Formation of Thioaldehyde Intermediates by Thermolysis of Sulfoxides Bearing Some Heteroaromatics

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Thermal reactions of phenacyl sulfoxide bearing heterocycles, such as a 2-benzothiazolyl or *N*-oxypyridyl group, in the presence of 2,3-dimethyl-1,3-butadiene afforded 6-benzoyl-5,6-dihydro-3,4-dimethyl-2*H*-thiapyran in good yield. This product is considered to be formed by the Diels−Alder reaction of a diene with thioaldehyde formed initially by the decomposition of sulfoxides.

Introduction

The thermolysis of alkyl sulfoxides having a β-hydrogen is well-known to form sulfenic acid and alkene through an Ei elimination mechanism.[1] Mislow and co-workers reported that thermolytic reactions of alkyl sulfoxides having no β-hydrogen, such as benzyl *p*-tolyl sulfoxide, afforded bibenzyl and *p*-tolylthiolsulfinate, and on the thermal reaction of an optically active sulfoxide the racemization of the sulfoxide was observed.[2] They also reported that the first step of this reaction is the homolytic cleavage of S−C (alkyl) of benzyl *p*-tolyl sulfoxide, and that no rearrangement of sulfoxide to a sulfenate ester was observed. Recently, Jenks and Guo have reported that photolytic reaction of benzyl *p*-tolyl sulfoxide afforded benzaldehyde, benzyl alcohol, mercaptotoluene, and tolyl disulfide as major products, and from the mechanistic study it was reported these products were formed through a benzyl *p*-tolylsulfenate intermediate arising from the initial photolytic rearrangement of the starting sulfoxide.[3] Furukawa and co-workers have also reported a similar intermediate in the photolysis of naphtho[1,8-*de*]dithiin monoxide.[4]

Recently, we have reported that the thermolytic reaction of phenacyl sulfoxide bearing heterocycles such as benzothiazole or *N*-oxypyridine, in the presence of 2,3-dimethyl-1,3-butadiene afforded 6-benzoyl-5,6-dihydro-3,4-dimethyl-2*H*-thiapyran and the hydroxy-substituted heterocycle in good yield.[5] The former product is considered to be formed by the Diels−Alder reaction of thioaldehyde formed by the 1,2-elimination of aryl phenacyl sulfenate generated by the rearrangement of the starting sulfoxide, which resulted in the cleavage of the S−C (aryl) bond and recombination of the C (aryl)−O (sulfoxide) bond.

Although a similar photolytic reaction has been reported in the carbonyl methyl cyclic sulfoxide system,[6] this reaction mode is the first example under a thermolytic condition and, thus, the studies of its scope and limitations are interesting.

Concerning the synthetic methods to generate rather labile thioaldehydes, a recent review[7] and many reports have already been published. For example, Vedejs et al. used a photochemical fragmentation of α-thioacetophenone derivatives to generate a variety of substituted thioaldehydes which were finally trapped as adducts with 1,3-diene derivatives.[8] Baldwin and Lopez studied the thermolysis of thiolsulfinates in which thioaldehydes were trapped as 9,10-dimethylanthracene adducts.[9] In a more convenient procedure, Kirby et al. demonstrated that base-promoted reaction of sulfenyl compounds, such as sulfenyl chloride,[10] *N*-thiophthalimide,[11] sodium thiosulfate *S*-ester,[12] and thiolsulfonate derivatives,[13] can be widely used for the generation of thioaldehydes.

To compare with these results and to gain further insight into this reaction, we studied the thermolytic reaction of various sulfoxides bearing heterocycles in the presence of dienes.

Results and Discussion

Thermal Reactions of Phenacyl Sulfoxides Having Heteroaromatics. Thermolytic reactions of phenacyl sulfoxides bearing aromatic or heteroaromatic groups in dioxane at 100 °C in the presence of 2,3-dimethyl-1,3-butadiene for 24 h were studied. The results are summarized in Table 1. In the case of phenacyl sulfoxide having an *N*-oxypyridyl group (**1a**), 6-benzoyl-5,6-dihydro-3,4-dimethyl-2*H*-thiapyran (**7a**) was obtained in 85%

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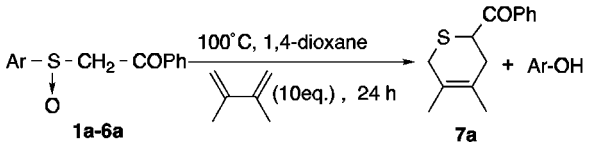
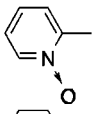
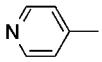
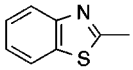
Table 1. The Reaction of Phenacyl Sulfoxide Bearing Heterocycle in the Presence of Dimethyl Butadiene



1a-6a 7a

entry	Ar		yield %[a] 7a	Ar-OH
1		**1a**	85	trace
2		**2a**	10	0
3		**3a**	19	trace
4		**4a**	26	0
5		**5a**	0	0
6		**6a**	73	83

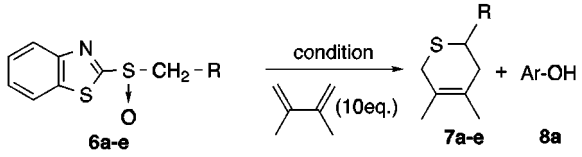
[a] isolated yield

yield, although the isolated yield of hydroxypyridine *N*-oxide was extremely low (entry 1). The reason for low yield is considered to be due to the polar nature of this product, as the NMR analysis of the crude reaction mixture indicated quantitative formation. In the cases of phenacyl sulfoxides bearing a 2-pyridyl (**2a**), 4-pyridyl (**3a**), and 2-pyrimidyl group (**4a**), **7a** was also obtained albeit in rather lower yields of 10, 19, and 26%, respectively (entries 2, 3, and 4), though other desired products, i.e., 2-hydroxy- and 4-hydroxypyridine and 2-hydroxypyrimidine were hardly obtained, or not isolated.

