Convenient Syntheses of Chiral Cyclic Sulfinates (Sultines) from Unsaturated Alcohols

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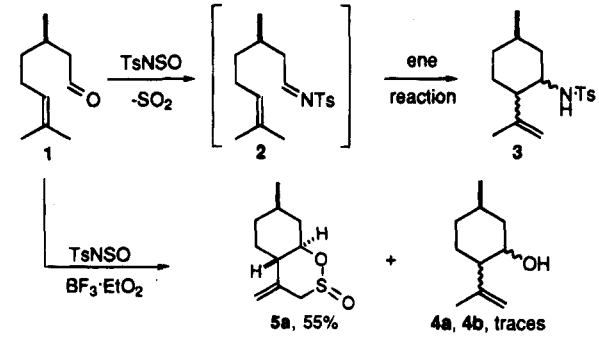
The reaction of unsaturated alcohols with *N*-sulfinyl-*p*-toluenesulfonamide (TsNSO) is shown to lead stereoselectively to chiral cyclic or bicyclic sulfinates (sultines). The reactions occur at ambient temperatures and afford a general route to δ- and ϵ-sultines which are notable for their crystallinity and thermal stability. These studies confirm the preservation of stereochemical integrity of the carbon atom α to the oxygen atom in the sultine ring. Some unsaturated aldehydes furnish sultines *via* a tandem oxo-ene cyclization and subsequent ring closure to the sultine. In some reactions, *N*-toluenesulfonamide derivatives of sultines (compounds of type **11**) were isolated, and since those were converted into the sultines by the action of $BF_3{\cdot}OEt_2$, such sulfonamides are considered to be intermediates in the reaction pathway.

Introduction

N-Toluenesulfonyl imines are extremely reactive and have been used to great effect by Weinreb and others as reactants in both imino-ene[1] and imino-Diels–Alder[2] reactions. During investigations into the imino-ene reaction,[1,3] we adopted known procedures[1,2,4] to obtain *N*-toluenesulfonyl imines such as **2** from aldehydes and *N*-sulfinyl-*p*-toluenesulfonamide (TsNSO) involving the elimination of sulfur dioxide. However, we have found that the more usual (formal) imino-ene reaction can be suppressed in favor of the formation of cyclic sulfinates (sultines). Thus, when (*R*)-citronellal (**1**) was reacted with TsNSO in the presence of boron trifluoride etherate the sultine **5a** was obtained, together with traces of the alcohols **4a** and **4b**. The ene products **3**, formed by reaction of TsNSO with the aldehyde and subsequent cyclization of the *N*-toluenesulfonyl imine **2**, were not detected (Scheme 1).

Cyclic sulfinates (sultines) are a fundamental heterocyclic system, and so a new general synthesis that proceeds stereoselectively and at ambient temperatures would be of value.[5] Although sultines have been long-known,[6] there are few relatively general methods for their synthesis,[5,7,8] and those usually proceed without stereocontrol.[9] Sultines can be versatile synthetic intermediates:[5] for example, they undergo ring-opening reactions,

Scheme 1



alkylation, and oxidation at sulfur to give sultones,[10] and reductive desulfurization. The stereogenic center at sulfur is of potential value in asymmetric synthesis. The generality of the reaction of unsaturated alcohols with TsNSO is herein described.

Results and Discussion

The structure of sultine **5a** was confirmed by single crystal X-ray crystallography.[11] The identification of the alcohols **4a** and **4b** indicated that these alcohols might be intermediates in the formation of the sultines. This hypothesis was tested using (−)-isopulegol **4a** and (+)-*neo*-isopulegol **4b**, the two major oxo-ene[12] products derived from (*R*)-citronellal (**1**). A commercial mixture of alcohols **4a** and **4b** was separated by column chromatography, and each alcohol was reacted with TsNSO under the conditions used for the corresponding reaction of (*R*)-citronellal (**1**).

Alcohol **4a** afforded sultine **5a** in 55% yield, and alcohol **4b** gave the sultine **5b** (75%) (Scheme 2). The reactions of alcohols **4a** and **4b** to give sultines **5a** and **5b**, respectively, suggest that the first step of the conversion of **1** into **5a** is the relatively fast oxo-ene reaction of (*R*)-citronellal to give a mixture of alcohols (of which iso-

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(1) (a) Tschaen, D. M.; Turos, E.; Weinreb, S. M. *J. Org. Chem.* **1984**, *49*, 5058. (b) Melnick, M. J.; Freyer, A. J.; Weinreb, S. M. *Tetrahedron Lett.* **1988**, *29*, 3891.

(2) (a) Sisko, J.; Weinreb, S. M. *Tetrahedron Lett.* **1989**, *30*, 3037. (b) Weinreb, S. M. *Bull. Soc. Chim. Belg.* **1992**, *101*, 381.

(3) For imino-ene reactions in nonactivated systems see: Demailly, G.; Solladie, G. *J. Org. Chem.* **1981**, *46*, 3102. Sakane, S.; Maruoka, K.; Yamamoto, H. *Tetrahedron* **1986**, *42*, 2203. For those in activated systems see: (a) Achmatowicz, O.; Pietrazkiewicz, M. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2680. (b) Achmatowicz, O.; Pietrazkiewicz, M. *Tetrahedron Lett.* **1981**, *22*, 4323.

(4) Kresze G.; Wucherpfennig, W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 149.

(5) Dittmer D. C.; Hoey M. D. In *The Chemistry of Sulfinic acids, Esters and Their Derivatives*; Patai, S., Ed.; Wiley: Chichester, 1990; p 240.

