Novel Type Elimination Reactions of Sulfoxides Bearing Several Heteroaromatics: Trapping of Sulfines with 2,3-Dimethyl-1,3-butadiene

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Previously we reported the novel thioaldehydes generation via thermolyses of phenacyl sulfoxides bearing some heteroaromatics. Thermolysis of sulfoxides (**1a**,**b** and **2a**−**4a**) bearing other heterocycles such as thiadiazole, triazole, and tetrazole in the presence of 2,3-dimethyl-1,3-butadiene in dioxane at 100 °C led to the unexpected products 6-substituted-5,6-dihydro-3,4-dimethyl-2*H*-thiapyran 1-oxide (**5a**,**b**). These products were considered to be formed by the Diels−Alder reaction of the diene with the sulfines formed initially by the thermal decomposition of the sulfoxides. The rate acceleration and the improvement of the yield by addition of 1.5 equiv of triethylamine, especially in the case of ethoxycabonylmethyl sulfoxide **1c**, was observed. The *cis*−*trans* selectivity for sulfine cycloadducts was also studied by NMR spectrometry. The reactions of α-substituted phenacyl sulfoxides **1d**−**f** bearing a phenyl-substituted tetrazolyl group in the presence of the same diene were also studied.

Introduction

Recently, we have reported that the thermolytic reaction of phenacyl sulfoxide bearing a heterocycle such as the 2-*N*-oxypyridyl, 2-pyridyl, 4-pyridyl, or 2-benzothiazolyl group in the presence of 2,3-dimethyl-1,3-butadiene at 100 °C for 24 h afforded 6-benzoyl-5,6-dihydro-3,4-dimethyl-2*H*-thiapyran.[1] This product was considered to be formed by the hetero Diels−Alder reaction of the diene with the thioaldehyde, which was probably formed by elimination of the sulfenate ester intermediate generated by rearrangement of the starting sulfoxide. To gain further details and limitations of this reaction, the thermolytic reactions of phenacyl sulfoxide derivatives bearing another heterocycle, the 5-(1-phenyl)tetrazolyl group, under the same conditions were studied. The products in the case of the thermal reaction of 5-(1-phenyl)-1,2,3,4-tetrazolyl phenacyl sulfoxide (**1a**) in the presence of 2,3-dimethyl-1,3-butadiene at 100 °C for 3 h were 1-phenyl-1,2,3,4-tetrazole (**6**) and 6-benzoyl-5,6-dihydro-3,4-dimethyl-2*H*-thiapyran 1-oxide (**5a**), in contrast to the previous results.[1] The product **5a** is considered to be formed by the Diels−Alder reaction of sulfine and butadiene.[2]

Sulfines are generally formed by the oxidation of thioketones[3] or the elimination reactions of sulfinyl halide derivatives.[4] Therefore, the facile direct formation of sulfine under mild thermal conditions from β-ketosulfoxides is interesting from the synthetic and mechanistic aspect, and hence, we synthesized several β-ketosulfoxides and further studied their behavior under similar conditions.

Results and Discussions

Reaction of Phenacyl Sulfoxides 1a−4a Bearing Heteroaromatics with 2,3-Dimethyl-1,3-butadiene. Thermolytic reactions of phenacyl sulfoxides having 1-phenyltetrazolyl, 1-methyltetrazolyl, 2-methylthiadiazolyl, and 4-methyl-1,2,4-triazolyl groups were carried out in dioxane at 100 °C for 3 h in the presence of 2,3-dimethyl-1,3-butadiene. The results are summarized in Table 1. The thermolytic reaction of 5-(1-phenyl)-1,2,3,4-tetrazolyl phenacyl sulfoxide (**1a**) in the presence of diene afforded 6-benzoyl-5,6-dihydro-3,4-dimethyl-2*H*-thiapyran 1-oxide (**5a**) and 1-phenyl-1,2,3,4-tetrazole (**6**) in quantitative and 60% yields, respectively (entry 1). In the case of 5-(1-methyl)-1,2,3,4-tetrazolyl phenacyl sulfoxide (**2a**), the reaction also afforded **5a** and 1-methyl-1,2,3,4-tetrazole (**7**) in quantitative yields (entry 2). The reaction of 5-(2-methyl)-1,3,4-thiadiazolyl phenacyl sulfoxide (**3a**) afforded **5a** and 2-methyl-1,3,4-thiadiazole (**8**) in rather poor yields of 20 and 30%, respectively (entry 3). This reaction for 16 h afforded the corresponding products in quantitative yields (entry 4). In the case of 3-(4-methyl)-1,2,4-triazolyl phenacyl sulfoxide (**4a**), **5a** and 4-methyl-1,2,4-triazole (**9**) were obtained quantitatively (entry 5). The yields of these reactions were

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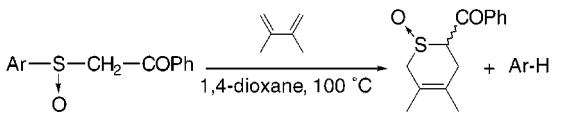
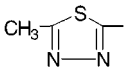
Table 1. Thermolysis of Phenacyl Sulfoxide Bearing Heteroaromatics in the Presence of 10 equiv of Butadiene in Dioxane at 100 °C



1a–4a **5a** **6–9**

entry	Ar		reaction time	yield % **5a** (*cis*:*trans*)	**6–9**
1		**1a**	3 h	99 (1:5)[a]	60[a]
2		**2a**	3 h	99 (1:3.7)[b]	99[b]
3		**3a**	3 h	20 (only *trans*)[b,c]	30[b,c]
4			16 h	99 (1:30.0)[b]	99[b]
5		**4a**	3 h	99 (2.1:1)[b]	99[b]

[a] isolated yield (reactions were not optimized).
[b] calculated yield from NMR analysis of the reaction mixture.
[c] 70% of the starting material was recovered.

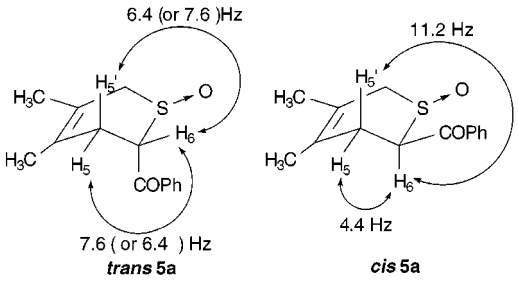


Figure 1. Coupling constants between H-5 and H-6 of cis and trans **5a**.