In the reaction of phenacyl sulfoxides attached to simple aromatics, e.g., a phenyl group, none of the desired product was formed; only the starting material and the corresponding sulfide in 15% yield were isolated. The reason phenyl phenacyl sulfoxide did not afford **7a** seemed to be the lower electron-withdrawing effect of the phenyl group compared with an *N*-oxypyridyl group. Therefore, the thermolytic reactions of phenacyl sulfoxides having electron-withdrawing groups on the phenyl ring such as *p*-nitrophenyl and 2,3,5,6-tetrafluorophenyl were studied. However, the thermolytic reactions of both *p*-nitrophenyl and 2,3,5,6-tetrafluorophenyl sulfoxides did not proceed at all, and the complete recovery of the starting material was observed. In contrast, the thermolysis of phenacyl sulfoxide having electron-rich heterocyclic rings, such as thiophene (**5a**), was also studied, but again resulted in complete recovery of the starting material (entry 5).

It seems clear that not only a simple electron-withdrawing effect but also the nitrogen-containing heterocyclic system play an important role to afford the product **7a** in this reaction. To study the effect of nitrogen-containing heterocycles other than pyridine, the thermolysis of 2-benzothiazolyl phenacyl sulfoxide (**6a**) was carried out under quite similar conditions (entry 6). In this case the desired product, dihydrothiapyran **7a**, was obtained in 73% yield together with 2-hydroxybenzothiazole (**8a**) in good isolated yield of 83%, probably

Table 2. Thermal Reaction of 2-Benzothiazolyl Sulfoxide Derivatives in the Presence of Dimethylbutadiene



6a-e 7a-e 8a

entry	R		condition	yield %[a] 7	8a
1	COPh	**6a**	in dioxane, 100°C,24h	73	83
2			in dioxane, 100°C,24h 20eq. BHT[b]	69	97
3			in MeOH, 100°C,24h	78	99
4	Ph	**6b**	in dioxane, 100°C,24h	0	0
5			in dioxane, 1.5eq. Et_3N 100°C, 24h	0	0
6	CN	**6c**	in dioxane, 100°C,24h	0	0
7			in dioxane, 1.5eq. Et_3N 100°C, 24h	0	0
8	COOEt	**6d**	in dioxane, 100°C,24h	0	0
9			in dioxane, 2eq. Et_3N 100°C, 24h	0	0
10	$COCH_3$	**6e**	in dioxane, 100°C,24h	0	0
11			in dioxane, 5eq. Et_3N 100°C, 24h	39	70

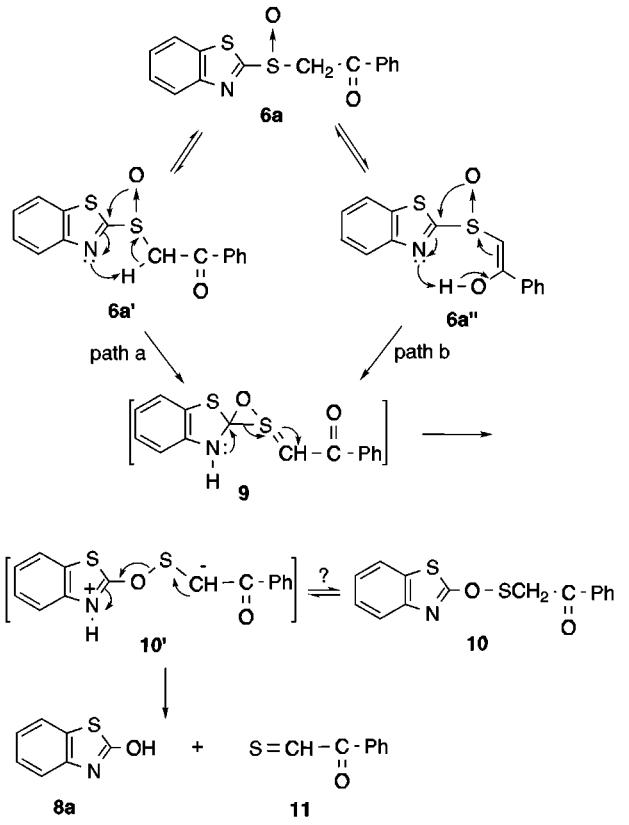
[a] isolated yield [b] 2,6-di-*tert*-butyl-4-methylphenol

because of the less polar nature of **8a** when compared to hydroxypyridine *N*-oxide. Therefore, various benzothiazolyl sulfoxide derivatives were prepared and used to obtain further mechanistic details of this thermolytic reaction.

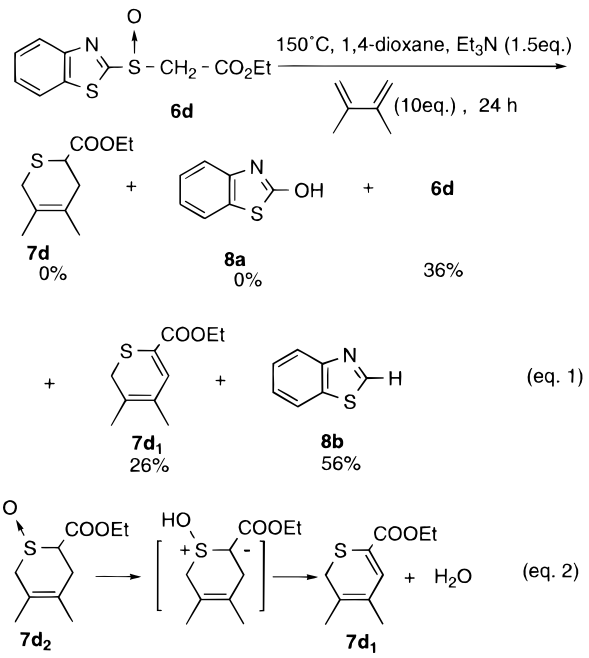
Thermal Reactions of Benzothiazolyl Sulfoxide Derivatives in the Presence of Diene and Base. Thermal reactions of benzyl-(**6b**), cyanomethyl-(**6c**), (ethoxycarbonyl)methyl-(**6d**), acetylmethyl-substituted sulfoxide (**6e**) having a 2-benzothiazolyl group under similar conditions in the presence of a diene were studied, and the results are summarized in Table 2. The compound **6b** did not show the desired reaction, giving complete recovery of starting material. Introduction of acidic α-hydrogens in the benzothiazolyl substituted sulfoxides, as in **6c**−**e**, unexpectedly, did not effect the thermal reaction, and hence resulted in the recovery of the starting material. One reason the thermolytic reactions of 2-benzothiazolyl sulfoxides in entries 8 and 10 did not proceed may be due to the relatively poor acidity of α-hydrogens when compared with benzoyl-substituted sulfoxide **6a**. In the case of **6c** the α-hydrogen acidity is expected to be stronger than that of **6a**; however, **6c** did not afford the desired product at all. This result suggests that not only the α-hydrogen acidity but also another factor is related to effect the reaction. One possibility is that the reaction is initiated from the enol **6a″** rather than keto form **6a′** as mentioned later.