(6) Baumann, E.; Walter, G. *Chem. Ber.* **1893**, *26*, 2836.

(7) Sharma, N. K.; De Reinach-Hirtzbach, F.; Durst, T. *Can. J. Chem.* **1976**, *54*, 3012.

(8) King J. F.; Rathore, R. *Tetrahedron Lett.* **1989**, *30*, 2763.

(9) (a) Liskamp, R. M. J.; Blom, H. J.; Nivard, R. J. F.; Ottenheijm, H. C. J. *J. Org. Chem.* **1983**, *48*, 2733. (b) Liskamp, R. M. J.; Zeegers, H. J. M.; Ottenheijm, H. C. J. *J. Org. Chem.* **1981**, *46*, 5408.

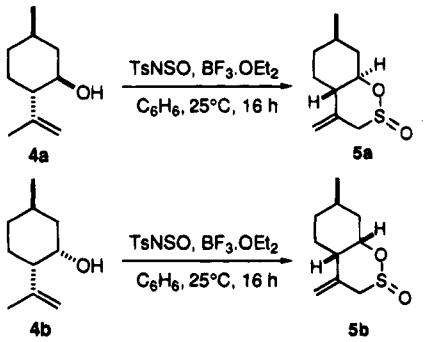
(10) Roberts D. W.; Williams, D. L. *Tetrahedron* **1987**, *43*, 1027.

(11) (a) Giles, P. R. Ph.D. Thesis, University of Sheffield, 1993. (b) Marson, C. M.; Giles, P. R.; Adams, H.; Bailey, N. A. *J. Chem. Soc., Chem. Commun.* **1993**, 1195.

(12) The cyclization of citronellal to isopulegols has been achieved using Lewis acids: Nakatani Y.; Kawashima, K. *Synthesis* **1978**, 147 and also thermally: Schulte-Elte, K. H.; Ohloff, G. *Helv. Chem. Acta* **1967**, *50*, 153.

0022-3263/95/1960-8067$09.00/0

Scheme 2



pulegol (**4a**) is the major isomer). The initial oxo-ene reaction may be a result of Lewis acid catalysis,[12] or more likely, a stepwise process catalyzed by residual Brönsted acid[12] present in the TsNSO.[13] The unsaturated alcohols subsequently react with TsNSO to yield the respective bicyclic sultines **5a** and **5b** (Scheme 2).

Having demonstrated that sultines could be satisfactorily prepared and with good stereocontrol from (−)-isopulegol (**4a**) and (+)-*neo*-isopulegol (**4b**), we reacted a range of cyclic and acyclic unsaturated alcohols **4c**−**r** (Table 1) with TsNSO in benzene in the presence of boron trifluoride etherate. It was possible that the acyclic alcohols, 2-methyl-2-propen-1-ol (**4m**) and 3-methyl-3-buten-1-ol (**4e**), would give five-membered (γ-sultine) and six-membered (δ-sultine) rings, respectively. The study was extended by examining whether the new heterocyclization could deliver a seven-membered ring (ϵ-sultine), derived from 4-methyl-4-penten-1-ol (**4o**).[14]

Each of the alcohols **4a**−**r**[15] was reacted with a solution of TsNSO[13] (1.5 equiv) in benzene at 20 °C; $BF_3{\cdot}OEt_2$ (1.5 equiv) was then added. The mixture was stirred for 12 h, water added, and the sultine and/or *N*-toluenesulfonamide isolated by column chromatography. The results are presented in Table 1. Entries 1 and 2 show that the reaction of the *cis*- and *trans*-cyclohexanols **4a** and **4b** with TsNSO are relatively selective, and afford the corresponding, thermally stable, sultines **5a** and **5b** in moderate to good yields. The structures of sultines **5a** and **5b** were confirmed by X-ray analysis.[11] As required, the relative configuration of **5b** as determined from its X-ray structure is consistent with the relative configuration of (+)-*neo*-isopulegol.[12] Both sultines **5a** and **5b** exhibit the preferred axial orientation of the sulfur−oxygen bond.[16]

Entries 3 and 4 show that although the unsaturated cyclopentanols **4c** and **4d** do afford the corresponding sultines, the reactions are not as efficient as for the cyclohexanols **4a** and **4b**. This may be due to facile rearrangements and oxidations of these substrates under acidic conditions, as reported by Ladner[15] and Snider,[17] although the reactions were carried out in the presence of a catalytic amount of sodium acetate to minimize rearrangement.[14] The *cis*-cyclopentanol **4d** (entry 4) afforded a fair yield of the sultine **5d**, while the *trans*-alcohol (entry 3) was somewhat poorer in its selectivity and yields. Additionally, the sulfonamides **6c** and **6d** were isolated from these reactions, each as a single diastereoisomer, and were fully characterized. The structure and configuration of compound **6c** was also elucidated by X-ray crystallography.[11]

In order to distinguish whether the sulfonamides **6c** and **6d** were byproducts or intermediates in the reactions, both sulfonamides were reacted with 2 equiv of $BF_3{\cdot}OEt_2$ in dichloromethane (owing to the poor solubility of those sulfonamides in benzene). After 12 h at 20 °C ^{1}H NMR spectra[18] of the reaction mixtures after workup showed *only* the corresponding sultines **5c** and **5d**, together with *p*-toluenesulfonamide ($TsNH_2$) and a trace of starting material. Similarly, the alcohol **4e** (entry 5) afforded the lesser substituted sultine **5e** together with the sulfonamide **6e**. The notion that the sulfonamide was a possible intermediate in the reaction was tested by reacting sulfonamide **6e** with $BF_3{\cdot}OEt_2$. Again, only the sultine **5e** and $TsNH_2$ were detected in the ^{1}H NMR spectrum of the crude material. These observations strongly suggest that sulfonamides such as **6c**, **6d**, and **6e** are intermediates in the reaction pathway.

