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Green synthesis of thiiranes from oxiranes under solvent- and catalyst-free conditions

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Green synthesis of thiiranes from oxiranes under solvent- and catalyst-free conditions

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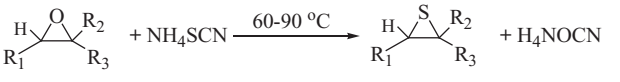
A simple and efficient method for the conversion of oxiranes to thiiranes using ammonium thiocyanate (NH_4SCN) under solvent- and catalyst-free conditions is described. These conditions enable clean and fast conversion of oxiranes to the corresponding thiirane.



1-20

Keywords: oxirane; thiirane; catalyst-free; solvent-free; ammonium thiocyanate

1. Introduction

Organic sulfur compounds have become increasingly useful and important in organic synthesis. Thiiranes, which are the simplest sulfur heterocycles, are important and useful building blocks for the synthesis of polymers, pharmaceuticals, pesticides, and herbicides (*1*, *2*). Various methods have been developed for the synthesis of thiiranes. The most general procedure for the synthesis of thiiranes is the conversion of epoxides by an oxygen–sulfur exchange reaction with thiourea (*3*), inorganic thiocyanates (*4*), Dowex-50WX8-supported thiourea (*5*), and polymer-supported thiocyanates (*6*). Along with each of these sulfur transfer reagents, a protic acid such as $Mg(HSO_4)_2$ (*3g*), etidronic acid (*7*), oxalic acid (*4k*), SiO_2-HBF_4 (*4d*) or a Lewis acid such as NH_4Cl (*3a*), $Al(DS)_3 \cdot 3H_2O$ (*3b*), SiO_2-$AlCl_3$ (*3c*), $LiBF_4$ (*3h*), $RuCl_3$ (*3i*), $SbCl_3$ (*3j*), montmorillonite K-10 (*3k*), I_2 (*4a*), $LiClO_4$ (*4b*), $Sn^{IV}(TPP)(BF_4)_2$ (*4c*), 2,4,6-trichloro-1,3,5-triazine (*4f*), TiO_2 (*4g*), $Sn^{IV}(TPP)(OTf)_2$ (*4h*), $InBr_3$ (*4l*), $Bi(TFA)_3$ (*4m*), $Bi(OTf)_3$ (*4m*), $BiCl_3$ (*4n*), $TiO(CF_3CO_2)_2$

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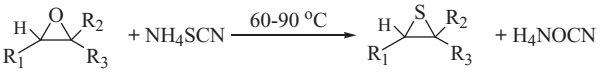
(*4o*), $TiCl_3(CF_3SO_3)$ (*4o*), ceric ammonium nitrate (*4p*), metalloporphyrins, (*4q*, *4r*, *4s*), SiO_2-Cl (*4t*) and ionic liquid (*8*) is employed.

However, some of these methods suffer from drawbacks such as long reaction times, high temperatures, low yields of the products, use of organic solvents, the need to use aqueous and/or alcoholic media, use of highly acidic catalysts, rapid increase of pH during the reaction, difficulties in the separation of the product from the original reactant and catalyst, formation of polymeric byproducts, high catalytic loading, and, in most of the cases, the use of an expensive (*4g*, *9*) and unrecoverable catalyst. Also the toxicity and volatility of many organic solvents, particularly chlorinated hydrocarbons that are widely used in organic synthesis, have posed a serious threat to the environment. Consequently, methods that successfully minimize use of catalysts and solvents are the focus of much attention. In this paper, we wish to report an improved, efficient, and easy synthesis of thiiranes from oxiranes that is environmental-friendly and more economical than previously reported procedures. This new method produces thiiranes in high yields under solvent- and catalyst-free conditions from the reaction of oxiranes with ammonium thiocyanate.

2. Results and discussion

Herein, we report a novel and simple solvent- and catalyst-free method for conversion of oxiranes to thiiranes (Scheme 1).