To clarify this consideration, reactions with the diene in the presence of triethylamine were studied, expecting the effect of "an outer-base". In the cases of **6b**−**d**, the reactions still did not proceed at all (entries 5, 7, and 9), while, as expected, the reaction of acetylmethyl sulfoxide **6e** in the presence of 1.5 equiv of triethylamine afforded 6-acetyl-5,6-dihydro-3,4-dimethyl-2*H*-thiapyran (**7e**) and

Scheme 1



Scheme 2



8a in 39% and 70% yield, respectively (entry 11). A possible reason the reactions of sulfoxides **6b** and **6d** did not proceed is that triethylamine was not a strong enough base to afford the intermediate **9** and/or **10′** as shown in Scheme 1. The reaction of **6a** with a diene in the presence of the stronger base potassium *tert*-butoxide was then studied; however, in dioxane at 60 °C it afforded a complex mixture of products containing **8a** and benzothiazole (**8b**), in 38 and 20% yield, respectively.

The reaction of **6d** with 10 equiv of 2,3-dimethyl-1,3-butadiene in the presence of 1.5 equiv of triethylamine under more forcing conditions, i.e., at 150 °C, was also studied. (cf. eq 1 in Scheme 2.) Unexpectedly, 2-(ethoxycarbonyl)-2*H*-thiapyran (**7d$_1$**) and benzothiazole (**8b**) were formed in 26 and 56% yield, respectively, and **6d** was recovered in 36% yield; however, **6c** was still unreactive under these conditions. In this reaction, a different mechanism is obviously operating because of the complete lack of the products **7d** and **8a**. The product **7d$_1$** was considered to be formed via Pummerer rearrangement of the corresponding dihydrothiapyran *S*-oxide **7d$_2$** initially formed (cf. eq 2 in Scheme 2). The same reactions with similar compounds were reported by Zwanenburg and co-workers previously.[14] The concomitant formation of **8b** instead of **8a** also support the sulfine formation pathway in the thermolysis of **6d** under these conditions; however, the mechanism for the sulfine formation is not certain at present.

The reaction of 2-benzothiazolyl phenacyl sulfoxide (**6a**) in the presence of 20 equiv of 2,6-di-*tert*-butyl-4-methylphenol (BHT) was carried out in order to test the effect of the radical scavenger under similar conditions (entry 2). The reaction of **6a** in methanol (entry 3) was also studied. These results ruled out a radical mechanism as there was no significant effect of either additive or solvent on the product distribution.

Concerning the mechanism, the results in Tables 1 and 2 suggest the following: (i) In this reaction, a phenacyl group is necessary to provide highly enough acidic α-hydrogens (entries 1−4 and 6 in Table 1 and entries 1−3 in Table 2). (ii) A simple electron-withdrawing effect is not enough for this reaction to proceed as entry 6 in Table 2 demonstrates. (iii) An electron-rich aromatic ring, such as a thienyl group, is not effective for this reaction (entry 5 in Table 1). (iv) A 2-benzothiazole moiety is useful as well as an *N*-oxide moiety as a heterocyclic substituent. 2-Pyridyl and 2-pyrimidyl sulfoxides (entries 2 and 4 in Table 1) also lead to the desired products though the yields are rather poor. This result seems to indicate that these nitrogen-containing heteroaryl groups are related in the hydrogen abstraction step as internal bases forming a five- or six-membered cyclic transition state. However, even 4-pyridyl sulfoxide **3a** as in entry 3 in Table 1 was found to afford the desired product; hence, an intermolecular hydrogen abstraction mechanism is also involved. In fact, as already mentioned, the addition of triethylamine in the thermolysis increased the yield of the desired product as in entries 10 and 11 in Table 2.

The above considerations suggest a possible mechanism for the thermolytic reaction of phenacyl sulfoxides attached to heterocycles as illustrated in Scheme 1 using benzothiazole as the representative heterocycle. This involves the abstraction of an α-hydrogen atom (path a) or of a hydroxy-hydrogen after enolization (path b) by the nitrogen atom of the benzothiazolyl group to afford an intermediate **9**, by *ipso*-attacking of the oxygen atom of the sulfinyl group to the α-carbon of the benzothiazole ring. Path b would be more plausible despite the formation of seven-membered transition state **6a″** because of the complete recovery of the starting material in the case of cyanomethyl sulfoxide **6c** as already mentioned. Similar *ipso*-substitutions on the heteroaromatic rings with nucleophiles are widely accepted.[15] The

(14) Lenz, B. G.; Regeling, H.; van Rozendaal, H. L. M.; Zwanenburg, B. *J. Org. Chem.* **1985**, *50*, 2930.

Scheme 3

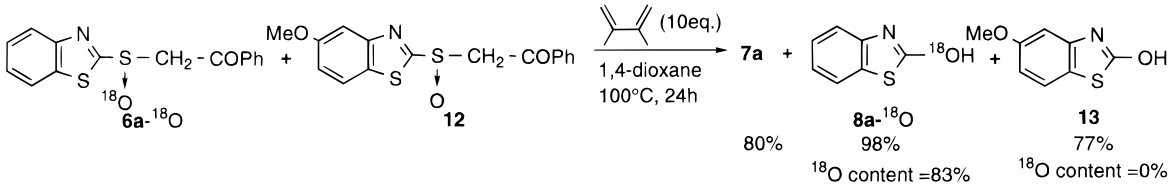
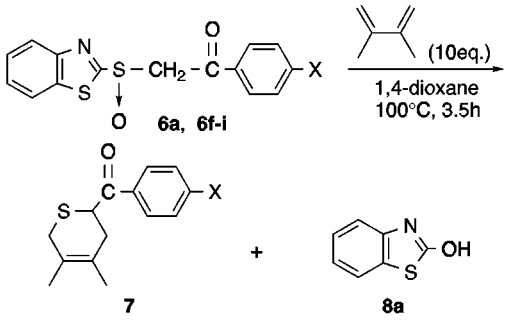