The effect of 1- *versus* 2-monosubstitution is shown in the pairs of entries 7 and 8, and 9 and 10. Such substitutions limit the flexiblity of the alkyl chain and might be expected to enhance the cyclization in terms of the Thorpe−Ingold effect.[19] Conversely, the much lower yields of sultines obtained from the 1,1-disubstituted alcohols can be accounted for by irreversible ionization with loss of sulfur dioxide[20] and recombination of the resulting ion-pair to give the *N*-toluenesulfonamide **6k**, thus disfavoring cyclization of the reaction intermediate(s) to form the sultine **5k**.

It was considered that the use of allylic alcohols such as **4m** might furnish γ-sultines (entries 11 and 12). However, when 2-methylprop-2-en-1-ol was reacted with

(13) TsNSO was prepared as described in: Hori, T.; Singer, S. P.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1456. TsNSO may be also be prepared under nonacidic conditions: Kim, Y. H.; Shin, J. M. *Tetrahedron Lett.* **1985**, *26*, 3821.

(14) Ansell, M. F.; Thomas, D. A. *J. Chem. Soc.* **1958**, 449.

(15) The *trans*- and *cis*-cyclopentanols **4c** and **4d** were prepared by the cyclization of 3,3,7-trimethylhept-6-enal with tin(IV) chloride: Anderson, N. H.; Ladner, D. W. *Synth. Commun.* **1978**, 449. Cyclopentanone, cyclohexanone, and cyclododecanone afforded the alcohols **4f**: Crane, G.; Boord, C. E.; Henne, A. L. *J. Am. Chem. Soc.* **1945**, *67*, 1237; **4g**: Murai, A.; Ono, M.; Masamune, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1226 and **4h** on reaction with 2-methyl-2-propenylmagnesium chloride. The alcohol **4i** was prepared from benzaldehyde: Wulff, J; Huisgen, R.; *Chem. Ber.* **1969**, *102*, 1841. 3-Phenyl-4-hydroxybutan-2-one, prepared as described by: (a) Pickering, J. Ph.D. Thesis, University of Sheffield, 1993. (b) Marson, C. M.; Walker, A. J.; Pickering, J.; Hobson, A. D.; Wrigglesworth, R.; Edge, S. J. *J. Org. Chem.* **1993**, *58*, 5944 underwent methylenation (27%) using the procedure described by: Lombardo, L. *Org. Synth.* **1987**, *65*, 81. Propanone and 2-methyl-2-propenylmagnesium chloride afforded alcohol **4k** by inverse addition. 2,2,3-Trimethyl-3-buten-1-ol **4l** (23%) was prepared by Wittig methylenation of the corresponding ketone. *trans*-2-(2-Methyl-2-butenyl)cyclopentan-1-ol (**4p**) was prepared from cyclopentene oxide and 2-methyl-2-propenylmagnesium chloride: (a) Hegedus, L. S.; Holden, M. S.; McKearin, J. M. *Org. Synth.* **1984**, *62*, 48. (b) McGregor, J. Ph.D. Thesis, University of Sheffield, 1993. The acyclic alcohols **4q** and **4r** were prepared by reacting *cis*- and *trans*-2,3-epoxybutane, respectively, with 2-methyl-2-propenylmagnesium chloride in the presence of copper(I) iodide: (a) Huynh, C.; Derguini-Boumechal, F.; Linstrumelle, G. *Tetrahedron Lett.* **1979**, *20*, 1503. (b) Linstrumelle, G.; Lorne, R.; Dang, H. P. *Tetrahedron Lett.* **1978**, *19*, 4069.

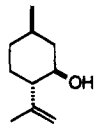
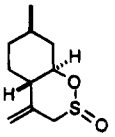
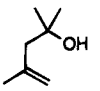
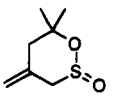
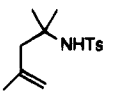
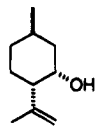
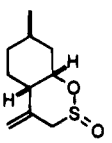
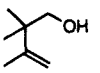
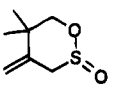
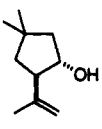
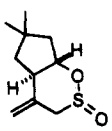
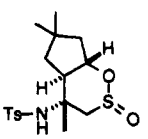
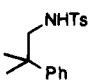
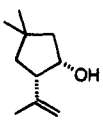
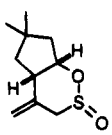
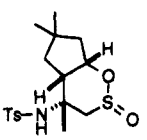
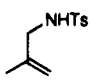
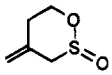
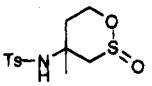
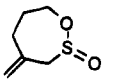
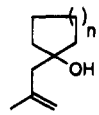
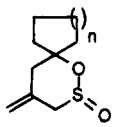
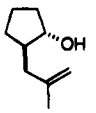
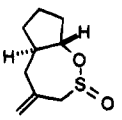
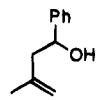
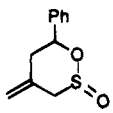
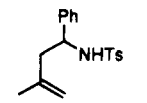
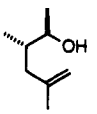
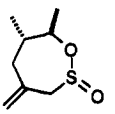
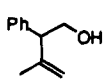
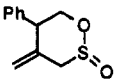
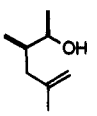
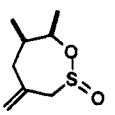
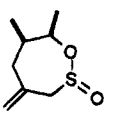
(16) For X-ray structural determinations of sultines, see: (a) Breau, L.; Sharma, N. K.; Butler, I. R.; Durst, T. *Can. J. Chem.* **1991**, *69*, 185. (b) Gray, M. D. M.; Russell, D. R.; Smith, D. H. J.; Durst, T.; Gimbarzevsky, B. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1826. (c) Surcouf, E. *Acta Cryst.* **1979**, *35B*, 1922 and 1925.