determined by NMR spectrometry of the reaction mixture directly. Compound **5a** has two stereoisomers, *cis* and *trans* forms, which are incidentally separable by recrystallization; *cis* **5a** was obtained as a pure form by repeated recrystallization from benzene, while *trans* **5a** was only obtained as a syrup, which contained a slight amount of *cis* isomer **5a** (approximately less than 5%). The relative stereochemistry of *cis* and *trans* **5a** was established by vicinal $^1H-^1H$ coupling constants. H-6 of *trans* **5a** exhibits a rather small coupling as $J = 7.6$ and 6.4 Hz to either of H-5 and H-5′, respectively, implying that the dihedral angles between H-6 and H-5 and between H-6 and H-5′ are both around 40−60°; these two coupling constants mean obviously that the relationship between the methyne proton at C-6 and the sulfinyl group is *cis* (cf. left side of Figure 1). In contrast to *trans* **5a**, a set of large coupling ($J = 11.2$ Hz) and rather small coupling ($J = 4.4$ Hz) in the NMR spectrum of *cis* **5a** revealed the *trans* relationship between the methyne proton at C-6 and the sulfinyl group, indicating that the former large value and the latter small value are due to the difference in the two dihedral angles (ca. 150° and 60°, respectively, estimated by the molecular model study) between H-6 and H-5 and H-6 and H-5′, respectively (cf. right side of Figure 1). The *cis* isomer of **5b** was also purified by repeated recrystallization from benzene; however, the *trans* isomer could not be obtained in a pure form and was shown to contain ca. 40% of *cis* **5b** by NMR spectrometry. The determination of *cis* **5b** was easily performed by the comparison of the spectra of *cis* and *trans* **5a**, while assignment of *trans* **5b** was possible by subtraction of the signals of the pure *cis* isomer from the spectrum of the impure sample. In the case of **5c**, both *cis* and *trans* isomers could not be obtained as pure material. Therefore, assignment of the *cis* and *trans* isomers was established by comparing the NMR spectra of pure *cis* and *trans* **5a** and an $^1H-^1H$ COSY experiment of this mixture. In the COSY spectrum the set of correlation peaks facilitated finding the set of peaks of both *cis* and *trans* **5c**, and finally the ratio determination of *cis* and *trans* isomers was performed by the integration of both C-6 protons. Thus, the *cis*−*trans* ratio of **5a** obtained in each entry was found to be 1:5 in entry 1, 1:3.7 in entry 2, 1:30.0 in entry 4, and 2.1:1 in entry 5 by NMR spectrometry (cf. Table 1).[5]

In general, sulfines are known to have two geometrical isomers, i.e., *E* and *Z*,[6] with a significant barrier of interconversion between them.[7] The preferred retention of configuration of the starting sulfines is also known to be common during the formation of cycloadducts in the Diels−Alder reaction.[2a,b,5b] For example, the reaction of (*Z*)-chloro phenyl thioketone *S*-oxide with 2,3-dimethyl-1,3-butadiene afforded mainly *cis* cycloadduct (*cis*:*trans* = 3.9: 1),[8] while in the case of (*E*)-chloro phenyl thioketone *S*-oxide *cis* and *trans* cycloadducts are reported to be formed in 12 and 67% yields (*cis*:*trans* = 1:5.6), respectively.[7] The kinetic studies of these cyclizations were also reported: activation parameter $\Delta H^{\ddagger} = 18.4$ kcal/mol and $\Delta S^{\ddagger} = -15$ eu for (*E*)-chloro phenyl thioketone *S*-oxide; $\Delta H^{\ddagger} = 20$ kcal/mol, $\Delta S^{\ddagger} = -15$ eu for (*Z*)-chloro phenyl thioketone *S*-oxide. The negative $\Delta S^{\ddagger}$ values for both cases, although not very large, are suggestive of a concerted cycloaddition process.[8]

More recently, for the monoaryl and monoalkyl sulfines, Barbaro et al. reported that the rate of isomerization of *Z* to *E* isomer was competitive with that of [4 + 2] cycloaddition with a diene at a low diene/sulfine ratio,[5b] and the *Z* isomer is reported to be more stable than the *E* isomer because of a "*syn* effect", i.e., the interaction between the α-hydrogen in the alkyl group or the *o*-hydrogen in the benzene ring and sulfinyl oxygen.[9] However, in benzoyl-substituted sulfine, the *E* isomer is considered to be more stable than the *Z* isomer, probably due to the steric repulsion between the benzoyl and sulfinyl groups because the "*syn* effect" is not present in this case. Furthermore, according to Zwanenburg and coworkers, the cycloaddition of benzoyl-substituted sulfine

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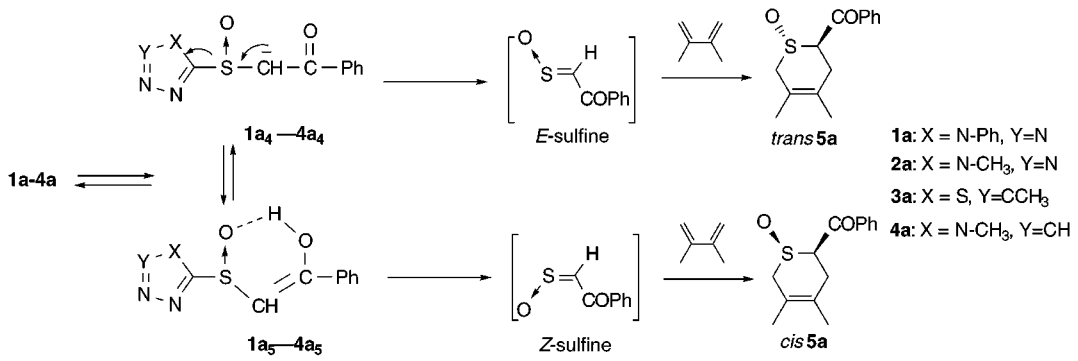
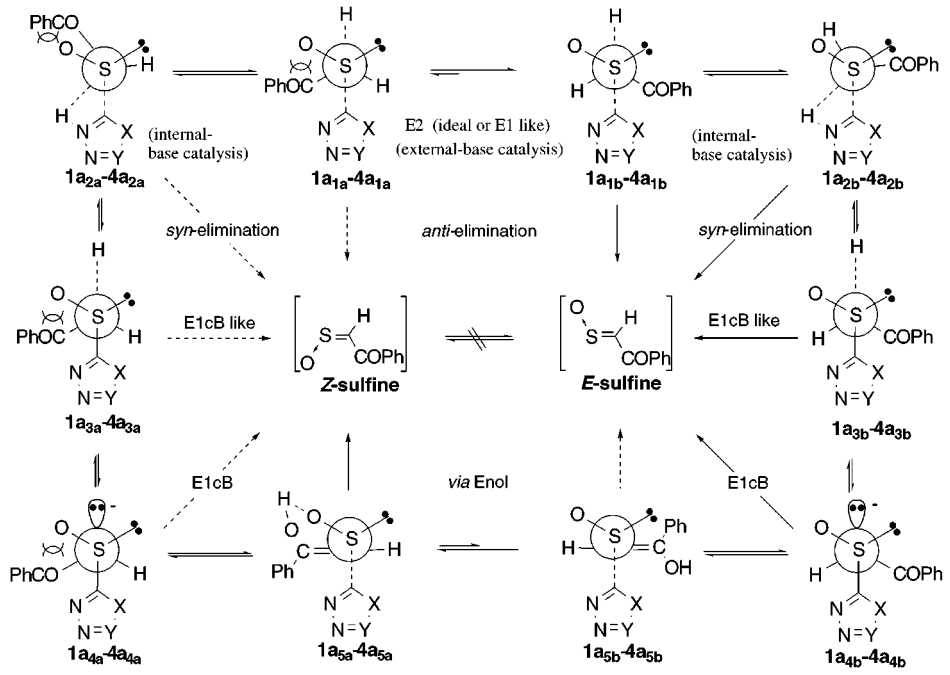
Scheme 1



Scheme 2



with butadiene was reported to be fast, even at temperatures lower than −78 °C.[4c]

As a result, the stereoselectivity of the *cis* and *trans* cycloadducts is considered to be controlled by the sulfine formation step, i.e., the elimination step of nitrogen-containing heteroaromatics and/or isomerization of (*Z*)- to (*E*)-sulfine. In the thermolytic reaction of **1a**, the formation of benzoyl-substituted sulfine was not observed; this means the cycloaddition step is rather fast in our case, the same as in Zwanenburg's results.[5c] Furthermore, the interconversion between *cis* and *trans* **5a** at 100 °C in dioxane was also studied independently and it was revealed that no detectable change in *cis* to *trans* isomer ratio was observed by NMR spectroscopy.

