 4.12.

4.3.4. 2-Benzothiazolyl 2-deutryl-2-hydroxy-2-(1-naphthyl)ethyl sulfide (2c′). Yield 95%; ^{1}H NMR ($CDCl_3$): δ 3.65 (d, J=14.8 Hz, 1H), 3.80 (d, J=14.8 Hz, 1H), 7.32–7.36 (m, 1H), 7.44–7.51 (m, 3H), 7.55–7.58 (m, 1H), 7.60 (d, J=8.4 Hz, 1H), 7.83–7.88 (m, 3H), 7.93–7.95 (m, 2H).

4.3.5. 2-Benzothiazolyl (1,2-diphenyl-2-hydroxy)ethyl sulfide (2d, diastereomeric mixture). Yield 90%; diastereomeric mixtures **A** and **B** (ratio of A/B, 1.0/6.0 by ^{1}H NMR) were separated by the repeated silica gel preparative thin layer chromatography. Diastereomeric mixtures **A** and **B** showed the following ^{1}H and ^{13}C NMR spectra, respectively.

Diastereomeric mixture **A**: colorless oil; ^{1}H NMR ($CDCl_3$): δ 3.78 (br, 1H), 5.28 (d, J=4.4 Hz, 1H), 5.32 (d, J=4.4 Hz, 1H), 7.08–7.15 (m, 10H), 7.19 (t, J=7.6 Hz, 1H), 7.32 (t, J=7.6 Hz, 1H), 7.61 (d, J=8.0 Hz, 1H), 7.81 (d, J=8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 59.5, 76.5, 121.0, 121.6, 124.5, 126.1, 126.9, 127.8 (2C), 127.9, 128.1, 129.2, 135.4, 136.2, 140.2, 152.6, 166.1; IR (KBr): ν=3350, 3057, 3027, 1453, 1424 cm^{-1}.

Diastereomeric mixture **B**: white solid; mp 120–122 °C (white solid from AcOEt–hexane), ^{1}H NMR ($CDCl_3$): δ 5.39 (d, J=4.4 Hz, 1H), 5.41 (d, J=4.4 Hz, 1H), 7.16–7.24 (m, 10H), 7.30 (t, J=7.8 Hz, 1H), 7.43 (t, J=7.8 Hz, 1H), 7.71 (d, J=8.0 Hz, 1H), 7.91 (d, J=8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 61.5, 78.8, 121.0, 121.5, 124.7, 126.2,

126.7, 127.7, 127.9, 128.0, 128.3, 128.5, 135.5, 137.8, 141.6, 152.3, 167.6; IR (KBr): ν=3307, 3056, 3028, 1453, 1423 cm^{-1}. Anal. Calcd for $C_{21}H_{17}NOS_2$: C, 69.39; H, 4.71; N, 3.85. Found: C, 69.49; H, 4.89; N, 3.95.

4.3.6. 2-Benzothiazolyl 2-(2-dibenzofuranyl)-2-hydroxyethyl sulfide (2e). Yield 94%; mp 108–110 °C (white solid from CH_2Cl_2–hexane); ^1H NMR ($CDCl_3$): δ 3.64 (dd, J=14.4, 8.4 Hz, 1H), 3.79 (dd, J=14.4, 3.2 Hz, 1H), 4.89 (br, 1H), 5.38 (dd, J=8.4, 6.0 Hz, 1H), 7.31–7.36 (m, 2H), 7.43–7.47 (m, 2H), 7.51–7.57 (m, 3H), 7.75 (d, J=8.0 Hz, 1H), 7.94 (t, J=7.6 Hz, 1H), 7.10 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 43.2, 73.8, 111.5, 111.7, 118.1, 120.7, 121.1, 121.3, 122.7, 124.1, 124.4, 124.8, 125.0, 126.4, 127.2, 135.3, 137.5, 152.1, 155.8, 156.6, 168.1; IR (KBr): ν=3328, 3058 cm^{-1}. Anal. Calcd for $C_{21}H_{15}NO_2S_2$: C, 66.82; H, 4.01; N, 3.79. Found: C, 66.35; H, 4.17; N, 3.57.