The optimum reaction parameters, shown in Scheme 1, were chosen after examining a variety of reaction factors. In a set of experiments, the reaction of styrene oxide as a model substrate with ammonium thiocyanate was studied in different solvents in the absence of any catalyst. 2-Phenyl thiirane was not obtained when the reaction was performed in dichloromethane, chloroform, nitromethane, and 1,4-dioxane at room temperature (Table 1, Entries 1–4). Under the same reaction



1-20

1-17 :

R_1 = Ph, $PhOCH_2$, 4-$CNC_6H_4OCH_2$, 4-$NO_2C_6H_4OCH_2$, 4-$FC_6H_4OCH_2$, 4-$ClC_6H_4OCH_2$, 4-$BrC_6H_4OCH_2$, 4-*tert*-$BuC_6H_4OCH_2$, 2-*tert*-Bu-4-$MeC_6H_4OCH_2$,2-Me-4-*tert*-$BuC_6H_4OCH_2$, 1-naphthylOCH_2 , 2-naphthylOCH_2 , $CH_3(CH_2)_3$., $ClCH_2$,$CH_2CHCH_2OCH_2$, $(CH_3)_2CHOCH_2$, $CH_2CH(CH_3)CO(CH_2)_2$

$R_2 = R_3$ = H

18-20 :

cyclohexeneoxide , 1-methylcyclohexeneoxide , *trans*-stilbeneoxide

Scheme 1. Conversion of oxiranes to thiiranes under solvent- and catalyst-free condition.

Table 1. Conversion of styrene oxide to 2-phenyl thiirane in various solvents, different molar ratios of H_4NSCN/styrene oxide, and different temperatures.

Entry	Solvent	Molar ratio of NH_4SCN/ styrene oxide	Temp. (°C)	Time	Conversion %[a]
1	Nitromethane	1/1	r.t.	24 h	0
2	Dichloromethane	1/1	r.t.	24 h	0
3	Chloroform	1/1	r.t.	24 h	0
4	1,4-Dioxane	1/1	r.t.	24 h	0
5	Acetone	1/1	r.t.	24 h	20
6	Acetonitrile	1/1	r.t.	24 h	40
7	Tetrahydrofuran	1/1	r.t.	24 h	50
8	–	1/1	r.t.	6.5 h	100
9	Dichloromethane	1/1	Reflux	24 h	0
10	Chloroform	1/1	Reflux	24 h	0
11	1,4-Dioxane	1/1	Reflux	24 h	0
12	Acetone	1/1	Reflux	24 h	60
13	Acetonitrile	1/1	Reflux	24 h	90
14	Tetrahydrofuran	1/1	Reflux	20 h	100
15	Nitromethane	1/1	Reflux	20 min	100
16	Nitromethane	1/1	90	30 min	100
17	Nitromethane	1/1	80	45 min	100
18	Nitromethane	1.5/1	90	10 min	100
19	Nitromethane	1.2/1	80	30 min	100
20	Nitromethane	1.5/1	80	25 min	100
21	Nitromethane	2/1	90	5 min	100
22	Nitromethane	2/1	80	17 min	100
23	Nitromethane	3/1	80	17 min	100
24	Nitromethane	4/1	80	15 min	100
25	Nitromethane	1/1	65	4 h	100
26	Nitromethane	1/1	55	24 h	0
27	–	2/1	90	15 min	100
28	–	1/1	90	15 min	100
29	–	1/1	75	60 min	100

conditions when the reaction was performed in acetone, acetonitrile, and tetrahydrofuran, 20–50% of 2-phenyl thiirane was produced (Table 1, Entries 5–7). At room temperature and under solvent-free conditions, styrene oxide was completely converted to 2-phenyl thiirane after 6.5 h (Table 1, Entry 8).

To improve styrene oxide conversion, the effect of temperature was examined in all of the solvents mentioned above. No product was obtained in dichloromethane, chloroform, and 1,4-dioxane after 24 h even at reflux (Table 1, Entries 9–11). However, in refluxing acetone, acetonitrile, and tetrahydrofuran, conversion of styrene oxide to 2-phenyl thiirane was improved significantly (Table 1, Entries 12–14).

Refluxing nitromethane surprisingly provides an efficient medium for conversion of styrene oxide to 2-phenyl thiirane in a short reaction time (Table 1, Entry 15). Consequently, the effect of temperature and of the molar ratio of H_4NSCN/styrene oxide was studied in nitromethane (Table 1, Entries 16–26). Lowering the temperature increased the reaction time (*e.g.* compare Entry 16 with 17), which when the molar ratios of H_4NSCN/styrene oxide were increased (*e.g.* compare Entry 16 with 21), the reaction was completed in a shorter reaction time. The best result was obtained at 90°C with a 2/1 molar ratio of H_4NSCN/styrene oxide in nitromethane (Table 1, Entry 21). Finally, the optimized conditions (90°C and 2/1 molar ratio of H_4NSCN/styrene oxide) were used with our new solvent-free reaction conditions (Table 1, Entry 27). Styrene oxide in the presence of H_4NSCN was completely converted to 2-phenyl thiirane with a 2/1 molar ratio of H_4NSCN/styrene oxide at 90°C under these solvent- and catalyst-free conditions. Decreasing the molar ratio of H_4NSCN/styrene oxide at the same temperature has no effect on

Table 2. Conversion of different oxiranes to thiiranes under solvent- and catalyst-free conditions.