In view of these results and discussions, all the reactions in Table 1 are considered to afford (*E*)-benzoylthioformaldehyde *S*-oxide predominantly or exclusively (cf. entries 1−4). The speculative mechanism is illustrated in Scheme 1. The abstraction of a carbonyl-substituted α-methyl hydrogen of the starting sulfoxide takes place easily to afford the ionic intermediate $\mathbf{1a_4}$−$\mathbf{4a_4}$ or enol $\mathbf{1a_5}$−$\mathbf{4a_5}$, which leads to (*Z*)- or (*E*)-sulfine, respectively, as shown in more detail in Scheme 2. If the elimination reaction of tetrazole from the intermediate or transition state $\mathbf{1a_1}$−$\mathbf{4a_1}$ is similar to that of the usual E2 or E1-like E2 elimination mechanism and, hence, the carbanion lobes or hydrogen atom on the α-position are assumed to be fixed in an antiperiplanar position to the tetrazolyl group in the transition state, apparently $\mathbf{1a_{1a}}$−$\mathbf{4a_{1a}}$ are less stable than $\mathbf{1a_{1b}}$−$\mathbf{4a_{1b}}$ in view of the larger steric repulsion existing between sulfinyl and the benzoyl group and, reversely, $\mathbf{1a_5}$−$\mathbf{4a_5}$ may be more stable than $\mathbf{1a_4}$−$\mathbf{4a_4}$, if the stabilization effect due to hydrogen bonding between the enol hydrogen and the sulfinyl group is working. Therefore, the cycloaddition reaction via (*Z*)- or (*E*)-sulfine thus formed initially resulted in the formation of the cycloadducts *cis* or *trans* **5a** stereoselectively with the diene. Consequently, the results in the Table 1 seem to indicate the importance of the path via $\mathbf{1a_{1b}}$−$\mathbf{4a_{1b}}$ (or $\mathbf{1a_{2b}}$−$\mathbf{4a_{2b}}$; *syn*-elimination) as shown in entries 1−4.

However, in the case of the **4a** (heteroaryl = 3-(4-methyl)-1,2,4-triazolyl, entry 5 in Table 1), the *cis*−*trans* selectivity of cycloadduct **5** was reversed. This result is,

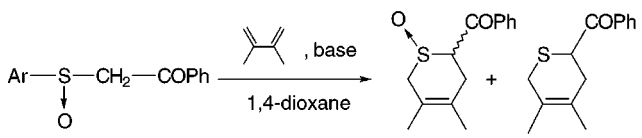
presumably, considered to be the difference of the acidity of the α-methylene protons and the basicity and the leaving ability of the heteroaromatic ring.

The H−D Exchange Study at Methylene Hydogen of Phenacyl Sulfoxide bearing Tetrazole, Triazole, and Thiadiazole. Among the nature of the mother nuclei of heteroaromatics, such as diazole, triazole, tetrazole, thiazole, thiadiazole, etc., no basicity or acidity data under the same conditions are available. Therefore, to obtain further clues for the acidity of the α-methylene hydrogens, the kinetic experiments of the H−D exchange reaction of **1a**, **2a**, **3a**, and **4a** were carried out in $CDCl_3$/CD_3OD at 37 °C (NMR probe temperature) by monitoring the decrease of the integration value of methylene hydrogens by NMR spectroscopy.

The calculated first-order kinetic constants for the H−D exchange reaction of α-methylene hydrogens of **1a**, **2a**, **3a**, and **4a** under these conditions were 7.77×10^{-3}, 9.14×10^{-3}, 9.78×10^{-3}, and 4.7×10^{-2} min^{-1}, respectively, and the relative rates were 1.0, 1.2, 1.3, and 6.0, respectively. Compound **4a** has a rate ca. 6 times faster than that of the other three sulfoxides, **1a**, **2a**, and **3a**, which, unexpectedly, showed almost the same reactivities. These results clearly indicates that the acidity of the methylene hydrogens of triazolyl phenacyl sulfoxide is the highest among the tetrazolyl- and thiadiazolyl-substituted sulfoxides **1a**, **2a**, and **3a**. This increasing order of H−D exchange rate constants also seems to imply the tendency of the increasing basicity of the heteroaromatic moieties, because these parts apparently catalyzed the H−D exchange reactions either intra- or intermolecularly, although no such values are reported in the literature for their mother nuclei, namely 1-phenyl-1,2,3,4-tetrazole, 1-methyl-1,2,3,4-tetrazole, 2-methyl-1,3,4-thiadiazole, and 4-methyl-1,2,4-triazole, under the same conditions. Concerning the leaving ability for these heteroaromatic moieties, no useful data exists using the same conditions; however, the 1-phenyl- or 1-methyl-1,2,3,4-tetrazolyl group is apparently much better than the 4-methyl-1,2,4-triazolyl or 2-methyl-1,3,4-thiadiazolyl group, in view of number of electron-withdrawing nitrogen atoms in the five-membered ring. Therefore, in the case of **4a**, the rate-determining step is not the α-methylene hydrogen abstraction step but the elimination step of the 4-methyl-1,2,4-triazolyl group; this means that the possible mechanism for **4a** will be via an E1cB or an E1cB-like transition state and, consequently, the possibility of existing as enol transition state $\mathbf{1a_{5a}}-\mathbf{4a_{5a}}$ will be increased, stabilized by hydrogen bonding between the hydroxy and sulfinyl groups, successively, to form (*Z*)-sulfine predominantly. In the case of **1a**, and **2a**, the α-methylene hydrogen abstraction step is, probably, the rate-determining step in view of the good leaving nature of the phenyl-substituted tetrazolyl group; this means that the possible mechanism will be via an E2 or an E1-like transition state.

In view of the rather low reactivity of **3a** compared with that of the other sulfoxides, **1a**, **2a**, and **4a** (compare the yields of **5a** in Table 1), the leaving ability of the 2-methyl-1,3,4-thiadiazolyl group does not appear to be substantially high. In addition, the acidity of the α-methylene hydrogen is also not as high as that of **4a.** Therefore, in the case of **3a**, the elimination reaction would be shifted to via an ideal E2 mechanism (*anti*-elimination, external base catalysis route, or *syn*-elimination, internal base catalysis route). Consequently, the more preferable transition state for **3a** is $\mathbf{1a_{1b}}-\mathbf{4a_{1b}}$ or $\mathbf{1a_{2b}}-\mathbf{4a_{2b}}$, which leads to the (*E*)-sulfine preferentially and, successively to *trans* **5a**.

Table 2. Effect of External Base for *Cis*−*Trans* Selectivity of 5a on the Reaction of 1a−4a in the Presence of 10 equiv of 2,3-Dimethyl-1,3-butadiene



1a–4a ***cis*** or ***trans*** **5a** **10** + Ar-H **6** + Ar-OH[a]

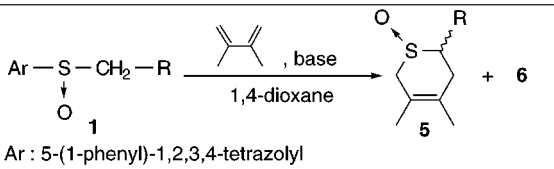
entry	compd.	conditions	base (1.5 equiv)	yield % **5a**	*cis*:*trans*[b]	**6**	**10**
1	**1a**	100 °C, 3 h	none	99	1:5.0	60	0
2	**1a**	70 °C, 1 h	Et_3N	67	1:4.0	62	trace
3	**1a**	70 °C, 1 h	MeONa	82	1:3.0	91	3
4	**2a**	100 °C, 3 h	none	99	1:3.7	99	0
5	**2a**	70 °C, 1 h	Et_3N	81	1:1.1	63	trace
6	**2a**	70 °C, 1 h	MeONa	98	1:2.0	30	1.3
7	**3a**	100 °C, 16 h	none	99	1:30	99	0
8	**3a**	70 °C, 6 h	Et_3N	27	1:1.4	3	39
9	**3a**	70 °C, 4.5 h	MeONa	56	1:4.3	61	6
10	**4a**	100 °C, 3 h	none	99	2.1:1	99	0
11	**4a**	70 °C, 0.5 h	Et_3N	99	49.5:1	99	trace
12	**4a**	70 °C, 0.25 h	MeONa	98	1:2.3	trace	1.7

[a] yields are not determined.