Table 3. Thermal Reaction of 2-Benzothiazolyl Substituted-Phenacyl Sulfoxides in the Presence of Diene



entry	X		conversion (%)	yield[a] % 7	8a
1	OCH_3	**6f**	31	28 (**7f**)	27
2	CH_3	**6g**	64	63 (**7g**)	60
3	H	**6a**	76	75 (**7a**)	73
4	Cl	**6h**	94	85 (**7h**)	79
5	NO_2	**6i**	100	89 (**7i**)	90

[a] yield from ^{1}H NMR spectrometry

cleavage between the S−O bond of sulfenate intermediate **10′** affords thioaldehyde **11** which is subsequently trapped as the cycloadduct, 6-benzoyl-5,6-dihydro-3,4-dimethyl-2*H*-thiapyran (**7a**), with 2,3-dimethyl-1,3-butadiene by the hetero Diels−Alder reaction.[16] The direct detection of a sulfenate ester intermediate in the case of **6a** was unsuccessfully attempted by ^{1}H NMR spectrometry, suggesting the rapid decomposition of the sulfenate ester intermediate **10′** to products.

The Effect of Substituents on the Phenyl Ring in the 2-Benzothiazolyl 4′-Substituted Phenacyl Sulfoxide. The effect of several substituents on the isolated yield was examined in the 2-benzothiazolyl sulfoxide system because of the difficulty of the determination of substituent effects by direct kinetic measurements. The results are summarized in Table 3. In the reaction of *p*-methoxy-substituted phenacyl sulfoxide (**6f**, entry 1) in dioxane at 100 °C for 3.5 h, conversion of the starting sulfoxide **6f** was observed as 31% with the recovery of the starting material, and methoxy-substituted products **7f** and **8a** were obtained in 28 and 27% yield, respectively, by NMR analysis. Under the same conditions, changing the phenyl substituent, to methyl (**6g**) and then hydrogen (**6a**) and further to chloro (**6h**) and nitro (**6i**) increased the conversion % of the thermolysis gradually to 64, 76, 94, and 100%, respectively. These results also suggest that a rather large substituent effect rules out the radical mechanism and the hydrogen abstraction step in Scheme 1 is rather important as already mentioned.

Crossover Experiment Using Sulfoxide (12) and ^{18}O Labeled-Sulfoxide (6a-^{18}O). In considering Scheme 1 as depicted, it is important to clarify the existence of equilibrium between the sulfenate intermediate **10′** and the starting sulfoxide and also to define the origin of the oxygen in the hydroxy heterocycles, such as **8a**, formed in this reaction. Therefore, the crossover reaction between methoxy-substituted benzothiazolyl phenacyl sulfoxide (**12**) and 2-benzothiazolyl phenacyl ^{18}O-sulfoxide (**6a**-^{18}O) was studied. **6a**-^{18}O was prepared by the reaction of the corresponding sulfide and *tert*-butyl hypochlorite in the presence of excess $H_2{}^{18}O$ (97 atom %).[17] The estimation of ^{18}O-content in this sulfoxide was not performed directly by mass spectrometry, because of the absence of the molecular ion peak of this sulfoxide in mass analysis. However, in the IR spectrum of this ^{18}O-labeled sulfoxide, the absorption band of S−O stretching vibration shifted completely to a lower wavenumber by 40 cm^{-1} than that of ^{16}O sulfoxide at 1020 cm^{-1}. From this difference of absorption band, the content of the ^{18}O atom of (**6a**-^{18}O) prepared was sufficiently high for the ^{18}O tracer experiment. The thermolytic reaction of a 1:1 mixture of **12** and **6a**-^{18}O under the usual conditions was carried out. The results are shown in Scheme 3. Dihydrothiapyran derivative **7a** and 2-hydroxybenzothiazole-^{18}O (**8a**-^{18}O) and 2-hydroxy-5-methoxybenzothiazole (**13**) were isolated using PLC eluting with ethyl acetate/hexane (1:5) in 80, 98, and 77% yield, respectively. The ^{18}O content of **8a** and **13** was found to be 83 and 0% by comparing the mass spectrum with those of products obtained in the reaction of unlabeled phenacyl sulfoxide. These results indicate clearly that the rearrangement of the corresponding sulfoxide to sulfenate intermediate **10′** takes place intramolecularly.

Experimental Section

All melting points were uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded using EI (E_a = 70 eV) ionization. The elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemical and Biochemical Engineering of Toyama University. All the reactions were monitored by TLC using Silica Gel 60 F_{254} TLC plates, and products were separated by column chromatography using Silica Gel 60 and also by preparative layer chromatography using 60 PF_{254} with UV detection. All reagents were of highest quality and were further purified by distillation or recrystallization. Solvents were further purified by general methods.

General Procedure for Preparation of Sulfoxides 1a−5a, 6a−i, 12. To a stirred solution of sulfide in $CHCl_3$ or CH_2Cl_2 was added *m*-CPBA (>70%) in $CHCl_3$ or CH_2Cl_2 at 0 °C. Addition of an equimolar amount of peracid calculated from the activity of the used *m*-CPBA resulted in the formation of sulfone; therefore, a ca. 30% less amount of the peracid was

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(17) Kobayashi, M.; Ohkubo, H.; Shimizu, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 503.

used, and the reaction mixture was stirred at 0 °C until the starting sulfide had disappeared by TLC monitoring. The reaction mixture was washed with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with $CHCl_3$. The combined organic layer was washed with brine and dried over $MgSO_4$. After evaporation of the solvent, the crude product was obtained. Purification of the sulfoxide was done by chromatography on silica gel and/or recrystallization.

N-Oxypyridyl Phenacyl Sulfoxide (1a). Spectral data: yield 27%: mp 126 °C (white crystals from EtOAc−hexane). ^{1}H NMR ($CDCl_3$) δ 4.56 (d, J = 14.0 Hz, 1H), 5.24 (d, J = 14 Hz, 1H), 7.44−7.61 (m, 5H), 7.81 (dd, J = 2.0, 8.0 Hz, 1H), 7.94−7.97 (m, 2H), 8.22−8.24 (m, 1H). ^{13}C NMR ($CDCl_3$) 57.8, 124.6, 126.9, 127.2, 128.7, 128.7, 134.0, 136.2, 139.1, 153.0, 190.9. IR (KBr) 1670, 1050 cm^{-1}. Anal. Calcd for $C_{13}H_{11}NO_3S$: C, 59.76; H, 4.24; N, 5.36%. Found: C, 59.56; H, 4.26; N, 5.18%.