(17) Snider, B. B.; Phillips, G. B. *J. Org. Chem.* **1984**, *49*, 183.

(18) The axial and equatorial isomers could be readily distinguished by ^{1}H NMR spectroscopy. Additionally, an axial S=O linkage induces a large difference in chemical shift (0.4−0.8 ppm) of the two adjacent methylene hydrogen atoms, typically $\delta_{Hax} - \delta_{Heq} = 0.4$ ppm. For conformational analysis of sultines by NMR spectroscopy, see: Harpp, D. N.; Gleason, J. G. *J. Org. Chem.* **1971**, *36*, 1314. Buchanan, G. W.; Sharma, N. K.; De Reinach-Hirtzbach, F.; Durst, T. *Can J. Chem.* **1977**, *55*, 44.

(19) (a) Jung, M. E.; Gervay, J. *J. Am. Chem. Soc.* **1991**, *113*, 224. (b) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc.* **1915**, *107*, 1080. (c) Ingold, C. K. *J. Chem. Soc.* **1921**, *119*, 3054.

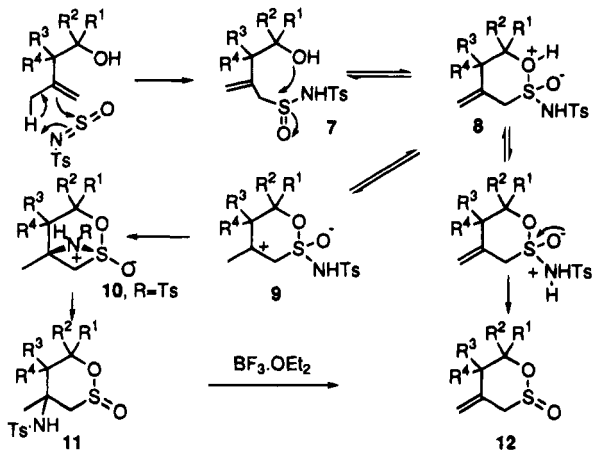
Table 1

Entry	Alcohol[a]	Sultine[b]	*N*-Toluenesulfonamide	Entry	Alcohol	Sultine	*N*-Toluenesulfonamide
1	 **4a**	 **5a**, 55%	–	9	 **4k**	 **5k**, 17%	 **6k**, 26%
2	 **4b**	 **5b**, 75%	–	10	 **4l**	 **5l**, 64%	–
3	 **4c**	 **5c**, 17%	 **6c**, 26%	11	 **4m**	–	 **6m**, 26%
4	 **4d**	 **5d**, 49%	 **6d**, 14%	12	 **4m**	–	 **6n**, 25%
5	 **4e**	 **5e**, 32%	 **6e**, 6%	13	 **4o**	 **5o**, 47%	–
6[c]	 **4f**, n=1; **4g**, n=2; **4h**, n=7	 **5f-5h**	–	14	 **4p**	 **5p**, 47%	–
7	 **4l**	 **5l**, 11%	 **6l**, 11%	15	 **4q**	 **5q**, 38%	–
8	 **4j**	 **5j**, 69%	–	16	 **4r**	 **5r**, 10%	 **6r**, 10%

[a]Standard reaction conditions: TsNSO-$BF_3 \cdot OEt_2$ in benzene, 12 h,20°C. [b]Epimer ratios of axial:equatorial S=O: 9:1 (**5c**), 1:1 (**5d**), 5:2 (**5j**), 7:2 (**5p**). [c]unstable products identified by ^1H NMR spectroscopy.

TsNSO in benzene, only the *N*-toluenesulfonamide **6m** was isolated. Amide **6m** is presumably formed by the ionization and subsequent trapping of the tertiary carbocation by benzene, resulting in a Friedel–Crafts alkylation. Not unexpectedly, preclusion of Friedel–Crafts alkylation by using dichloromethane as the reaction solvent afforded the unsaturated *N*-toluenesulfonamide **6n** as the only product isolated. Notably, signals for the exocyclic alkene or the hydrogen atoms α to the sulfur center were absent in the crude NMR spectra of both reactions. Since it appeared that γ-sultines could not be formed by this process, our attention turned to the possible synthesis of ε-sultines. Entry 13 illustrates that a seven-membered sultine **5o** can be formed from alcohol **4o**, and entry 14 shows that a *trans*-fused 5,7-ring system **5p** is formed in fair yield by the TsNSO reaction. Sultine **5p** is sufficiently stable, which contrasts markedly with the *cis*- or *trans*-5,6-systems **5c** and **5d** (stable for at most 2–3 days), possibly indicating that ring strain in sultines may be contributing to the lowering of yields. Entries 15 and 16 illustrate once more that the substitution of the alkyl chain is crucial to the outcome of the reaction. *trans*-1,2-Disubstitution of the alkyl chain cleanly gave the sultine **5q**, no *N*-toluenesulfonamide being detected. However, the analogous *cis*-1,2-disubstitution (entry 16) afforded a 1:1 mixture of the sultine **5r** and the amide **6r**. The far greater yield of **5q** as compared with the epimeric **5r** is consistent with the development of nonbonding eclipsing interactions between the methyl groups in the transition state leading to **5r**. In all cases, the S=O linkage was found to adopt an axial orientation, attributable to dipole minimization.[18]