[b] ratios were obtained by NMR analysis of the reaction mixture.

Effect of an External Base on the *Cis*−*Trans* Selectivity of 5a. As shown in Schemes 1 and 2, the formation of the ionic intermediate $\mathbf{1a_4}-\mathbf{4a_4}$ or enol $\mathbf{1a_5}-\mathbf{4a_5}$ is expected to be accelerated by the abstraction with an external base added, if the α-hydrogen abstraction step is related to the rate-determining step. Therefore, to obtain further mechanistic details, the reactions of **1a**−**4a** with 2,3-dimethyl-1,3-butadiene in the presence of triethylamine or sodium methoxide as an external base were studied and these results are summarized in Table 2 (the results of Table 1 are included for comparison). First of all, in all cases of addition of the external bases, the reaction was apparently accelerated substantially (lower reaction temperature and shoter reaction time) to afford **5a** and, interestingly, the formation of product **10** was observed in trace to low yields in every case. Product **10** was apparently formed via a different mechanism which involves thioaldehyde formation by 1,2-elimination of heteroaryl phenacyl sulfenate generated by the rearrangement of the starting sulfoxide as reported in our precedent study.[1c] In the case of **3a** in the presence of triethylamine (entry 8) the yield of **10** is extreamely high. The reason is not certain at present; however, the relatively lower leaving ability of the 2-methyl-1,3,4-thiadiazolyl group of **3a** seems to be important. The tendency of *trans* predominace of **5a** in the reaction of **1a**−**2a** in the presence or absence of triethylamine or sodium methoxide is unchanged, although the selectivity seems to become lower with the stronger base (entries 1−3 and 4−6). In the case of **3a** in the presence of an external base (entries 7−9), the *trans*-selectivity became very low compared with that in the absence of base, suggesting that the elimination mechanism shifts to an E1cB-like or E1cB mechanism which will raise the possibility of *cis*-selectivitiy. As mentioned previously, because of the high acidity of the methylene proton of

Table 3. Thermolysis of 1-Phenyl-1,2,3,4-tetrazolyl Sulfoxide in the Presence of 10 equiv of Butadiene



Ar : 5-(1-phenyl)-1,2,3,4-tetrazolyl

entry	R		conditions	base (1.5 equiv)	yield %[a] 5 (*cis*:*trans*)		6
1	PhCO	**1a**	100 °C, 3 h	none	99 (1:5)	**5a**	60
2	PhCO	**1a**	70 °C, 1 h	Et_3N	67 (1:4)	**5a**	62
3	CH_3CO	**1b**	100 °C, 3 h	none	82 (1:1.2)	**5b**	66
4	CH_3CO	**1b**	70 °C, 1 h	Et_3N	90 (1:1)	**5b**	70
5	EtOCO	**1c**	100 °C, 3 h	none	0[b]	**5c**	0[b]
6	EtOCO	**1c**	100 °C, 3 h	Et_3N	73 (1:1)	**5c**	68

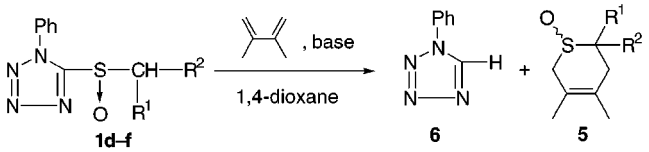
[a] isolated yield (reactions were not optimized).
[b] complete recovery of starting material.

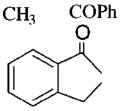
4a, which apparently was derived from the higher basicity of the triazolyl moiety, the reaction of **4a**, probably, procceds via an E1cB or E1cB-like mechanism and, hence, the formation of the enol $\mathbf{4a}_{\mathbf{5a}}$ is involved both in the absence and the presence of triethylamine. In contrast to this result, when a strong base is used, sodium methoxide as an external base (entry 12), the mechanism shifts to the ideal E1cB, in which case the enol form $\mathbf{4a}_{\mathbf{5a}}$, stabilized by internal hydrogen bonding, cannot exist because of the absence of protons (a strong basic media), resulting in predominant formation of the (*E*)-sulfine mainly via the transition state $\mathbf{4a}_{\mathbf{4b}}$ rather than $\mathbf{4a}_{\mathbf{4a}}$.

The Reaction of *β*-Keto Sulfoxides 1b,c Bearing 5-(1-Phenyl)-1,2,3,4-tetrazole with 2,3-Dimethyl-1,3-butadiene. The reactions of **1b**,**c** with 2,3-dimethyl-1,3-butadiene in the presence of triethylamine were further studied, and the results are summerized in Table 3. In the case of 5-(1-phenyl)-1,2,3,4-tetrazolyl acetylmethyl sulfoxide (**1b**), the reaction in dioxane was accelerated by the addition of triethylamine to afford **5b** and **6** in 90 and 70% yields, respectively (see entries 3 and 4). In both cases, whether a base is present or not, the *cis*−*trans* isomer ratios of **5b** are almost identical. This means that the mechanism is considered to be the same or quite similar in both the presence and absence of a base; if other mechanisms are operating as illustrated in Scheme 2, the *cis*−*trans* product ratios will be changed significantly. In entry 5, the reaction of 5-(1-phenyl)-1,2,3,4-tetrazolyl ethoxycarbonylmethyl sulfoxide **1c** with 2,3-dimethyl-1,3-butadiene without a base did not afford the desired cycloadduct product. However, the addition of triethylamine was found to accelerate the reaction dramatically to afford 6-ethoxycarbonyl-5,6-dihydro-3,4-dimethyl-2*H*-thiapyran 1-oxide (**5c**)[11] and **6** in 73 and 68% yields, respectively (entry 6). In entry 6, the *cis*−*trans* isomer selectivity of **5c** was completely lost. The loss of the *cis*−*trans* selectivity in entries 3, 4, and 6, compared to the results in the case of the sulfoxide **1a**, is probably due to the sterical difference between the benzoyl and acetyl or ethoxycarbonyl groups.