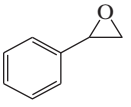
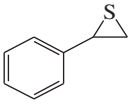
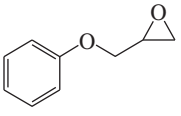
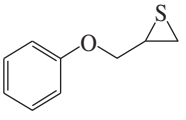
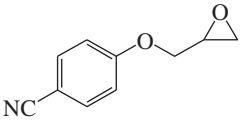
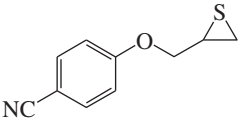
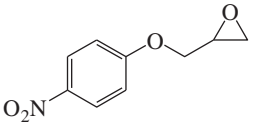
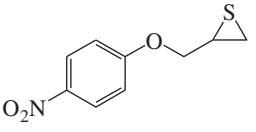
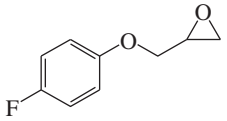
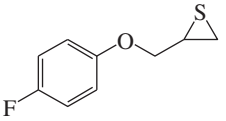
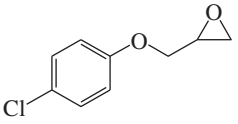
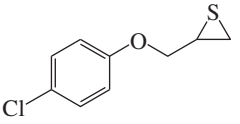
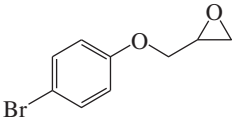
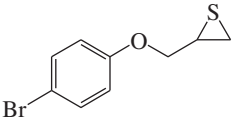
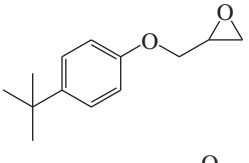
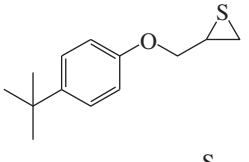
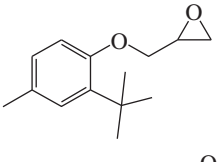
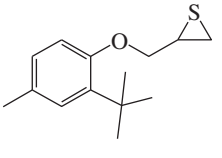
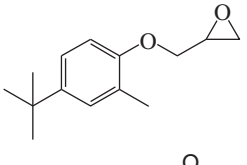
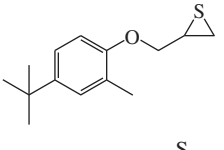
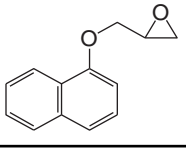
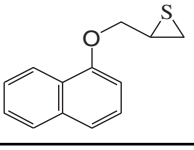
Entry	Substrate	Product[a]	Temp (°C)	Time	Isolated yield%
1			90	15 min	98
2			90	15 min	96
3			90	9 min	97
4			90	7 min	98
5			90	10 min	98
6			90	11 min	94
7			90	13 min	96
8			90	15 min	93
9			90	18 min	95
10			90	17 min	95
11			90	10 min	98

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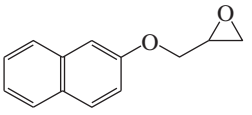
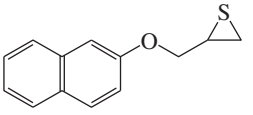
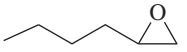
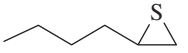
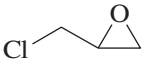
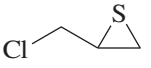
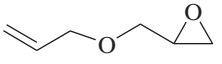
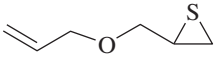
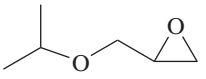
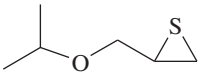
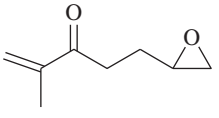
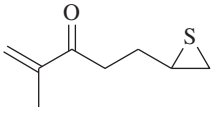
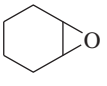
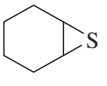
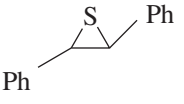
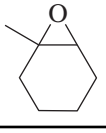
Table 2. Continued