2-Pyridyl Phenacyl Sulfoxide (2a). Spectral data: yield 66%: mp 92 °C (white crystals from EtOAc−hexane). ^{1}H NMR ($CDCl_3$) δ 4.44 (d, J = 14 Hz, 1H), 4.78 (d, J = 14 Hz, 1H), 7.36−7.47 (m, 3H), 7.55−7.61 (m, 1H), 7.89−8.00 (m, 4H), 8.60−8.63 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 62.6, 120.4, 124.9, 128.6, 133.9, 136.0, 138.0, 149.5, 163.6, 191.2. IR (neat) 1680, 1050 cm^{-1}. Anal. Calcd for $C_{13}H_{11}NO_2S$: C, 63.66; H, 4.52; N, 5.71%. Found: C, 64.02; H, 4.48; N, 5.67%.

4-Pyridyl Phenacyl Sulfoxide (3a). Spectral data: yield 41%: mp 114−118 °C (white crystals from EtOAc−hexane) dec. ^{1}H NMR ($CDCl_3$) δ 4.39 (dd, J = 0.8, 14.8 Hz, 1H), 4.60 (dd, J = 0.8, 14.8 Hz, 1H), 7.47−7.50 (m, 2H), 7.61−7.65 (m, 2H), 7.87−7.99 (m, 3H), 8.78−8.79 (m,2H). ^{13}C NMR ($CDCl_3$) δ 65.5, 118.5, 128.7, 128.9, 134.5, 135.5, 150.5, 153.8, 190.9. IR (neat) 1660, 1040 cm^{-1}. Anal. Calcd for $C_{13}H_{11}NO_2S$: C, 63.66; H, 4.52; N, 5.71%. Found: C, 63.70; H, 4.52; N, 5.70%.

2-Pyrimidyl Phenacyl Sulfoxide (4a). Spectral data: 44%: mp 114−119 °C (white crystals from EtOAc−hexane) dec. ^{1}H NMR ($CDCl_3$) δ 4.67 (d, J = 15.0 Hz, 1H), 4.88 (d, J = 15.0 Hz, 1H), 7.28−7.58 (m, 3H), 7.59−7.60 (m, 1H), 7.93−7.95 (m, 2H), 8.89 (d, J = 4.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 61.5, 121.9, 128.7, 134.0, 135.9, 158.5, 172.6, 191.2. IR (KBr) 1680, 1070 cm^{-1}. Anal. Calcd for $C_{12}H_{10}N_2O_2S$: C, 58.52; H, 4.09; N, 11.37%. Found: C, 58.65; H, 4.10; N, 11.19%.

2-Thienyl Phenacyl Sulfoxide (5a). Spectral data: yield 49%: mp 87 °C (white crystals from EtOAc−hexane). ^{1}H NMR($CDCl_3$) δ 4.53 (dd, J = 0.8, 14.8 Hz, 1H), 4.83 (dd, J = 0.8, 14.8 Hz, 1H), 7.08−7.10 (m, 1H), 7.47−7.50 (m, 3H), 7.59−7.66 (m, 2H), 7.90−7.92 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 66.9, 127.5, 128.7, 128.9, 130.0, 131.5, 134.3, 135.7, 145.2, 191.2. IR (KBr) 1670, 1040 cm^{-1}. Anal. Calcd for $C_{12}H_{10}O_2S_2$: C, 57.58; H, 4.03%. Found: C, 57.78; H, 4.02%.

2-Benzothiazolyl Phenacyl Sulfoxide (6a). Spectral data: yield 33%: mp 117−120 °C (white crystals from EtOAc−hexane) dec. ^{1}H NMR ($CDCl_3$) δ 4.80 (d, J = 14.8 Hz, 1H), 4.90 (d, J = 14.8 Hz, 1H), 7.26−7.63 (m, 5H), 7.94−7.96 (m, 2H), 8.00−8.02 (m, 1H), 8.05−8.08 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 65.3, 122.3, 124.1, 126.4, 127.0, 128.8, 128.9, 134.4, 135.6, 136.3, 153.7 176.5, 190.5. IR (KBr) 1670, 1060 cm^{-1}. Anal. Calcd for $C_{15}H_{11}NO_2S_2$: C, 59.78; H, 3.68; N, 4.65%. Found: C, 59.98; H, 3.68; N, 4.54%.

2-Benzothiazolyl Benzyl Sulfoxide (6b). Spectral data: yield 57%: mp 123 °C (white crystals from EtOAc−hexane). ^{1}H NMR ($CDCl_3$) δ 4.34 (d, J = 13 Hz, 1H), 4.52 (d, J = 13 Hz, 1H), 7.16−7.31 (m, 5H), 7.46−7.60 (m, 2H), 7.93−7.95 (m, 1H), 8.09−8.11 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 62.8, 122.2, 123.9, 126.1, 126.9, 128.3, 128.7, 130.4, 133.7, 136.0, 153.7. IR (KBr) 1050 cm^{-1}. Anal. Calcd for $C_{14}H_{11}NOS_2$: C, 61.51; H, 4.06; N, 5.12%. Found: C, 61.89; H, 4.19; N, 5.04%.

2-Benzothiazolyl Cyanomethyl Sulfoxide (6c). Spectral data: yield 77%: mp 138 °C (white crystals from EtOAc−hexane). ^{1}H NMR ($CDCl_3$) δ 4.11 (d, J = 16.4 Hz, 1H), 4.31 (d, J = 16.4 Hz, 1H), 7.53−7.64 (m, 2H), 8.03−8.05 (m,1H), 8.10−8.12 (m,1H). ^{13}C NMR ($CDCl_3$) δ 44.2, 110.3, 122.5, 124.4, 126.9, 127.4, 136.3, 153.5, 173.4. IR (KBr) 2225, 1060 cm^{-1}. Anal. Calcd for $C_9H_6NOS_2$: C, 48.63; H, 2.72; N, 12.60%. Found: C, 48.58; H, 2.67; N, 12.43%.