Reaction of α-Substituted Phenacyl Sulfoxide with 2,3-Dimethyl-1,3-butadiene. To study the possibility of the thioketone oxide formation, the thermolyses of α-methyl or α-substituted-methyl phenacyl sulfoxide (**1d**−**f**) in the presence of 2,3-dimethyl-1,3-butadiene using bases such as triethylamine or sodium methoxide were also carried out, and the results are summarized in Table 4. The reaction of 5-(1-phenyl)-1,2,3,4-tetrazolyl α-methylphenacyl sulfoxide (**1e**) in the presence of 2,3-dimethyl-1,3-butadiene without base afforded 4-benzoyl-1,2-dimethyl-1-cyclohexene (**15**) and **6** in 85 and 29% yields, respectively (entry 1 in Table 4). Product **15** is considered to be formed by the Diels−Alder reaction of the diene with **12** which was initially formed by the *β*-elimination of the starting sulfoxide **1d** together with the corresponding unstable sulfenic acid (**13**) (cf. Scheme 3). Therefore, next, in the absence of the diene and a base, the reaction of **1d** in dioxane at 100 °C for 4.8 h was carried out to afford 5-(1-phenyl)-1,2,3,4-tetrazole (**6**), phenyl vinyl ketone (**12**), and 5-(1-phenyl)-1,2,3,4-tetrazolyl benzoylethyl sulfoxide (**14**) in 60, 12, and 30% yields, respectively. Product **14** is considered to be formed by the Michael addition of sulfenic acid **13** to **12**. This result, apparently, revealed that the *β*-elimination of sulfoxide took place to afford **12** and the corresponding unstable sulfenic acid **13** which probably led to complex reaction mixtures. Further, to confirm this consideration a trapping experiment of the corresponding sulfenic acid with methyl propiolate was carried out under similar conditions; however, the corresponding trapped product of sulfenic acid, the methyl 1-tetrazolylsulfinylacrylate derivative, was not obtained, and products **6** and **12** were formed in 73 and 45% yields, respectively.

Table 4. Thermolytic Reaction of 5-(1-Phenyl)-1,2,3,4-tetrazolyl α-Substituted Phenacyl Sulfoxide in the Presence of 10 equiv of 2,3-Dimethyl-1,3-butadiene



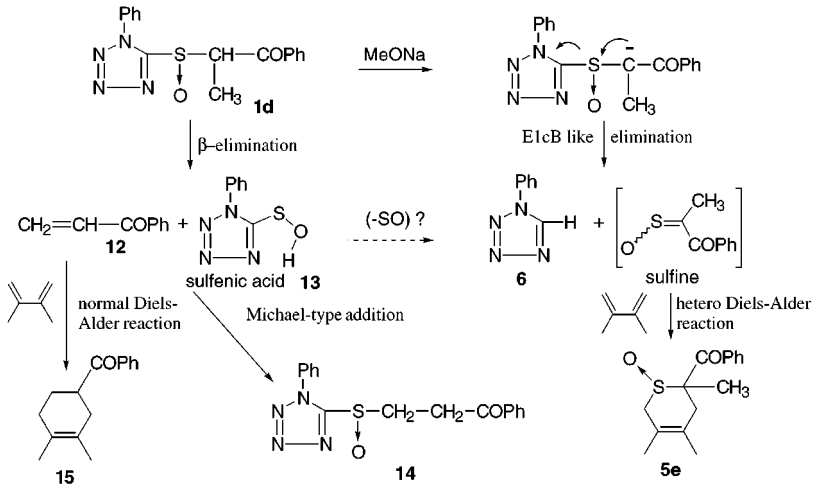
entry	R^1	R^2		conditions	base (1.5 equiv)	yield %[a] 6	5
1	CH_3	COPh	**1d**	100 °C, 1 h	none	29	0[b]
2	CH_3	COPh	**1d**	70 °C, 1 h	Et_3N	91	0[b]
3	CH_3	COPh	**1d**	70 °C, 1 h	MeONa	37	41
4			**1e**	70 °C, 0.25 h	MeONa	57	33
5	Ph	COPh	**1f**	70 °C, 1.3 h	Et_3N	86	73

[a] isolated yield (reactions were not optimized) .
[b] 4-benzoyl-1,2-dimethyl-1-cyclohexene was obtained.

The reaction of **1d** with triethylamine at 70 °C afforded **6** in 91% yield (entry 2). However, no Diels−Alder cycloadduct of sulfine with butadiene was obtained under these conditions, in contrast with the result of entry 2 in Table 3. This is rationalized by the lower α-methyne hydrogen acidty of **1d** than that of **1a** by introduction of an electron-releasing methyl group to the sulfoxide **1a**. Therefore, in this case the *β*-elimination reaction path to **12** and **13** may be competing with the elimination reaction path to the sulfine and **6** as shown in Scheme 3. Consequently, in this case the complex product mixture was obtained under these conditions. Using a stronger base, sodium methoxide, than triethylamine, the reaction

(10) (a) Block, E.; Wall. A. *J. Org. Chem.* **1987**, *52*, 809. (b) Kice, J. L.; Kupczyk-Subotkowska, L. *J. Org. Chem.* **1991**, *56*, 1424.
(11) Freer, A. A.; Kirby, G. W.; Lewis, R. A *J. Chem. Soc., Chem. Commun.* **1987**, 718.

Scheme 3



afforded the corresponding product **5d** in 41% yield (entry 3). Similarly, the reaction of 2-(5′-(1′-phenyl)-1,2,3,4-tetrazolylsulfinyl)-1-indanone (**1e**) using sodium methoxide afforded the corresponding cycloadduct **5e** in 33% yield (entry 4). Zwanenburg and co-workers also have reported the formation of **5e** via the sulfine which was generated by reaction of the corresponding silyl enol ether with thionyl chloride.[12] In the case of no possibility of β-elimination, such as with **1f**, which has no β-hydrogens, expectedly, this reaction gave the corresponding cycloadduct **5f** in rather high yield, 73% (entry 5).

Experimental Section

All melting points are uncorrected. ^{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 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, 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 the Preparation of Sulfoxide (1a−4a, 1b−f). To a stirred solution of sulfide in chloroform or methylene chloride was added *m*-chloroperbenzoic acid (*m*-CPBA, >70%) in chloroform or methylene chloride at 0 °C. This reaction mixture was stirred at 0 °C until starting sulfide disappeared by TLC monitoring. The reaction mixture was washed with saturated aqueous $NaHCO_3$. The aqueous layer was extracted well with chloroform. This combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, and condensed to afford the crude product. Purification was performed by chromatography on silica gel and/or recrystallization.

5-(1-Phenyl)-1,2,3,4-tetrazolyl phenacyl sulfoxide (1a): 89% yield; white crystals from EtOAc/hexane; mp 105.9 °C. Spectral data: ^{1}H NMR δ 5.22 (d, J = 16.4 Hz, 1H), 5.81 (d, J = 16.4 Hz, 1H), 7.51−7.55 (m, 2H), 7.65−7.70 (m, 4H), 7.80−7.82 (m, 2H), 7.93−7.95 (m, 2H); ^{13}C NMR δ 62.1, 124.9, 128.6, 129.1, 130.1, 131.3, 132.8, 134.6, 135.0, 157.0, 192.3; IR (KBr) 1670, 1080 cm^{-1}. Anal. Calcd for $C_{15}H_{12}N_4O_2S$: C, 57.68; H, 3.87; N, 17.94. Found: C, 57.66; H, 3.89; N, 17.96.

5-(1-Methyl)-1,2,3,4-tetrazolyl phenacyl sulfoxide (2a): 75% yield; white crystals from CH_2Cl_2/hexane; mp 125.7−127.0 °C (dec). Spectral data: ^{1}H NMR δ 4.37 (s, 3H), 4.83 (d, J = 15.2 Hz, 1H), 5.00 (d, J = 15.2 Hz, 1H), 7.49−7.53 (m, 2H), 7.63−7.67 (m, 1H), 7.93−7.96 (m, 2H); ^{13}C NMR δ 35.3, 62.8, 128.6, 129.1, 134.8, 134.9, 155.9, 190.9; IR (KBr) 1670, 1070 cm^{-1}. Anal. Calcd for $C_{10}H_{10}N_4O_2S$: C, 47.99; H, 4.03; N, 22.39. Found: C, 48.04; H, 3.98; N, 22.62.