Entry	Substrate	Product[a]	Temp (°C)	Time	Isolated yield%
12			90	8 min	95
13			60	22 min	97
14			65	15 min	96
15			65	14 min	98
16			65	20 min	95
17			65	12 min	96
18			60	25 min	93
19			60	2 h	90
20			60	40 min	98

[a]The products were identified by the comparison of its physical constants, IR and NMR spectral data with those of an authentic sample (see Supplementary material).

the reaction time (compare Entries 27 and 28). On the basis of these data, the best molar ratio of H_4NSCN/styrene oxide is 1/1 at 90°C, under solvent- and catalyst-free conditions, for the formation of 2-phenyl thiirane (Table 1, Entry 28). According to the data in Table 1, it seems that conversion of styrene oxide to 2-phenyl thiiranes under solvent- and catalyst-free conditions is very sensitive to temperature (*e.g.* compare Entries 28 and 29).

The reaction of different oxiranes with ammonium thiocyanate was also studied under solvent- and catalyst-free conditions at 90°C (Table 2). As a result of the low boiling points of the aliphatic oxiranes, the reaction temperatures were lowered to 60–65°C (Table 2, Entries 13–20).

With these optimized solvent- and catalyst-free conditions, a wide variety of different aryl and alkyl oxiranes react with ammonium thiocyanate to provide an efficient conversion to the corresponding thiiranes with 100% conversions. According to the data in Table 2, this method is efficient in conversion of monosubstituted, disubstituted, and trisubstituted oxiranes to the corresponding thiiranes.

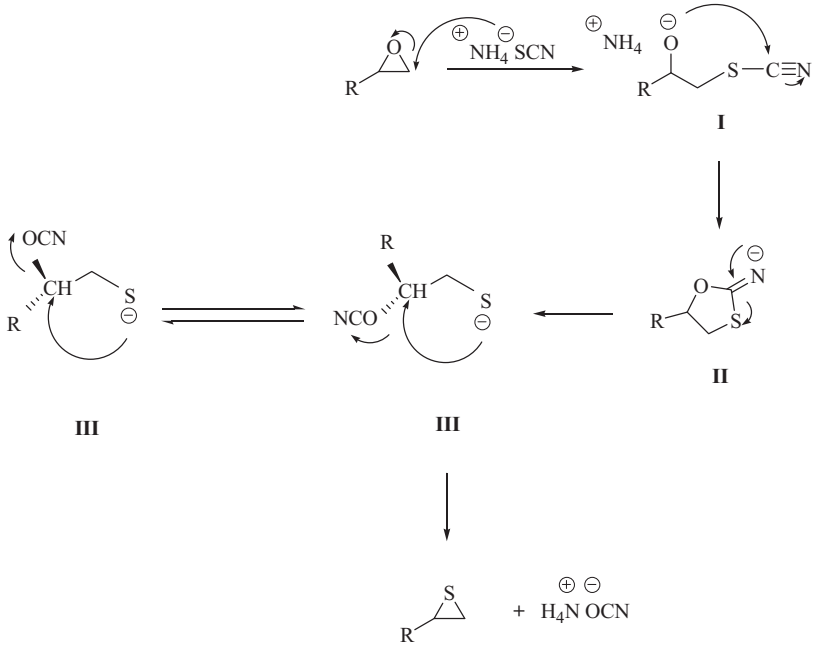
Although various methods for the preparation of thiiranes have been extensively reported, this type of results for reactions on optical active epoxides is very rare (*14*, *15*). The conversion of

optically active styrene oxide to 2-phenyl thiirane using NH_4SCN is studied under solvent- and catalyst-free conditions. When we reacted optically active (R) - (+) styrene oxide with ammonium thiocyanate by applying a 1/1 molar ratio of NH_4SCN/styrene oxide at 90°C, 2-phenyl thiirane (styrene episulfide) was obtained in 98% yield with 0% optical purity (Scheme 2).

The mechanism of these transformations is not clear. We believe that nucleophilic attack of thiocyanate ions opens the epoxide ring and leads to formation of **I**. Subsequently, intramolecular nucleophilic attack of oxygen at the nitrile carbon will give a five-membered ring intermediate **II** which then opens to **III**. Finally, intramolecular nucleophilic substitution with the negatively charged sulfur leads to the formation of thiirane and cyanate ions (Scheme 3). The result of Scheme 2 suggests that the nucleophilic attack is performed on two equally stable conformers of intermediate **III**. However, further mechanistic studies are required to confirm this mechanism.