2-Benzothiazolyl (Ethoxycarbonyl)methyl Sulfoxide (6d). Spectral data: yield 77%: mp 59 °C (white crystals from CH_2Cl_2−hexane). ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 7.2 Hz, 3H), 4.12 (d, J = 14.4 Hz, 1H), 4.24 (d, J = 14.4 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 7.49−7.60 (m, 4H), 8.00−8.03 (m, 2H), 8.06−8.08 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 14.0, 60.6, 62.5, 122.3, 124.1, 126.5, 127.1, 136.2, 153.6, 164.0, 175.9. IR (KBr) 1720, 1060 cm^{-1}. Anal. Calcd for $C_{11}H_{11}NO_3S_2$: C, 49.05; H, 4.12; N, 5.20%. Found: C, 48.79; H, 3.99; N, 5.01%.

2-Benzothiazolyl Acetylmethyl Sulfoxide (6e). Spectral data: yield 76%: mp 127 °C (white crystals from EtOAc−hexane). ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 3H), 4.21 (d, J = 14.8 Hz, 1H), 4.36 (d, J = 14.8 Hz, 1H) 7.50−7.61 (m, 2H), 8.00−8.02 (m, 1H), 8.06−8.09 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 31.7, 67.7, 122.3, 124.1, 126.5, 127.1, 136.2, 153.7, 175.9, 198.0. IR (KBr) 1710, 1050 cm^{-1}. Anal. Calcd for $C_{10}H_9NO_2S_2$: C, 50.19; H, 3.79; N, 5.85%. Found: C, 50.36; H, 3.80; N, 5.85%.

2-Benzothiazolyl 4′-Methoxyphenacyl Sulfoxide (6f). Spectral data: yield 64%: mp 143 °C (white crystals from EtOAc−hexane). ^{1}H NMR ($CDCl_3$) δ 3.87 (s, 3H), 4.75 (d, J = 15.2 Hz, 1H), 4.84 (d, J = 15.2 Hz, 1H), 6.91−6.94 (m, 2H), 7.50 (dt, J = 1.2, 8.0 Hz, 1H), 7.57 (dt, J = 1.6, 7.6 Hz, 1H), 7.90−7.94 (m, 2H), 7.99−8.02 (m, 1H), 8.06−8.08 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 55.61, 65.24, 114.1, 122.3, 124.1, 126.3, 127.0, 128.7, 131.3, 136.3, 153.7, 164.6, 176.7, 188.8. IR (KBr) 1650, 1580, 1050 cm^{-1}. Anal. Calcd for $C_{16}H_{13}NO_3S_2$: C, 57.99; H, 3.95; N, 4.23%. Found: C, 57.97; H, 4.00; N, 4.11%.

2-Benzothiazolyl 4′-Methylphenacyl Sulfoxide (6g). Spectral data: yield 57%: mp 147.5−153.3 °C (white crystals from EtOAc−hexane) dec. ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 3H), 4.77 (d, J = 15.1 Hz, 1H), 4.87 (d, J = 15.1 Hz, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.50 (dt, J = 0.8, 8.4 Hz, 1H), 7.58 (dt, J = 1.2, 7.2 Hz, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.99−8.02 (m, 1H), 8.06−8.08 (m, 1H), 7.99−8.02 (m, 1H), 8.06−8.08 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 21.8, 65.4, 122.3, 124.1, 126.3, 127.0, 128.9, 129.6, 133.2, 136.3, 145.7, 153.7, 190.1. IR (KBr) 1650, 1290, 1050 cm^{-1}. Anal. Calcd for $C_{16}H_{13}NO_2S_2$: C, 60.93; H, 4.15; N, 4.44%. Found: C, 60.47; H, 4.15; N, 4.20%.

2-Benzothiazolyl 4′-Chlorophenacyl Sulfoxide (6h). Spectral data: yield 70%: mp 152−158 °C (white crystals from EtOAc−hexane) dec. ^{1}H NMR ($CDCl_3$) δ 4.76 (d, J = 14.9 Hz, 1H), 4.86 (d, J = 14.9 Hz, 1H), 7.42−7.46 (m, 2H), 7.51 (dt, J = 1.2, 8.0 Hz, 1H), 7.58 (dt, J = 0.8, 7.2 Hz, 1H), 7.87−7.90 (m, 2H), 7.99−8.02 (m, 1H), 8.05−8.07 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 64.9, 122.3, 124.1, 126.5, 127.1, 129.3, 130.2, 134.0, 136.2, 141.1, 153.6, 176.1, 189.4. IR (KBr) 1660, 1060 cm^{-1}. Anal. Calcd for $C_{15}H_{10}ClNO_2S_2$: C, 53.64; H, 3.00; N, 4.17%. Found: C, 53.02; H, 3.03; N, 3.95%.

2-Benzothiazolyl 4′-Nitrophenacyl Sulfoxide (6i). Spectral data: yield 57%: mp 177−181 °C (white crystals from EtOAc−hexane) dec. ^{1}H NMR ($CDCl_3$) δ 4.83 (d, J = 14.8 Hz, 1H), 4.94 (d, J = 14.8 Hz, 1H), 7.05−7.40 (m, 2H), 7.46−7.71 (m, 1H) 8.00−8.12 (m, 3H), 8.18−8.38 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 64.6, 122.4, 124.0, 124.1, 126.7, 127.3, 129.9, 136.2, 140.6, 150.8, 153.6, 175.4, 189.3. IR (KBr) 1680, 1520, 1350, 1050 cm^{-1}. Anal. Calcd for $C_{15}H_{10}N_2O_4S_2$: C, 52.04; H, 2.91; N, 8.08%. Found: C, 52.07; H, 2.92; N, 7.95%.

5-Methoxy-2-benzothiazolyl Phenacyl Sulfoxide (12). Spectral data: yield 90%: mp 143 °C (white crystals from EtOAc−hexane). ^{1}H NMR($CDCl_3$) δ 3.91 (s, 3H), 4.78 (d, J = 15.2 Hz, 1H), 4.71 (d, J = 15.2 Hz, 1H), 7.15 (dd, J = 2.4, 8.8 Hz, 1H), 7.46−7.51 (m, 3H), 7.62 (t, J = 7.6 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.94−7.96 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 55.7, 65.3, 105.8, 117.1, 122.5, 128.3, 128.8, 128.9, 134.4, 135.6, 155.1, 159.5, 190.6. IR (KBr) 1670, 1050 cm^{-1}. Anal. Calcd for $C_{16}H_{13}NO_3S_2$: C, 57.99; H, 3.95; N, 4.23%. Found: C, 58.05; H, 4.03; N, 4.26%.