2-(5-Methyl)-1,3,4-thiadiazolyl phenacyl sulfoxide (3a): 72% yield; white crystals from CH_2Cl_2/hexane; mp 118.5−129.7 °C (dec). Spectral data: ^{1}H NMR δ 2.88 (s, 3H), 5.05 (d, J = 16.4 Hz, 1H), 5.41 (d, J = 16.4 Hz, 1H), 7.50−7.55 (m, 2H), 7.65−7.69 (m, 1H), 7.92−7.95 (m, 2H); ^{13}C NMR δ 16.2, 65.0, 128.7, 129.0, 134.6, 135.4, 169.7, 176.9, 190.5; IR (KBr) 1650, 1030 cm^{-1}. Anal. Calcd for $C_{11}H_{10}N_2O_2S_2$: C, 49.61; H, 3.78; N, 10.52. Found: C, 49.74; H, 3.75; N, 10.48.

5-(4-Methyl)-4*H*-1,2,4-triazolyl phenacyl sulfoxide (4a): 75% yield; white crystals from CH_2Cl_2/hexane; mp 127.0−134.3 °C (dec). Spectral data: ^{1}H NMR δ 4.03 (s, 3H), 5.10 (d, J = 16.0 Hz, 1H), 5.55 (d, J = 1.6, 16.0 Hz, 1H), 7.50−7.54 (m, 2H), 7.64−7.68 (m,1H), 7.97−8.00 (m, 2H), 8.29 (s, 1H); ^{13}C NMR δ 31.9, 61.6, 128.5, 128.9, 134.5, 135.0, 146.8, 154.0, 191.7; IR (KBr) 1640, 1050 cm^{-1}. Anal. Calcd for $C_{11}H_{11}N_3O_2S$: C, 53.00; H, 4.45; N, 16.86. Found: C, 52.79; H, 4.49; N, 16.82.

5-(1-Phenyl)-1,2,3,4-tetrazolyl acetylmethyl sulfoxide (1b): 66% yield; white crystals from CH_2Cl_2/hexane; mp 119.8 °C. Spectral data: ^{1}H NMR δ 2.37 (s, 3H), 4.68 (d, J = 16.4 Hz, 1H), 5.17 (d, J = 16.4 Hz, 1H), 7.63−7.66 (m, 2H), 7.73−7.75 (m, 3H); ^{13}C NMR δ 30.6, 64.5, 124.9, 130.1, 131.3, 200.4; IR (KBr) 1710, 1050 cm^{-1}. Anal. Calcd for $C_{10}H_{10}N_4O_2S$: C, 47.99; H, 4.03; N, 22.39. Found: C, 47.97; H, 4.06; N, 22.73.

5-(1-Phenyl)-1,2,3,4-tetrazolyl ethoxycarbonylmethyl sulfoxide (1c): 35% yield; white crystals from CH_2Cl_2/hexane; mp 68.2−69.4 °C. Spectral data: ^{1}H NMR δ 1.26 (t, J = 7.2 Hz, 3H), 4.17−4.23 (m, 2H), 4.50 (d, J = 15.6 Hz, 1H), 4.92 (d, J = 15.6 Hz, 1H), 7.62−7.66 (m, 3H), 7.71−7.74 (m, 2H); ^{13}C NMR δ 19.9, 56.5, 62.8, 125.0, 130.1, 131.4, 132.8, 156.3, 164.4; IR (KBr) 1740, 1070 cm^{-1}. Anal. Calcd for $C_{11}H_{12}N_4O_3S$: C, 47.14; H, 4.31; N, 19.99. Found: C, 46.83; H, 4.30; N, 20.41.

2-[5′-(1′-Phenyl)-1,2,3,4-tetrazolylsulfinyl]propiophenone (1d): 78% yield; white crystals from CH_2Cl_2/hexane; mp 119.8−123.4 °C (dec). Spectral data: ^{1}H NMR ($CDCl_3$) δ 1.96 (d, J = 7.6 Hz, 3H), 5.97 (t, J = 7.6 Hz, 1H), 7.51−7.62 (m, 2H), 7.65−7.73 (m, 4H), 7.76−7.80 (m, 2H), 7.82−7.94 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.9, 67.1, 124.9, 128.8, 129.2, 130.0, 131.2, 132.8, 133.6, 134.8, 156.9, 198.3. Anal. Calcd for $C_{16}H_{14}N_4O_2S$: C, 58.88; H, 4.32; N, 17.17. Found: C, 58.76; H, 4.54; N, 17.16.

2-[5′-(1′-Phenyl)-1,2,3,4-tetrazolylsulfinyl]indanone (1e): 69% yield; white crystals from CH_2Cl_2/hexane; mp 103.2−131.5 °C (dec). Spectral data: ^{1}H NMR ($CDCl_3$) δ 3.80−3.86 (m, 1H), 4.03−4.09 (m, 1H), 4.85−4.89 (m, 1H), 7.42−7.46 (t, J = 7.2 Hz, 1H), 7.58−7.73 (m, 7H), 7.79 (d, J = 7.6 Hz, 1H); ^{13}C NMR

(12) Lenz, B. G.; Regeling, H.; Zwanenburg, B. *Tetrahedron Lett.* **1984**, *25*, 5947.

($CDCl_3$) δ 25.6, 67.5, 124.7, 125.0, 126.8, 128.3, 130.1, 131.4, 132.9, 135.4, 136.4, 153.8, 197.6. Anal. Calcd for $C_{16}H_{12}N_4O_2S$: C, 59.25; H, 3.73 N, 17.27. Found: C, 59.17; H, 3,78; N, 17.29.

2-[5′-(1′-Phenyl)-1,2,3,4-tetrazolylsulfinyl]-2-phenylacetophenone (1f): 79% yield; white crystals from CH_2Cl_2/hexane; mp 150.0−161.1 °C (dec). Spectral data: ^{1}H NMR ($CDCl_3$) δ 6.91 (s, 1H), 6.97−7.00 (m, 2H), 7.16−7.28 (m, 5H), 7.46 (m, 4H), 7.52−7.61 (m, 2H), 8.00−8.01 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 79.1, 124.8, 126.2, 129.0, 129.9, 129.32, 129.7, 129.8, 130.2, 131.1, 132.3, 134.4, 134.7, 157.0, 192.0. Anal. Calcd for $C_{21}H_{16}N_4O_2S$: C, 64.93; H, 4.15; N, 14.42. Found: C, 64.72; H, 4.19; N, 14.32.