The present method has the following advantages: the procedure is simple, the reaction times are short, the workup is easy, and the yield of thiiranes is high. Most importantly, it can be performed with a wide range of oxiranes with any kind of functional groups under solvent- and catalyst-free conditions.

Scheme 2. Conversion of optically active (R) - (+) styrene oxide to a racemic mixture of styrene episulfide.



Scheme 3. The proposed mechanism of the conversion of oxiranes to thiiranes.

3. Experimental

3.1. *General*

The products were purified by column chromatography. The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of the products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on an Avatar 370 FT-IR Therma Nicolet spectrometer. The NMR spectra were provided on Brucker Avance 100 and 400 MHz instruments in $CDCl_3$. All of the products were known compounds and characterized by the IR and ^{1}H NMR spectra and comparison of their melting points (or those of the derivatives) with known compounds. Different structurally oxiranes were prepared and purified by the method described previously (*10*). Elemental analyses were performed using a Elementar, Vario EL III instrument. Mass spectra were recorded with a Shimadzu GC-17A&MS-QP5050instrument at 70 eV; in m/z (rel.%). The optical rotation was determined using a Atabo AP300 polarimeter.

3.2. *Typical procedure for conversion of styrene oxide to 2-phenyl thiirane*

Ammonium thiocyanate (0.0761 g, 1 mmol) was added to styrene oxide (0.1202 g, 1 mmol) in a round-bottomed flask equipped with a condenser. The reaction mixture was stirred magnetically at 90°C. The progress of the reaction was followed by TLC. Upon completion of the reaction, the viscous mass was subjected to silica gel flash column chromatography using *n*-hexane/ethylacetate (20/1) as an eluent. 2-Phenyl thiirane was obtained in 98% yield (0.1334 g) after removing the solvent under reduced pressure.

2-phenyl thiirane (Table 2*, Entry 1)*

Oil (*4n*). IR (neat, cm^{-1}) ν: 3060, 3027, 2963, 1490, 1454, 1261, 1073, 801, 761, 695, 610. ^{1}H NMR (400 MHz $CDCl_3$, 25°C, ppm) δ: 7.35 (m, 5H), 3.95 (t, 1H, $J = 6.0$ Hz), 2.92 (dd, 1H, $J = 6.4$ Hz, $J = 1.2$ Hz), 2.71 (dd, 1H, $J = 5.2$ Hz, $J = 1.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 139.2, 128.7, 127.7, 126.8, 36.2, 27.5.

2-(Phenoxymethyl)thiirane (Table 2*, Entry 2)*

Oil (*4n*). IR (neat, cm^{-1}) ν: 3060, 3039, 2921, 2872, 1599, 1496, 1243, 1034, 754, 691. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 7.36 (t, 2H, $J = 8.0$ Hz), 7.04 (t, 1H, $J = 8.0$ Hz), 6.98 (dd, 2H, 1H, $J = 8.8$ Hz, $J = 0.8$ Hz), 4.26 (dd, 1H, $J = 10.0$ Hz, $J = 5.6$ Hz), 395 (dd, 1H, $J = 10.0$ Hz, $J = 6.8$ Hz), 3.33(q, 1H, $J = 5.6$ Hz), 2.66 (d, 1H, $J = 6$ Hz), 2.38 (dd, 1H, $J = 5.2$ Hz, $J = 1.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 158.5, 129.6, 121.3, 114.8, 72.6, 31.5, 24.1.

2-((4-Cyanophenoxy)methyl)thiirane (Table 2*, Entry 3)*

IR (KBr, cm^{-1}) ν: 3096, 2982, 2932, 2217, 1605, 1509, 1300, 1259, 1177, 1024, 843. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 7.60 (d, 2H, $J = 8.8$ Hz), 6.97 (d, 2H, $J = 8.8$ Hz), 4.21 (dd, 1H, $J = 10$ Hz, $J = 6$ Hz), 4.04 (dd, 1H, $J = 10$ Hz, $J = 6.8$ Hz), 3.29 (q, 1H, $J = 6$ Hz), 2.65 (d, 1H, $J = 6$ Hz), 2.36 (dd, 1H, $J = 4.80$ Hz, $J = 1.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 161.6, 134.1, 119.1, 115.3, 104.5, 72.8, 30.9, 23.7. EI-MS: m/z 192 (M^+); Elemental analysis data: C%: 62.90 (calc. 62.8); H%: 4.60 (calc. 4.74); N%: 7.36 (calc. 7.32); S%: 16.5 (calc. 16.70).