4.3.7. 4-(4-Methyl)-4*H*-1,2,4-triazolyl 2-hydroxy-2-(2-naphthyl)ethyl sulfide (2f). Yield 90%; mp 97–98 °C (white solid from CH_2Cl_2–ether–hexane); ^1H NMR ($CDCl_3$): δ 3.47 (s, 3H), 3.50 (dd, J=14.4, 8.0 Hz, 2H), 3.64 (dd, J=14.4, 3.2 Hz, 2H), 4.96 (br, 1H), 5.28 (dd, J=8.0, 3.2 Hz, 2H), 7.44–7.47 (m, 2H), 7.50 (dd, J=8.8, 1.6 Hz, 1H), 7.79–8.82 (m, 3H), 7.89 (s, 1H), 8.04 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 31.0, 41.8, 73.4, 123.9, 124.7, 125.8, 126.1, 127.6, 128.0, 128.1, 132.9, 133.1, 140.1, 145.0, 151.8; IR (KBr): ν=3181, 1510, 1079 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{15}N_3OS$: 285.0936. Found: m/z 285.0923 (M^+).

4.3.8. 5-(1-Phenyl)-1*H*-1,2,3,4-tetrazolyl 2-hydroxy-2-(2-naphthyl)ethyl sulfide (2g). Yield 94%; mp 120–122 °C (white crystal from CH_2Cl_2–diethylether–hexane); ^1H NMR ($CDCl_3$): δ 3.18 (br, 1H), 3.60 (dd, J=14.0, 8.4 Hz, 1H), 3.90 (dd, J=14.0, 3.2 Hz, 1H), 5.36 (dd, J=8.4, 3.2 Hz, 1H) 7.46–7.52 (m, 8H), 7.82–7.86 (m, 3H), 7.91 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 41.8, 72.9, 123.6, 123.8, 124.8, 126.2, 126.3, 127.7, 128.1, 128.5, 129.8, 130.17, 133.18, 133.5, 139.2, 154.6; IR (KBr): ν=3497 cm^{-1}. Anal. Calcd for $C_{19}H_{14}N_4OS$: C, 65.50; H, 4.63; N, 16.08. Found: C, 65.49; H, 4.83; N, 15.99.

4.3.9. 2-Pyridyl 2-hydroxy-2-(2-naphthyl)ethyl sulfide (2h). Yield 93%; mp 57–58 °C (white crystal from CH_2Cl_2–diethylether–hexane); ^1H NMR ($CDCl_3$): δ 3.46 (dd, J=14.4, 7.6 Hz, 1H), 3.50 (dd, J=14.4, 3.2 Hz, 1H), 5.25 (dd, J=7.6, 3.2 Hz, 1H), 6.65 (br, 1H), 7.03 (ddd, J=7.2, 5.2, 0.8 Hz, 2H), 7.27 (d, J=8.0 Hz, 2H), 7.41–7.48 (m, 3H), 7.53 (dd, J=8.4, 1.6 Hz, 1H), 7.80–7.84 (m, 3H), 7.93 (s, 1H), 8.41–8.43 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 40.8, 74.5, 120.1, 123.0, 124.1, 124.6, 125.6, 125.9, 127.6, 127.9, 128.0, 132.9, 133.2, 136.6, 141.3, 148.7, 159.0; IR (KBr): ν=3292 cm^{-1}. Anal. Calcd for $C_{17}H_{15}NOS$: C, 72.57; H, 5.37; N, 4.98. Found: C, 72.83; H, 5.56; N, 5.00.

4.3.10. 2-Benzothiazolyl 2-hydroxy-1,2,2-triphenylethyl sulfide (2i). To a solution of 2-benzothiazolyl α-phenylphenacyl sulfide (**1d**) (890 mg, 2.46 mmol) in 10 ml of anhydrous THF was added 1.1 equiv of phenyl magnesium bromide solution in anhydrous THF with stirring at rt under N_2. After 6 h, 5.0 ml of 1.0 M aqueous HCl was added slowly to complete the reaction. The mixture was extracted with AcOEt (20 ml×4) and 50 ml of brine. The combined organic phase was dried over anhydrous $MgSO_4$. The solvent was removed to afford crude **2i**, which was purified by recrystallization from dichloromethane, diethylether, and hexane at rt with seeding. Yield 95%; mp 144–146 °C; ^1H NMR ($CDCl_3$): δ 3.83 (br, 1H), 6.17 (s, 1H), 7.02–7.13 (m, 6H), 7.19–7.32 (m, 6H), 7.37–7.41 (m, 3H), 7.63–7.66 (m, 1H), 7.68–7.71 (m, 2H), 7.89–7.92 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 61.2, 81.2, 120.9, 121.6, 124.2, 125.9, 126.1, 126.7, 127.29, 127.31, 127.6, 127.7, 128.2, 130.2, 135.7, 138.1, 144.4, 145.5, 152.9, 165.1; IR (KBr): ν=3328, 3058 cm^{-1}. Anal. Calcd for $C_{21}H_{15}NOS_2$: C, 73.77; H, 4.82; N, 3.19. Found: C, 73.60; H, 5.09; N, 3.04.