Thermolysis of 5-(1-Phenyl)-1,2,3,4-tetrazolyl Phenacyl Sulfoxide (1a) in the Presence of Diene. To a dioxane solution (3.0 mL) of **1a** (150 mg, 0.48 mmol) was added freshly distilled 2,3-dimethyl-1,3-butadiene (0.54 mL, 10 equiv). This mixture in a 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 h. The reaction mixture was chromatographed on a silica gel preparative plate using EtOAc/hexane (1:5) to afford 115 mg of **5a** (*cis*:*trans* = 1:5) and 52 mg of **6** in 99 and 60% yields, respectively. Spectral data of **5a**: *trans* and *cis* isomers were separated by recrystallization from benzene. IR (neat) 1680, 1050 cm^{-1}. *Trans* isomer: ^{1}H NMR δ 1.74 (s, 3H), 1.78 (s, 3H), 2.68 (s, 2H), 3.47 (d, J = 15.6 Hz, 1H), 3.59 (d, J = 15.6 Hz, 1H), 4.83 (dd, J = 6.4, 7.6 Hz, 1H), 7.49−7.53 (m, 2H), 7.61−7.65 (m, 1H), 8.02−8.04 (m, 2H); ^{13}C NMR δ 19.3, 10.0, 32.1, 53.5, 65.5, 117.6, 127.6, 128.7, 128.8, 134.1, 135.8, 195.5. *Cis* isomer: mp 128.8−138.5 °C. ^{1}H NMR δ 1.78 (s, 3H), 1.81 (s, 3H), 2.32−2.37 (m, 1H), 3.10−3.17 (m, 1H), 3.35 (d, J = 17.6 Hz, 1H), 3.48 (d, J = 17.6 Hz, 1H), 4.44 (dd, J = 4.4, 11.2 Hz, 1H), 7.48−7.52 (m, 2H), 7.60−7.64 (m, 1H), 7.92−7.94 (m, 2H); ^{13}C NMR δ 19.6, 19.9, 26.0, 52.3, 59.1, 155.3, 127.6, 128.7, 128.8, 133.8, 135.6, 194.4. Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49. Found: C, 67.57; H, 6.51.

General Procedure for Thermolysis of Sulfoxides (2a−4a). To a dioxane solution of a sulfoxide in a Pyrex tube was added 10 equiv of freshly distilled 2,3-dimethyl-1,3-butadiene. This mixture was degassed thoroughly in vacuo at dry ice−acetone temperature, and the glass tube was sealed and then was heated at 100 °C for 3 h. After cooling, solvent and butadiene were removed in vacuo and the NMR spectra of the residual products were measured directly to determine the *cis*−*trans* product ratio.

Thermolysis of 5-(1-Methyl)-1,2,3,4-tetrazolyl Phenacyl Sulfoxide (2a) in the Presence of Diene for 3 h. The above procedure was employed by using 29 mg of **2a**, 0.13 mL of 2,3-dimethyl-1,3-butadiene, and 1.0 mL of dioxane to afford **5a** (*cis*:*trans* = 1:3.7) and **7** in quantitative yield by NMR spectroscopy.

Thermolysis of 2-(5-Methyl)-1,3,4-thiadiazolyl Phenacyl Sulfoxide (3a) in the Presence of Diene for 3 h. The above procedure was employed using 39 mg of **3a**, 0.18 mL of 2,3-dimethyl-1,3-butadiene, and 1.2 mL of dioxane to afford the recovered **3a**, **5a** (only *trans)*, and **8** in 70, 20, and 30% yields by NMR spectroscopy.

Thermolysis of 2-(5-Methyl)-1,3,4-thiadiazolyl Phenacyl Sulfoxide (3a) in the Presence of Diene for 16 h. The above procedure was employed using 34 mg of **3a**, 0.15 mL of 2,3-dimethyl-1,3-butadiene, and 1.0 mL of dioxane to afford **5a** (*cis*:*trans* = 1:30.0) and **8** in quantitative yield by NMR spectroscopy.

Thermolysis of 3-(4-Methyl)-4*H*-1,2,4-triazolyl Phenacyl Sulfoxide (4a) in the Presence of Diene 3 h. The above procedure was employed using 39 mg of **4a**, 0.18 mL of 2,3-dimethyl-1,3-butadiene, and 1.2 mL of dioxane to afford **5a** (*cis*:*trans* = 2.1:1) and **9** in quantitative yield by NMR spectroscopy.

The Kinetic Study of H−D Exchange of Methylene Proton of 1a−4a in CD_3OD/$CDCl_3$. 1a−4a (0.05 mmol) was dissolved in $CDCl_3$ (0.015 mL). To this solution in an NMR tube was added 0.002 mL of dioxane as an internal standard. To this mixture was added 0.035 mL of CD_3OD, and then, the integration values of residual methylene protons were monitored by NMR spectroscopy. The pseudo-first-order rate constants (k_1) for the H−D exchange reaction of α-methylene hydrogens were correlated nicely (correlation coefficients: 0.998, 0.999, 0.978, and 0.997 for **1a**, **2a**, **3a**, and **4a**, respectively.) to the following first-order equation and the rate constants were calculated graphically:

$$k_1 = (\log(A_t/A_0))/t$$

t is the time (in min) from the addition of CD_3OD and A_t and A_0 are the integration values of CH_2 peaks of sulfoxides at $t = t$ and 0 min, respectively. The calculated first-order kinetic constants for the H−D exchange reaction of α-methylene hydrogens of **1a**, **2a**, **3a**, and **4a** under these conditions are 7.77×10^{-3}, 9.14×10^{-3}, 9.78×10^{-3}, and 4.7×10^{-2} min^{-1}, respectively, and the relative rates are 1.0, 1.2, 1.3, and 6.0, respectively.

General Procedure of Thermolysis of Sulfoxide (1a−4a) in the Presence of Diene with Base (Et_3N or MeONa). To a solution of the starting sulfoxide in 2 mL of dioxane were added 10 equiv of freshly distilled 2,3-dimethyl-1,3-butadiene (10 equiv) and 1.5 equiv of base. This mixture was heated at 70 °C. After cooling, this reaction mixture was evaporated and dried completely in vacuo to give the crude residue, which was used for the direct determination of the *cis*−*trans* isomer ratio of **5a** by NMR spectroscopy. Pure **5a** was obtained by a preparative thin-layer chromatography using EtOAc/hexane (1:5) as eluent.

Reaction of 1a in the presence of Et_3N: yield of **5a**, 67%; *cis*−*trans* ratio of **5a**, 1:5.0.

Reaction of 1a in the presence of MeONa: yield of **5a**, 82%; *cis*−*trans* ratio of **5a**, 1:3.0.

Reaction of 2a in the presence of Et_3N: yield of **5a**, 81%; *cis*−*trans* ratio of **5a**, 1:1.1.

Reaction of 2a in the presence of MeONa: yield of **5a**, 98%; *cis*−*trans* ratio of **5a**, 1:2.0.

Reaction of 3a in the presence of Et_3N: yield of **5a**, 27%; *cis*−*trans* ratio of **5a**, 1:14.

Reaction of 3a in the presence of MeONa: yield of **5a**, 56%; *cis*−*trans* ratio of **5a**, 1:4.3.

Reaction of 4a in the presence of Et_3N: yield of **5a**, 99%; *cis*−*trans* ratio of **5a**, 49.5:1.

Reaction of 4a in the presence of MeONa: yield of **5a**, 98%; *cis*−*trans* ratio of **5a**, 1:2.3.

Thermolysis of 5-(1-Phenyl)-1,2,3,4-tetrazolyl Acetylmethyl Sulfoxide (1b) in the Presence of Diene. To a dioxane solution (3.0 mL) of **1b** (100 mg, 0.40 mmol) was added 10 equiv of freshly distilled 2,3-dimethyl-1,3-butadiene (0.45 mL, 10 equiv). This mixture in a 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 h. The reaction mixture was chromatographed on a silica gel preparative plate using EtOAc/hexane (1:5) to afford 61 mg of **5b** (*cis*:*trans* = 1:1.2) and 35 mg of **6** in 82 and 66% yields, respectively. The *cis* isomer of **5b** was successfully separated as white crystals by recrystallization of the obtained *cis*−*trans* mixture from benzene. Spectral data of **5b**: IR (neat) 1710, 1030 cm^{-1}. *Trans* isomer: ^{1}H NMR δ 1.72 (s, 3H), 1.73 (s, 3H), 2.38 (s, 3H), 2.57 (d, J = 7.0 Hz, 1H), 3.50 (d, J = 16.8 Hz, 1H), 3.28−3.32 (m, 2H), 3.95 (t, J = 7 Hz, 1H); ^{13}C NMR δ 19.3, 19.7, 30.6, 31.2. 54.1, 69.3, 117.7, 127.4, 203.6. *Cis* isomer: mp 120.2−123.2 °C; ^{1}H NMR δ 1.75 (s, 3H), 1.78 (s, 3H), 2.28−2.34 (m, 1H), 2.40 (s, 3H), 2.87−2.94 (m, 1H), 3.28−3.38 (m, 2H), 3.51 (dd, J = 5, 10 Hz, 1H); ^{13}C NMR δ 19.8, 19.9, 25.5, 29.7, 51.9, 64.1, 115.4, 127.0. 202.4.