2-((4-Nitrophenoxy)methyl)thiirane (Table 2, Entry 4)

m.p. 93.5°C, Lit. (*11*): 93°C. IR (KBr, cm^{-1}) ν: 3113, 3076, 2917, 1597, 1511, 1343, 1262, 1180, 1021, 849, 755. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 8.22 (dd, 2H, $J = 10.4$ Hz, $J = 3.2$ Hz), 6.99 (d, 2H, $J = 8$ Hz),4.27 (dd, 1H, $J = 10.0$ Hz, $J = 5.6$ Hz), 4.09 (dd, 1H, $J = 10.0$ Hz, $J = 6.8$ Hz), 3.31 (q, 1H, $J = 6.0$ Hz), 2.67 (d, 1H, $J = 6.4$ Hz), 2.38 (dd, 1H, $J = 5.2$ Hz, $J = 1.6$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 163.3, 141.8, 126.0, 114.6, 73.1, 30.8, 23.7.

2-((4-Fluorophenoxy)methyl)thiirane (Table 2, Entry 5)

IR (neat, cm^{-1}) ν: 3053, 2992, 2926, 2871, 1505, 1467, 1208, 1097, 1049, 1033, 827, 763. ^{1}H NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 7.04–6.98 (m, 2H), 6.91–6.86 (m, 2H), 4.17 (dd, 1H, $J = 10.0$ Hz, $J = 6.0$ Hz), 3.92 (dd, 1H, $J = 10.4$ Hz, $J = 7.2$ Hz), 3.28 (q, 1H, $J = 6.0$ Hz), 2.63 (d, 1H, $J = 6$ Hz), 2.34 (t, 1H, $J = 4$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 154.59, 154.57, 116.1, 115.9, 73.4, 31.4, 23.8. EI-MS: m/z 184 (M^+); Elemental analysis data: C%: 58.28 (calc. 58.62); H%: 4.73 (calc. 4.92); S%: 17.28 (calc. 17.40).

2-((4-Chlorophenoxy)methyl)thiirane (Table 2, Entry 6)

Oil (*11*). IR (neat, cm^{-1}) ν: 3068, 2986, 2925, 1597, 1589, 1491, 1245, 1098, 1012, 820. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 7.28 (t, 2H, $J = 8.8$ Hz), 6.87 (d, 2H, $J = 8.8$ Hz), 4.18 (dd, 1H, $J = 10.0$ Hz, $J = 5.6$ Hz), 3.93 (dd, 1H, $J = 10.0$ Hz, $J = 6.8$ Hz), 3.28 (q, 1H, $J = 6.0$ Hz), 2.64 (d, 1H, $J = 6.0$ Hz), 2.35 (d, 1H, $J = 5.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 157.0, 129.5, 126.2, 116.0, 72.9, 31.2, 23.9.

2-((4-Bromophenoxy)methyl)thiirane (Table 2, Entry 7)

Oil (*11*). IR (neat, cm^{-1}) ν: 3072, 2990, 2925, 1588, 1488, 1284, 1243, 1173, 1030, 821. ^{1}H NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 7.44 (d, 1H, $J = 5$ Hz), 7.38 (d, 1H, $J = 5$ Hz), 6.85 (d, 1H, $J = 4$ Hz), 6.77 (d, 1H, $J = 4$ Hz), 4.15 (dd, 1H, $J = 10$ Hz, $J = 5$ Hz), 3.90 (dd, 1H, $J = 10$ Hz, $J = 5$ Hz), 3.28 (q, 1H, $J = 5$ Hz), 2.61 (dd, 1H, $J = 5$ Hz, $J = 2.5$ Hz), 2.32 (dd, 1H, $J = 5$ Hz, $J = 2.5$ Hz).

2-((4-tert-Butylphenoxy)methyl)thiirane (Table 2, Entry 8)

Oil (*4b*). IR (neat, cm^{-1}) ν: 3039, 2962, 2900, 2868, 1513, 1245, 1185, 1033, 1013, 829. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 7.36 (d, 2H, $J = 8.8$ Hz), 6.91 (d, 2H, $J = 8.4$ Hz), 4.27 (dd, 1H, $J = 10.0$ Hz, $J = 5.2$ Hz), 3.93 (dd, 1H, $J = 10.0$ Hz, $J = 7.6$ Hz), 3.32 (q, 1H, $J = 5.2$ Hz), 2.65 (d, 1H, $J = 6.0$ Hz), 2.36 (d, 1H, $J = 5.2$ Hz), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 156.2, 144.0, 126.4, 114.2, 72.7, 34.1, 31.6, 31.5, 24.1.