2-Benzothiazolyl Phenacyl ^{18}O-Sulfoxide (6a-^{18}O). To a stirred solution of 100 mg of 2-benzothiazolyl phenacyl sulfoxide (0.33 mmol) and 0.12 mL (6.6 mmol) of H_2O-^{18}O (97%) in 3 mL of CH_3CN was added 0.043 mL of *tert*-BuOCl (0.38 mmol) at 0 °C. After stirring for 10 min at 0 °C, this mixture was evaporated, and the residual product was rinsed with ether to afford a white product. This product was recrystallized from CH_2Cl_2−hexane to afford 35 mg of the pure **6a**-^{18}O in 33% yield as white crystals: ^{1}H NMR ($CDCl_3$) δ 4.80 (d, J = 14.8, 1H), 4.90 (d, J = 14.8, 1H), 7.26−7.63 (m, 5H), 7.94−7.96 (m, 2H), 8.00−8.02 (m, 1H), 8.05−8.08 (m, 1H). ^{13}C NMR

($CDCl_3$) δ 65.3, 122.3, 124.1, 126.4, 127.1, 128.8, 128.9, 134.4, 135.6, 136.3, 153.7, 176.5, 190.48. IR (KBr) 1670, 1020 cm^{-1}.

General Procedure of Thermolytic Reaction of Sulfoxide 1a−6a in the Presence of 2,3-Dimethyl-1,3-butadiene. A 100 mg amount of the starting sulfoxide was dissolved in 3 mL of dioxane, and into this solution was added freshly distilled 2,3-dimethyl-1,3-butadiene. This mixture in a 10-mL Pyrex tube was degassed thoroughly in vacuo at dry ice−acetone temperature, and the glass tube was sealed. The mixture was heated at 100 °C for 24 h and was chromatographed on a silica gel preparative plate using EtOAc−hexane as eluent.

Thermolysis of N-Oxypyridyl Phenacyl Sulfoxide (1a) in the Presence of Diene. The reaction mixture was purified on silica gel preparative plate using EtOAc−hexane (1:1) as eluent to afford 75.8 mg of **7a** (85%). Spectral data of **7a**: ^1H NMR ($CDCl_3$) δ 1.74 (s, 6H), 2.41−2.57 (m, 2H), 2.99 (s, 2H), 4.49 (m, 1H), 7.43−7.47 (m, 2H), 7.53−7.57 (m, 1H), 7.98−8.01 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 19.5, 20.1, 29.8, 32.7, 41.8, 122.6, 126.3, 128.5, 128.6, 133.0, 135.2, 195.6. IR (neat) 2900, 1670 cm^{-1}. Anal. Calcd for $C_{14}H_{16}OS$: C, 72.37; H, 6.94%. Found: C, 72.28; H, 7.14%.

Thermolysis of 2a. The reaction mixture was chromatographed on silica gel preparative plate using EtOAc−hexane (1:1) as eluent to afford 10 mg of **7a** (10%) and 23 mg of 2-pyridyl phenacyl sulfide (24%).

Thermolysis of 3a. The reaction mixture was chromatographed on silica gel preparative plate using EtOAc−hexane (1:1) as eluent to afford 13 mg of **7a** (19%) and 39 mg of 4-pyridyl phenacyl sulfide (58%).

Thermolysis of 4a. The reaction mixture was chromatographed on silica gel preparative plate using EtOAc−hexane (1:5) as eluent to afford 20 mg of **7a** and 23 mg of 2-pyrimidyl phenacyl sulfide in 26% and 14% yield, respectively.

Thermolysis of 6a. The reaction mixture was chromatographed on silica gel preparative plate using EtOAc−hexane (1:5) as eluent to afford 57 mg of **7a** (73%) and 42 mg of 2-hydroxybenzothiazole (**8a**) (83%). Spectral data of **8a**: ^1H NMR ($CDCl_3$): δ 7.14−7.18 (m, 2H), 7.26−7.31 (m, 1H), 7.40−7.42 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 111.7, 122.5, 123.3, 123.9, 126.5, 135.3, 172.9. IR (KBr) 3300−2400, 1640 cm^{-1}.

Thermolysis of 6e in the Presence of Diene and NEt_3. To 1.5 mL of 1,4-dioxane was added 100 mg of **6e** (0.418 mmol), and into this solution were added freshly distilled 2,3-dimethyl-1,3-butadiene (471 μL, 10 equiv) and 87 μL of triethylamine (1.5 equiv). This mixture in a 10-mL Pyrex tube was degassed thoroughly in vacuo at dry ice−acetone temperature, and the glass tube was sealed. Then the mixture was heated at 100 °C for 24 h. The reaction mixture was chromatographed on silica gel preparative plate using EtOAc−hexane (1:5) as eluent to afford 28 mg of 6-acetyl-5,6-dihydro-3,4-dimethyl-2*H*-thiapyran (**7e**) (39%), 40 mg of **8a** (70%), and 22 mg of 2-benzothiazolyl acetylmethyl sulfide (23%). Spectral data of **7e**: ^1H NMR ($CDCl_3$) δ 1.70 (s, 6H), 2.28−2.43 (m, 5H), 2.94 (s, 2H), 3.59 (t, J = 6.0 Hz, 1H). IR (neat) 3300−2400, 1640 cm^{-1}. HRMS Calcd for $C_9H_{14}OS$: 170.0765. Found: 170.0761.

Thermolysis of 2-Benzothiazolyl (Ethoxycarbonyl)-methyl Sulfoxide (6d) in the Presence of Diene and Base at 150 °C. To 3 mL of 1,4-dioxane was added 100 mg of **6d** (0.37 mmol), and into this solution were added freshly distilled 2,3-dimethyl-1,3-butadiene (0.42 mL, 10 equiv) and 77 μL of triethylamine (0.556 mmol). This mixture in a 10-mL Pyrex tube was degassed thoroughly in vacuo at dry ice−acetone temperature, and the glass tube was sealed. Then the mixture was heated at 150 °C for 24 h. The reaction mixture was chromatographed on silica gel preparative plate using EtOAc−hexane (1:5) as eluent to afford 19 mg of **7d$_1$** (26%), 28 mg of **7b** (56%) and 36% recovery of the starting material.