Thermolysis of 5-(1-Phenyl)-1,2,3,4-tetrazolyl Acetylmethyl Sulfoxide (1b) in the Presence of Diene with Base. The above procedure was employed using 100 mg of **1b**, 0.41 mL of 2,3-dimethyl-1,3-butadiene, 0.085 mL of triethylamine, and 3.0 mL of dioxane to afford **5b** (*cis*:*trans* = 1:1) and **6** in 90 and 70% yields, respectively.

Thermolysis of 5-(1-Phenyl)-1,2,3,4-tetrazolyl Ethoxycarbonylmethyl Sulfoxide (1c) in the Presence of Diene

with Base. In a Pyrex tube, 89 mg of **1c** (0.32 mmol), 0.36 mL of freshly distilled 2,3-dimethyl-1,3-butadiene, and 0.066 mL of triethylamine in 2.7 mL of dioxane were degassed thoroughly in vacuo at dry ice−acetone temperature, and the glass tube was sealed and then was heated at 100 °C for 3 h. The reaction mixture was chromatographed on a silica gel preparative plate using EtOAc/hexane (1:5) to afford 47 mg of **5c** (*cis*:*trans* = 1:1) and 34 mg of **6** in 68 and 73% yields, respectively. Spectral data of **5c**: IR (neat) 1730, 1030 cm^{-1}. *Trans* isomer: ^{1}H NMR δ 1.30 (t, J = 7.2 Hz, 3H), 1.72−1.79 (m, 6H), 2.56−2.62 (m, 1H), 2.71−2.77 (m, 1H), 3.31−3.32 (bs, 2H), 3.82 (dd, J = 5.6, 8.0 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H). *Cis* isomer: ^{1}H NMR δ 1.33 (t, J = 7.2 Hz, 3H), 1.73−1.79 (m, 6H), 2.40−2.43 (m, 1H), 2.90−2.99 (m, 1H), 3.2 8−3.32 (m, 1H), 3.39 (dd, J = 4.8, 12.0 Hz, 1H), 3.50 (d, J = 16.4 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H); ^{13}C NMR (*cis*−*trans* mixture) δ 14.0, 19.4, 19.5, 19.8, 19.9, 24.9, 29.9, 52.0, 52.4, 57.2, 61.9, 62.0, 62.1, 115.2, 117.2, 126.8, 126.9, 168.1, 168.5.

Thermolysis of 5-(1-Phenyl)-1,2,3,4-tetrazolyl α-Methylphenacyl Sulfoxide (1d) in the Presence of Diene. To a dioxane solution (3.0 mL) of **1d** (106 mg) was added 10 equiv of freshly distilled 2,3-dimethyl-1,3-butadiene (0.45 mL, 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 4 h. The reaction mixture was chromatographed on a silica gel preparative plate using EtOAc/hexane (1/5) as eluent to give 59 mg of 4-benzoyl-1,2-dimethyl-1-cyclohexene (**15**) and 14 mg of 1-phenyl-1,2,3,4-tetrazole (**6**) in 85 and 29% yields, respectively. Spectral data of **15**: colorless oil; ^{1}H NMR δ 1.65 (s, 6H), 1.67−1.74 (m, 1H), 1.92−2.34 (m, 5H), 3.46−3.54 (m, 1H), 7.46 (t, J = 7.2 Hz, 2H), 7.53−7.57 (m, 1H), 7.96 (d, J = 6.8 Hz, 2H); ^{13}C NMR δ 18.8, 19.0, 26.4, 31.4, 34.2, 42.5, 124.4, 125.3, 128.2, 128.6, 132.8, 136.4, 203.6; IR (neat) cm^{-1}; MS (*m*/*z*) 214.

Thermolysis of 1d−f with 2,3-Dimethyl-1,3-butadiene in the Presence of Base. To a solution of the starting sulfoxide **1d−f** in 3 mL of dioxane were added 1.5 equiv of 2,3-dimethyl-1,3-butadiene and 1.5 equiv of a base, sodium methoxide or triethylamine, at 70 °C with stirring. After cooling, the reaction mixture was evaporated and dried in vacuo. The residual product was separated on a silica gel preparative plate using AcOEt/hexane (1/1) as eluent to give the corresponding cycloadducts **5d−f** and **6**.

6-Benzoyl-5,6-dihydro-3,4,6-trimethyl-2*H*-thiapyran 1-oxide (5d): ^{1}H NMR δ 1.50 (s, 3H), 1.59 (s, 3H), 1.78 (s, 3H), 2.57 (d, J = 17.6 Hz, 1H), 2.81 (d, J = 17.6 Hz, 1H), 3,12 (d, J = 18 Hz, 1H), 3.32 (d, J = 18 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.76 (d, J = 7.6 Hz, 2H); ^{13}C NMR δ 19.1, 20.1, 20.8, 33.4, 50.2, 67.0, 117.0, 127.2, 127.9, 128.5, 132.8, 136.2, 201.5.

5,6-Dihydro-3,4-dimethyl-2*H*-thiapyran-6-spiro-2′-indanone 1-oxide (5e): ^{1}H NMR δ 1.69 (s, 3H), 1.78 (s, 3H), 2.34 (d, J = 18.4 Hz, 1H), 1.79 (d, J = 18.4 Hz, 1H), 3.02 (d, J = 17.6 Hz, 1H), 3.33 (d, J = 16.0 Hz, 1H), 3.68 (d, J = 14.4 Hz, 1H), 3.93 (d, J = 17.2, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.64 (t, J = 8.0, 1H), 7.78 (d, J = 7.6 Hz, 1H); ^{13}C NMR δ 19.4, 19.8, 29.2, 31.1, 39.1, 52.2, 118.5, 124.6, 126.5, 126.8, 128.0, 135.4, 135.8, 152.6, 202.4.

6-Benzoyl-5,6-dihydro-3,4-dimethyl-6-phenyl-2*H*-thiapyran 1-oxide (5f): mp 141.3−142.9 °C; ^{1}H NMR δ 1.25 (s, 3H), 1.65 (s, 3H), 2.75 (d, J = 17.2 Hz, 1H), 3.04 (d, J = 17.6 Hz, 1H), 3.52 (d, J = 16.8 Hz, 1H), 3.57 (d, J = 18.4 Hz, 1H), 2.29 (t, J = 8.0 Hz, 2H), 7.38−7.51 (m, 8H); ^{13}C NMR δ 19.1, 20.4, 30.8, 52.2, 74.1, 120.4, 126.3, 127.6, 128.3, 128.6, 129.11, 129.5, 132.6, 133.8, 186.0, 199.6; IR (neat) 1669, 1050 cm^{-1}. Anal. Calcd for $C_{20}H_{20}O_2S$: C, 74.04; H, 6.21. Found: C, 73.70; H, 6.23.

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