2-((2-tert-Butyl-4-methylphenoxy)methyl)thiirane (Table 2, Entry 9)

IR (neat, cm^{-1}) ν: 3031, 2954, 2867, 1497, 1221, 1095, 1033, 1013, 804, 774. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 7.15 (d, 1H, $J = 1.6$ Hz), 7.01 (d, 1H, $J = 8.4$ Hz), 6.76 (d, 1H, $J = 8.4$ Hz), 4.23 (dd, 1H, $J = 10.0$ Hz, $J = 5.6$ Hz), 4.01 (dd, 1H, $J = 10.0$ Hz, $J = 6.8$ Hz), 3.38 (q, 1H, $J = 6.0$ Hz), 2.67 (d, 1H, $J = 6.0$ Hz), 2.39 (d, 1H, $J = 5.2$ Hz), 2.34 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ:

155.1, 137.9, 129.8, 127.7, 127.2, 112.1, 72.6, 34.8, 31.7, 29.9, 23.9, 20.8. EI-MS: m/z 236 (M^+). Elemental analysis data: C%: 71.07 (calc. 71.14); H%: 8.22 (calc. 8.35); S%: 13.43 (calc. 13.57).

2-((4-tert-Butyl-2-methylphenoxy)methyl)thiirane (Table 2, Entry 10)

IR (neat, cm^{-1}) ν: 3027, 2962, 2867, 1508, 1469, 1302, 1269, 1246, 1142, 1034, 807, 619, 611. ^1H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 7.28 (s, 1H), 7.21 (dd, 1H, $J = 8.4$ Hz, $J = 2.0$ Hz), 6.82 (d, 1H, $J = 8.4$ Hz), 4.28 (dd, 1H, $J = 10.4$ Hz, $J = 5.6$ Hz), 3.98 (dd, 1H, $J = 10.4$ Hz, $J = 7.2$ Hz), 3.36 (q, 1H, $J = 5.6$ Hz), 2.67 (d, 1H, $J = 6.0$ Hz), 2.40 (d, 1H, $J = 5.2$ Hz), 2.35 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 154.5, 143.7, 128.1, 126.4, 123.3, 111.2, 72.9, 34.1, 31.8, 31.6, 24.0, 16.6. EI-MS: m/z 236 (M^+); Elemental analysis data: C%: 71.07 (calc. 71.14); H%: 8.22 (calc. 8.35); S%: 13.43 (calc.13.57).

2-((Naphthalen-4-yloxy)methyl)thiirane (Table 2, Entry 11)

Oil (*4b*). IR (neat, cm^{-1}) ν: 3051, 2929, 2864, 1634, 1580, 1462, 1392, 1274, 1102, 910, 751, 624. ^1H NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 8.32 (dd, 1H, $J = 8$ Hz, $J = 4$ Hz), 7.77 (dd, 1H, $J = 8$ Hz, $J = 4$ Hz), 7.66–7.1 (m, 4 H), 6.78 (dd, 1H, $J = 8$ Hz, $J = 4$ Hz), 4.33 (dd, 1H, $J = 10$ Hz, $J = 5$ Hz), 4.07 (dd, 1H, $J = 10$ Hz, $J = 5$ Hz), 3.40 (q, 1H, $J = 5$ Hz), 2.66 (d, 1H, $J = 5$ Hz), 2.42 (d, 1H, $J = 5$ Hz)

2-((Naphthalen-3-yloxy)methyl)thiirane (Table 2, Entry 12)

m.p. 74°C, Lit (*12*): 74°C. IR (KBr, cm^{-1}) ν: 3059, 2928, 2855, 1629, 1599, 1469, 1389, 1260, 1220, 1186, 840, 742. ^1H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 7.78 (m, 3H) 7.48 (t, 1H, $J = 7.6$ Hz), 7.39 (t, 1H, $J = 7.2$ Hz), 7.21 (d, 1H, $J = 8.8$ Hz), 7.17 (s, 1H), 4.37 (dd, 1H, $J = 10.0$ Hz, $J = 5.2$ Hz), 4.06 (dd, 1H, $J = 10.0$ Hz, $J = 7.2$ Hz), 3.38 (q, 1H, $J = 6.0$ Hz), 2.69 (d, 1H, $J = 6.0$ Hz), 2.42 (d, 1H, $J = 5.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 156.4, 134.5, 129.6, 129.2, 127.7, 126.8, 126.5, 123.9, 118.8, 107.0, 72.6, 31.4, 24.1.