Spectral data of **7d$_1$**: ^1H NMR ($CDCl_3$) δ 1.32 (t, J = 7.0 Hz, 3H), 1.84 (s, 3H), 1.92 (s, 3H), 3.22 (s, 2H), 4.27 (q, J = 7.0 Hz, 2H), 7.09 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 14.2, 17.3, 19.9, 31.6, 61.2, 124.1, 125.9, 127.6, 135.4, 164.9. IR (neat) 1730 cm^{-1}.

Spectral data of **8b**: ^1H NMR ($CDCl_3$): δ 7.20−7.53 (m, 2H), 7.67,−8.10 (m, 2H), 8.80 (s, CH, 1H). IR (neat) 1450, 1420, 870 cm^{-1}.

Thermolysis of 2-Benzothiazolyl Phenacyl Sulfoxide (6a) in the Presence of Diene and BHT. To 3 mL of 1,4-dioxane was added 100 mg of **6a** (0.335 mmol), and into this solution were added freshly distilled 2,3-dimethyl-1,3-butadiene (10 equiv) and 2,6-di-*tert*-butyl-4-methylphenol (20 equiv). This mixture in a 10-mL Pyrex tube was degassed thoroughly in vacuo at dry ice−acetone temperature, and the glass tube was sealed. Then the mixture was heated at 100 °C for 24 h. The reaction mixture was chromatographed on silica gel preparative plate using EtOAc−hexane (1:5) as eluent to afford 53 mg of **7a** (69%) and 48 mg of **8a** (97%).

The Effect of Substituents on the Phenyl Ring in the 2-Benzothiazolyl 4′-Substituted Phenacyl Sulfoxide. To 1 mL of 1,4-dioxane was added 20 mg of 2-benzothiazolyl 4′-substituted-phenacyl sulfoxide, and into this solution was added 2,3-dimethyl-1,3-butadiene (10 equiv) freshly distilled. This mixture in a 10-mL Pyrex tube was degassed thoroughly in vacuo at dry ice−acetone temperature, and the glass tube was sealed. Then the mixture was heated at 100 °C for 3.5 h. The solvent of this reaction mixture was evaporated and dried thoroughly in vacuo. The yields of products and recovery of the starting sulfoxide were found from the NMR spectrometry of this residue. The assignment of cycloadduct **7f**−**i** was easily performed by the comparison of the spectra of **7a**.

Spectral data of **7f**: yield 28%. ^1H NMR ($CDCl_3$) δ 1.75 (s, 6H), 2.39−2.59 (m, 2H), 2.99 (d, J = 15.6 Hz, 1H), 3.07 (d, J = 15.6 Hz, 1H), 3.87 (s, 3H), 2.46 (dd, J = 5.2, 6.0 Hz, 1H), 6.94 (d, J = 8.9 Hz, 2H), 7.99 (d, J = 8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 19.6, 20.2, 30.3, 33.1, 41.9, 55.5, 113.7, 122.7, 126.6, 128.1, 131.0, 163.5, 194.7. IR (neat) 3000−2900, 1670, 1600 cm^{-1}.

Spectral data of **7g**: yield 63%. ^1H NMR ($CDCl_3$) δ 1.74 (s, 6H), 2.35−2.08 (m, 5H), 2.74−3.08 (m, 2H), 4.55 (t, J = 5.5 Hz, 1H),7.22 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 19.6, 20.1, 21.6, 30.1, 32.9, 42.1, 122.7, 126.5, 128.8, 129.3, 132.7, 143.9, 195.6. IR (neat) 3000−2900, 1670, 1600, 1030 cm^{-1}.

Spectral data of **7h**: yield 85%. ^1H NMR ($CDCl_3$) δ 1.75 (s, 6H), 2.41−2.56 (m, 2H), 3.00 (bs, 2H), 4.26 (t, J = 5.4 Hz, 1H),7.43 (d, J = 8.9 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 19.6, 20.1, 29.8, 32.4, 41.7, 122.6, 126.2, 128.8, 130.1, 133.5, 139.4, 194.4. IR (neat) 3000−2950, 1680, 1090 cm^{-1}.

Spectral data of **7i**: yield 89%. ^1H NMR ($CDCl_3$) δ 1.76 (s, 3H), 1.78 (s, 3H), 2.52 (bs, 2H), 2.94 (s, 2H), 4.46 (t, J = 5.4 Hz, 1H), 8.14 (d, J = 8.8 Hz, 2H), 8.31 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 19.6, 20.1, 29.3, 31.8, 41.7, 122.4, 123.7, 125.9, 129.7, 140.1, 150.1, 193.3. IR (neat) 2950−3000, 1690, 1350 cm^{-1}.

Crossover Experiment between 5-Methoxy-Substituted-Benzothiazolyl Phenacyl Sulfoxide (12) and 2-Benzothiazolyl Phenacyl ^{18}O-Sulfoxide (6a-^{18}O) in the Presence of Diene. To 1.8 mL of 1,4-dioxane were added 33 mg of **12** (0.1 mmol) and 29 mg of **6a**-^{18}O (0.095 mmol), and into this solution was added freshly distilled 2,3-dimethyl-1,3-butadiene (10 equiv). This mixture in a 10-mL Pyrex tube was degassed thoroughly in vacuo at dry ice−acetone temperature, and the glass tube was sealed. Then the mixture was heated at 100 °C for 1 h. The reaction mixture was chromatographed on silica gel preparative plate using EtOAc−hexane (1:5) as eluent to afford 35 mg of **7a** (76%) and 14 mg of **8a**-^{18}O (98%) and **13** (77%). The ratio of the parent peak and parent peak plus 2 of **8a**-^{18}O (M = 151) and **13** (M = 165) in mass spectra is 0.19 and 14.8. On the other hand, in the control experiments using the unlabeled sulfoxide **6a** and **12** the ratio of M^+ and $M^+ + 2$ of both **8a** and **13** is 14.8. Therefore, ^{18}O content of **13** obtained in the crossover experiment was found to be 0%, and for **8a**-^{18}O it was calculated to be 83%.

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