4.4. Thermolysis of 2-benzothiazolyl β-hydroxyphenethyl sulfide (2a) at neat conditions

To a 2 ml of Pyrex tube was added 50 mg (0.175 mmol) of sulfide, and this tube was sealed after the replacement with N_2. The heating at 200 °C for 30 min followed by separation with preparative TLC, hexane–AcOEt (5/1), gave 24.4 mg of 2-hydroxybenzothiazole (**9**) in 92% yield as white solid and 16.6 mg of volatile mixture.

4.5. Thermolysis of 2-(2-naphthyl)-2-hydroxyethyl sulfide bearing several heteroaromatics

2-Benzothiazolyl 2-hydroxy-2-(2-naphthyl)ethyl sulfide (**2c**) of 10 mg dissolved in $CDCl_3$ was poured into a 2 ml Pyrex tube and this tube was sealed under N_2. After heating the sample at 140 °C for 5 h, the crude mixture was measured by ^1H NMR directly.

4.6. Time dependence study of thermolysis of 2-benzothiazolyl β-hydroxyphenethyl sulfide 2a

To 10 mg of sulfide dissolved in 1.0 ml of $CDCl_3$ was added 1.0 equiv of mesitylene, and this reaction mixture was put into a 2 ml Pyrex tube sealed under N_2. After sealing the tube followed by heating each samples at 140 °C for 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, and 5.0 h, the change of the component of reaction mixture was measured by ^1H NMR directly.

4.6.1. 1-Deuterium-1-(2-naphthyl) thiirane (4c′). ^1H NMR ($CDCl_3$): δ 2.76 (s, 1H), 2.94 (s, 1H), 7.29 (dd, J=8.8, 2.4 Hz, 1H), 7.43–7.52 (m, 3H), 7.73–7.85 (m, 4H).

4.6.2. 1-Deuterium-1-(2-naphthyl) ethylene (5c′). ^1H NMR ($CDCl_3$): δ 5.33 (s, 1H), 5.86 (t, J=2.4 Hz, 1H), 7.41–7.48 (m, 2H), 7.63 (dd, J=8.8, 1.6 Hz, 1H), 7.74 (s, 1H), 7.78–7.82 (m, 3H).

4.6.3. 2-Vinyldibenzofuran[15] (5e). ^1H NMR ($CDCl_3$): δ 5.27 (d, J=10.8 Hz, 1H), 5.79 (d, J=13.6 Hz, 1H), 6.87 (dd, J=13.6, 10.8 Hz, 1H), 7.34 (t, J=7.6 Hz, 1H), 7.43–7.47 (m, 1H), 7.51–7.56 (m, 3H), 7.94 (d, J=7.6 Hz, 1H), 7.96 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 111.6, 111.7, 113.0, 118.3, 120.7, 122.8, 124.1, 124.5, 127.2, 132.7, 136.7, 155.9, 156.6. HRMS (EI) calcd for $C_{14}H_{10}O$: 194.0727. Found: m/z 194.0732 (M^+).

4.6.4. 2-Triphenylvinylsulfanylbenzothiazole (8). Mp 137–139 °C (pale yellow solid); ^1H NMR ($CDCl_3$): δ 7.02–7.05 (m, 2H), 7.07–7.13 (m, 6H), 7.22–7.24 (m, 1H), 7.26–7.31 (m, 3H), 7.34–7.37 (m, 1H), 7.38–7.43 (m,

2H), 7.45–7.47 (m, 2H), 7.66–7.69 (m, 1H), 7.79–7.82 (m, 1H); IR (KBr): ν=3377, 3050, 1489, 747 cm^{-1}. HRMS (EI) calcd for $C_{27}H_{19}NS_2$: 421.0959. Found: m/z 421.0973 (M^+).

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