Scheme 3



The reaction of TsNSO with substituted alcohols which afford appreciably stabilized carbocations has been reported by McFarland[20] to give *N*-toluenesulfonamides in moderate to good yields, small amounts of ethers and sulfites being isolated as byproducts. Attack of the alcohol on TsNSO affords the corresponding *N*-sulfinyl ester which may undergo attack by another molecule of the alcohol at *sulfur*, forming a sulfite, or which may be attacked at *carbon*, leading to an ether.[20] If the carbocation that would be generated by loss of sulfur dioxide is sufficiently stabilized, then the *N*-sulfinyl ester may lose sulfur dioxide to give an ion pair which can recombine to form the substituted *N*-toluenesulfonamide. The thermal conditions used by McFarland favor the liberation of the sulfur dioxide. It seems likely that all of these reactions will occur to some extent for any given alcohol. Indeed, relatively unpolar compounds, detected by TLC, had been formed in the present reactions.

The first step may be the ene reaction of the N=S bond (a powerful enophile[1]) with the allylic moiety, to form the intermediate **7** (Scheme 3). Attack of the alcohol on the sulfur atom would give the zwitterion **8** which can eliminate $TsNH_2$ to form the sultine **12**. Alternatively, protonation of the alkene could afford the zwitterion **9**, which by intramolecular nucleophilic attack of nitrogen would give the sulfonamide **11**, *via* the intermediate **10**. In this study, several sulfonamides **11** were shown to be converted *only* into the sultines **12** (and $TsNH_2$) upon treatment with $BF_3{\cdot}OEt_2$.

An alternative pathway would involve attack of the hydroxy group at TsNSO as the first step. It seems likely that at least in some examples of 1-substituted or 1,1-disubstituted alcohols, that is the preferred pathway, with subsequent C–O bond cleavage being enhanced by the increased stability of the secondary or tertiary carbocation that would result. This would then account for the formation of the unsaturated *N*-toluenesulfonamides.

The initial steps of the reaction cannot currently be definitively stated. However, the formation of γ-sultines, *e.g.* as from alcohol **4m**, would not be expected, since by analogy a strained [3.1.1]bicyclo intermediate would be required. Consequently, alcohol **4m** gave products derived chiefly from sulfonamide fragmentation: in dichloromethane, the corresponding *N*-toluenesulfonamide **6n**, and in benzene, the Friedel–Crafts alkylation product **6m**.

New, convenient and stereocontrolled syntheses of functionalized δ- and ϵ-sultines from unsaturated alcohols have been provided. In most cases, the relative configuration of the sultines was determined, a notable feature being the isolation of new, highly crystalline and thermally stable sultines. These studies confirm that the stereochemical integrity of the carbon atom α to the ring oxygen is preserved. It is concluded that *N*-toluenesulfonamides of the type **11** are intermediates in the reaction pathway. A study of the effects of different solvents and Lewis acids is to be undertaken, and the interplay of intitial *O- versus C*-attack of the unsaturated alcohol is to be addressed.

Experimental Section

Materials and Methods. All melting points are uncorrected. NMR spectra were run in $CDCl_3$; chemical shifts are quoted in ppm downfield from internal tetramethylsilane. ^1H and ^{13}C NMR spectra were recorded at 250 MHz and at 62.8 MHz, respectively. Mass spectra were obtained operating in chemical ionization (CI) using methane or in electron impact (EI) mode. Infrared spectra were obtained as a thin film or a KBr disc. TLC was performed on aluminum-backed silica plates and visualized using ultraviolet radiation or developed using cerium(IV) sulfate spray or iodine. Column chromatography was performed using Merck silica gel 60 (230–400 mesh). Solutions were dried over sodium sulfate unless otherwise stated. Evaporation refers to the removal of solvent under reduced pressure.

The following compounds were prepared according to literature procedures: *N*-sulfinyltoluenesulfonamide;[13] 4-methylpent-4-en-1-ol;[14] 2,2,3-trimethyl-3-buten-1-ol.[21]

Reaction of *(R)*-Citronellal (1) with TsNSO–$BF_3{\cdot}OEt_2$. TsNSO (0.81 g, 3.47 mmol) was dissolved in benzene (20 mL) and cooled to 10 °C. *(R)*-Citronellal (**1**) (0.30 g, 1.95 mmol) was added, followed by $Et_2O{\cdot}BF_3$ (0.15 mL, 2.01 mmol). The yellow solution gradually darkened to deep red over 4 h. Water (10 mL) was then added, the mixture stirred for 5 min, and the organic layer separated, and the aqueous layers were extracted with dichloromethane (2 × 10 mL). The organic layers were combined, dried, and evaporated. The residue was dissolved in dichloromethane (50 mL) and silica (5 g) added; the solvent was carefully removed by rotary evaporation and the dry silica loaded onto a preprepared chromatography column. Column chromatography (9:1 petroleum ether–ethyl acetate) afforded the *cis*- and *trans*-sultines (165 mg, 42.5%) as an amorphous solid. This material was recrystallized from petroleum to give the *trans*-sultine **5a** as white needles: mp 96–99 °C; ν_{max} (KBr disc) 1650 (w), and 1120 cm^{-1}; $[\alpha]_D$ = +306° ($CHCl_3$); δ_H 5.10 (1H, bd s), 5.02 (1H, bd s), 4.33 (1H, t of d, J = 10 and 4.5 Hz), 3.60 (1H, d, J = 15 Hz), 3.20 (1H, d, J = 15 Hz), 2.08 (1H, bd t, J = 10 Hz), 1.9–1.0 (7H, m), and 0.97 (3H, d, J = 6 Hz); δ_C 135.5 (s), 115.2 (t), 75.2 (d), 60.7 (t), 46.4 (d), 40.5 (t), 33.7 (t), 31.7 (d), 26.5 (t), and 22.0 (q); m/z (CI) 218 (M + 18, 12%), 201 (M + 1), 184 (3), 170 (2), and 154 (100). Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.99; H, 8.05. Found: C, 59.83; H, 7.93.