2-Butyl thiirane (Table 2, Entry 13)

Oil (*3a*).IR (neat, cm^{-1}) ν: 2921, 1435, 1259, 1108, 798, 612. ^1H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 2.16 (m, 3H), 1.84 (m, 2H), 1.53 (m, 2H), 1.41 (m, 2H), 1.28 (t, 3H).

2-(Chloromethyl)thiirane (Table 2, Entry 14)

Oil (*4n*). IR (neat, cm^{-1}) ν: 2955, 2925, 2853, 1721, 1678, 1527, 1422, 1347, 1218, 920, 747. ^1H NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 3.70–3.5 (d, $J = 5$ Hz, 2H), 3.10–3.00 (m, 1H), 2.50 (t, $J = 5$ Hz, 1H), 2.20 (dd, $J = 7.5$ Hz, 1H).

2-((Allyloxy)methyl)thiirane (Table 2, Entry 15)

Oil (*4n*). IR (neat, cm^{-1}) ν: 2990, 2958, 2929, 1716, 1637, 1452, 1333, 1313, 1293, 1158, 1046, 942, 813, 657, 618. ^1H NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 5.91 (m, 1H), 5.35 (dd, 1H, $J = 10$ Hz, $J = 4$ Hz), 5.16 (dd, 1H, $J = 5$ Hz, $J = 1.1$ Hz), 4.10 (d, 2H, $J = 5$ Hz), 3.58 (dd, 2H, $J = 10$ Hz, $J = 5$ Hz), 3.11 (q, 1H, $J = 5$ Hz), 2.56 (d, 1H, $J = 5$ Hz), 2.25 (d, 1H, $J = 5$ Hz).

2-(Isopropoxymethyl)thiirane (Table 2, Entry16)

Oil (*4n*). IR (KBr, cm^{-1}) ν: 2963, 2923, 2858, 1714, 1454, 1373, 1266, 1119, 1082, 739, 611, 457. ^1H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 3.67 (m, 2H), 3.41 (dd, 1H, $J = 10.4$ Hz, $J = 7.2$ Hz), 3.09 (q, 1H, $J = 5.6$ Hz), 2.55 (d, 1H, $J = 6.4$ Hz), 2.23 (d, 1H, $J = 4.8$ Hz), 1.20 (t, 6H, $J = 4.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 72.9, 72.0, 32.7, 24.2, 22.2, 22.1.

2-Methyl-6-(thiiran-2-yl)hex-1-en-3-one (Table 2, Entry 17)

Oil (*3c*). IR (KBr, cm^{-1}) ν: 2994, 2958, 2933, 1720, 1637, 1452, 1313, 1293, 1159, 1046, 942, 813, 618. ^1H NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 6.10 (q, 1H, $J = 1.1$ Hz), 5.58 (q, 1H, $J = 1.1$ Hz), 4.28 (d, 1H, $J = 5$ Hz), 4.17 (d, 1H, $J = 5$ Hz), 3.16 (q, 1H, $J = 5$ Hz), 2.57 (d, 1H, $J = 5$ Hz), 2.32 (d, 1H, $J = 5$ Hz), 1.93 (t,3H, $J = 1.1$ Hz).

Cyclohexene episulfide (Table 2, Entry 18)

Oil (*4n*). IR (KBr, cm^{-1}) ν: 2935, 2855, 1728, 1444, 1351, 1275, 1194, 1002, 754. ^1H NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 2.80 (m, 2H), 1.89 (m, 2H), 1.64 (m, 2H), 1.49 (m, 2H), 1.20 (m, 2H).

trans-Stilben episulfide (Table 2, Entry 19)

m.p. 51–53°C, Lit (*3a*): 53–54°C. IR (KBr, cm^{-1}) ν: 3077, 3057, 3031, 3020, 2990, 1597, 1495, 1451, 1282, 1221, 1071, 963, 855, 765, 744, 692, 615, 526. ^1H NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 7.38 (s, 10H), 3.90 (s, 2H).

1-Methylcyclohexene episulfide (Table 2, Entry 20)

Oil (*16*). IR (neat, cm^{-1}) ν: 2966, 2935, 2871, 1739, 1642, 1618, 1544, 1464, 1378, 1227, 1136, 1086, 912, 747, 650. ^1H NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 2.50 (t, 1H), 1.50–1.30 (m, 4H), 1.10–0.90 (m, 4H), 1.00 (s, 3H).

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