(–)-Isopulegol (4a) and (+)-*neo*-Isopulegol (4b). Separation of commercial isopulegol was achieved by column chromatography using petroleum ether–ethyl acetate (9:1) as eluant to give (+)-*neo*-isopulegol (**4b**): R_f 0.39; δ_H 4.95 (1H, bd s), 4.78 (1H, bd s), 4.0 (1H, bd s), 1.8 (3H, s), and 0.90 (3H, d, J = 6 Hz); δ_C 147.3 (s), 111.3 (t), 66.3 (d), 48.4 (d), 40.9 (t), 34.7 (t), 25.8 (q), 23.9 (t), 22.7 (d), and 22.2 (q); and (–)-isopulegol (**4a**); R_f 0.28; $[\alpha]_D$ = −19° (lit.,[12] −22°); δ_H 4.85 (2H, m), 3.46 (1H, t of d, J = 10 and 4.5 Hz), 1.7 (3H, m, J = 0.5 Hz), and 0.90 (3H, d, J = 6 Hz); δ_C 146.6 (s), 112.7 (t), 70.3 (d), 54.0 (d), 42.6 (t), 34.2 (t), 31.4 (q), 29.6 (t), 22.2 (d), and 19.1 (q).

(20) McFarland, J. W.; Schmidt, D.; Zwanenburg, B. *Tetrahedron* **1981**, *37*, 389.

(21) Schneider, R. A.; Meinwald, J. *J. Am. Chem. Soc.* **1967**, *89*, 2023.

4,4-Dimethyl-2-(2-propenyl)-cyclopentan-1-ols (4c and 4d). To a solution of 3,3,7-trimethylhept-6-enal[14] (1.0 g, 6.5 mmol) in benzene (100 mL) and a trace of sodium acetate (20 mg) stirred at 0 °C was added tin(IV) chloride (2 mL, 0.5 M in benzene). The mixture was stirred for 1 h and then poured into ice-cold saturated ammonium chloride solution (50 mL), the aqueous layers were washed with ether (3 × 50 mL) and dried (K_2CO_3), and the solvent was removed. The residue was purified by column chromatography (9:1 petroleum ether–ethyl acetate) to give the *cis*-isomer **4d**[14] (191 mg, 19%) as a colorless oil: R_f 0.51; δ_H 4.99 (1H, m), 4.81 (1H, s), 4.2 (1H, t, J = 4 Hz), 2.60 (1H, m), 2.0–1.0 (4H, m), 1.8 (3H, s), 1.15 (3H, s), and 1.02 (3H, s); and the *trans*-isomer **4c**[14] (341 mg, 34%) as a colorless oil: R_f 0.35; δ_H 4.80 (2H, m), 4.05 (1H, t, J = 8 Hz), 2.52 (1H, m), 2.0–1.0 (4H, m), 1.71 (3H, s), 1.11 (3H, s), and 1.03 (3H, s).

General Procedure for the Preparation of Alcohols (4f–i,k,o–r). To powdered magnesium (1.56 g, 65 mmol) in THF (10–30 mL) were added a crystal of iodine and a few drops of 1-chloro-2-methylprop-2-ene. Once the exothermic reaction had commenced, the remainder of the chloride (to a total of 60 mmol) was added at such a rate so as to maintain gentle reflux. The cloudy suspension was allowed to cool and then added dropwise to the carbonyl compound or oxirane (1 equiv in 10–20 mL of THF). The mixture was stirred for 2–16 h (completion monitored by TLC) and then poured into saturated ammonium chloride solution. The aqueous layer was extracted with ether (3 × 50 mL), the combined organic layers were dried, and the solvent was evaporated to afford the crude product which was purified as specified below.

1-(2-Methylprop-2-enyl)dodecan-1-ol (4h). 2-Methyl-2-propenylmagnesium chloride was reacted with cyclododecanone (2.0 g, 11.1 mmol). The crude product was recrystallized from petroleum to afford the alcohol **4h** (2.46 g, 96%) as colorless oblong crystals: mp 53–55 °C; δ_H 4.95 (1H, m), 4.75 (1H, m), 2.12 (2H, s), 1.88 (3H, bd s), and 1.7–1.2 (22H, m); δ_C 142.9 (s), 114.8 (t), 74.9 (s), 48.1 (t), 34.9 (t, 2 signals), 26.6 (t, 2 signals), 26.0 (t), 25.2 (q), 22.7 (t, 2 signals), 22.3 (t, 2 signals), and 19.8 (t, 2 signals). Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.61. Found: C, 80.92; H, 12.68.

3-Methyl-2-phenylbut-3-en-1-ol (4j). A slurry of zinc dust (1.73 g, 26.5 mmol) and dibromomethane (0.61 g, 8.7 mmol) in THF (15 mL) was cooled to an external temperature of between −50 and −40 °C (acetone–CO_2 bath) under an atmosphere of nitrogen, prior to the dropwise addition of titanium tetrachloride (0.70 mL, 6.26 mmol) over 15 min. After the addition was complete, the flask was kept in a refrigerator for 3 days and stirred periodically. The flask was then placed in an ice-bath and dry dichloromethane (15 mL) added. 1-Hydroxy-2-phenylbutan-3-one[15] (0.8 g, 4.81 mmol in 10 mL of dichloromethane) was added dropwise over 10 min. The ice-bath was removed and the mixture allowed to stir at 20 °C for 1.5 h. Petroleum (70 mL) was added, followed by dropwise addition of a slurry of sodium hydrogen carbonate (4 g in 10 mL water) (CAUTION: initial addition must be slow in order to avoid vigorous effervescence). After the addition, the petroleum layer was decanted and the viscous inorganic materials were triturated with petroleum (2 × 50 mL). The combined organic layers were dried over a 1:1 mixture of sodium hydrogen carbonate and sodium sulfate for 10 min and filtered, the solvent was removed, and the residue was purified by column chromatography (9:1 petroleum ether–ethyl acetate) to give **4j** (219 mg, 27%): ν_{max} (film) 3400 (b), 1650 (w), 1600, and 1490 (w) cm^{-1}; δ_H 7.4–7.2 (5H, m), 5.0 (1H, m), 4.92 (1H, m), 3.96 (1H, d, J = 8 Hz), 3.84 (1H, d, J = 8 Hz), 3.45 (1H, t, J = 8 Hz), 1.7 (1H, s, OH), and 1.65 (3H, d, J = 8 Hz); δ_C 145.1 (s), 140.2 (s), 128.6 (d, 2 lines), 128.2 (d, 2 lines), 127.0 (d), 64.5 (t), 55.0 (d), and 21.9 (q); m/z (EI); 162 (3%, M); 144 (19), 131 (100), 115 (26), 103 (10), 91 (56), and 77 (15). HRMS calcd for $C_{11}H_{14}O$ 162.0145, found 162.1047.

1,1,3-Trimethylbut-3-en-1-ol (4k). 2-Methyl-2-propenylmagnesium chloride and excess propanone were reacted by inverse addition; purification by column chromatography (9:1 petroleum ether–ethyl acetate) gave **4k** as an oil: δ_H 4.95 (1H, m), 4.83 (1H, m), 2.22 (2H, s), 1.86 (3H, m), and 1.05 (6H, s); δ_C 143.0 (s), 114.7 (t), 70.5 (s), 51.2 (t), 29.7 (q, 2 signals), and 24.9 (q); m/z (EI) 123 (M − 1, 3%), 99 (72), and 83 (100). The intensity of the parent ion was too weak to obtain an accurate HRMS measurement.

***threo*-1,2,4-Trimethylpent-4-en-1-ol (4q).** To a suspension of copper(I) iodide (55 mg, 0.29 mmol) and *cis*-2,3-epoxybutane (0.50 g, 6.9 mmol) in THF (40 mL) was added dropwise 2-methyl-2-propenylmagnesium chloride, keeping the temperature at −40 °C. The mixture was stirred for 1 h and then poured into a saturated solution of ammonium chloride (40 mL). The aqueous layer was extracted with ether (3 × 50 mL), the combined organic layers were washed with brine and dried, and the solvent was evaporated to give a residue which was purified by column chromatography (9:1 petroleum ether–ethyl acetate), giving **4q** (502 mg, 50%) as an oil: δ_H 4.75 (1H, m), 4.71 (1H, m), 3.73 (1H, quintet), 2.2–0.9 (3H, m), 1.71 (3H, s), 1.15 (3H, d, J = 7 Hz), and 0.81 (3H, d, J = 6 Hz); δ_C 144.7 (s), 111.7 (t), 71.9 (d), 41.8 (t), 37.3 (d), 22.1 (q), 19.5 (q), and 14.6 (q); m/z (EI), 128 (M$^+$, 3%), 109 (52), 95 (100), and 83 (52). The intensity of the parent ion was too weak to obtain an accurate HRMS measurement.

***erythro*-1,2,4-Trimethylpent-4-en-1-ol (4r).** 2-Methyl-2-propenylmagnesium chloride and *trans*-2,3-epoxybutane (0.50 g, 2.9 mmol) were reacted as described above for *cis*-2,3-epoxybutane; the residues were purified by column chromatography (9:1 petroleum ether–ethyl acetate) to give **4r** (513 mg, 57%): δ_H 4.75 (1H, s), 4.71 (1H, s), 3.62 (1H, quintet), 2.2–1.6 (3H, m), 1.70 (3H, s), 1.50 (1H, bd s, OH), 1.15 (3H, d, J = 7 Hz), and 0.81 (3H, d, J = 7 Hz); δ_C 144.5 (s), 111.8 (t), 70.8 (d), 41.5 (t), 37.2 (d), 22.1 (q), 20.2 (q), and 13.7 (q); m/z (EI), 128 (M$^+$, 2%), 109 (50), 95 (100), and 83 (54). The intensity of the parent ion was too weak to obtain an accurate HRMS measurement.

General Procedure for the Reaction of Unsaturated Alcohols with TsNSO–BF_3·OEt_2. TsNSO (1.5 equiv)[13] was dissolved in benzene (10–20 mL). The appropriate alcohol (1 equiv) was added, followed by BF_3·OEt_2 (1.5 equiv). The yellow solution was stirred for 12 h, prior to addition of water (1–5 mL). The organic layer was separated, and the aqueous layers were extracted with dichloromethane (2 × 10 mL). The organic layers were combined and dried and the solvents removed. The residue was adsorbed onto silica as described for sultine **5a** and purified by column chromatography (9:1 petroleum ether–ethyl acetate) to give the products.

The following alcohols gave sultines and/or *N*-toluenesulfonamides:

Reaction of Isopulegol (4a) with TsNSO–BF_3·OEt_2. Alcohol **4a** (0.30 g, 1.95 mmol) gave the *trans*-sultine **5a** (218 mg, 55%). This sample was spectroscopically identical with the sultine prepared from the reaction of (*R*)-citronellal (**1**).

Reaction of *neo*-Isopulegol (4b) with TsNSO–BF_3·OEt_2. Alcohol **4b** (0.30 g, 1.95 mmol) gave the sultine **5b** (293 mg, 75%) as an amorphous solid, which was recrystallized from petroleum to give the product as white needles, mp 98–101 °C; ν_{max} (KBr disc) 1650 (bd, w), 1150, and 1120 cm^{-1}; δ_H 5.35 (1H, bd s), 5.11 (1H, m), 5.02 (1H, m), 3.80 (1H, d, J = 15 Hz), 3.12 (1H, d, J = 15 Hz), 2.41 (1H, d of m, J = 10 Hz), 2.05 (1H, bd t, J = 10 Hz), 2.1–1.0 (7H, m), and 1.05 (3H, d, J = 6 Hz); δ_C 136.6 (s), 117.5 (t), 69.0 (d), 54.5 (t), 44.6 (d), 38.9 (t), 33.7 (t), 26.0 (q), 25.4 (t), and 22.1 (q); m/z (CI) 218 (M + 18, 12%), 201 (22), 152 (6), 137 (100), 121 (13), 107 (10), 93 (15), 81 (39), and 68 (10). Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.96; H, 8.05. Found: C, 60.22; H, 8.14.

Reaction of Alcohol 4c with TsNSO–BF_3·OEt_2. Alcohol **4c** (0.302 g, 1.94 mmol) gave the *trans*-sultine **5c** (67 mg, 17%) as an oil (9:1 mixture of epimers at sulfur); and the *N*-toluenesulfonamide **6c** as a white powder (159 mg, 26%): mp 189–190.5 °C; ν_{max} (KBr disc) 3200 (bd), 1340, 1160, and 1120 cm^{-1}; δ_H 7.76 (2H, d, J = 8 Hz, ArH), 7.31 (2H, d, J = 8 Hz, ArH), 5.31 (1H, bd s, NH), 4.65 (1H, t of d, J = 4 and 10 Hz), 3.02 (2H, s), 2.45 (3H, s), 2.18 (1H, t of d, J = 4 and 10 Hz), 2.0–1.1 (4H, m), 1.5 (3H, s), 0.98 (3H, s), and 0.95 (3H, s); δ_C 143.6 (s), 140.0 (s), 129.8 (d, 2 lines), 126.8 (d, 2 lines), 71.0 (d), 59.4 (t), 57.5 (t), 49.5 (d), 44.7 (t), 37.0 (t), 32.6 (t), 32.1 (q), 31.8 (q), 21.5 (q), and 20.8 (q); m/z (CI), 372 (M+1, 91),

306 (54), 224 (21) and 137 (100). Anal. Calcd for $C_{17}H_{25}NO_4S_2$: C, 54.96; H, 6.78; N, 3.77. Found: C, 55.04; H, 7.04; N, 3.72.

Reaction of Alcohol 4d with TsNSO–BF_3·OEt_2. Alcohol **4d** (0.30 g, 1.94 mmol) gave the *cis*-sultine **5d** (178 mg, 49%) as an oil (1:1 mixture of epimers at sulfur); δ_H 5.07 (1H, m), 5.00 (1H, m), 4.97 (1H, m), 4.48 (1H, m), 3.70 and 3.32 (1H, d, J = 15 Hz), 3.52 and 2.98 (1H, d, J = 15 Hz), 2.88 (1H, m), 2.00–1.42 (4H, m), 1.07 and 1.05 (3H, s), 1.00 (3H, s); and the *N*-toluenesulfonamide **6d** (92 mg, 14%) as a white powder, mp 222–226 °C; ν_{max} (KBr disc) 3200 (bd), 1330, 1160, and 1130 cm^{-1}; δ_H 7.78 (2H, d, J = 8 Hz), 7.31 (2H, d, J = 8 Hz), 4.95 (2H, m), 3.05 (1H, d, J = 15 Hz), 2.60 (1H, d, J = 15 Hz), 2.42 (3H, s), 2.25 (1H, t of d, J = 4 and 9 Hz), 2.0–1.5 (4H, m), 1.16 (3H, s), 1.15 (3H, s) and 0.98 (3H, s); δ_C 143.7 (s), 139.9 (d, 2 lines), 129.8 (d, 2 lines), 127.0 (d), 74.0 (d), 55.4 (t), 54.8 (t), 49.5 (d), 47.4 (t), 39.7 (t), 36.4 (t), 30.9 (q), 30.5 (q), 27.0 (q), and 21.5 (q). Anal. Calcd for $C_{17}H_{25}NO_4S_2$: C, 54.96; H, 6.78; N, 3.77. Found: C, 55.11; H, 6.69; N, 3.82.

Reaction of 3-Methylbut-3-en-1-ol (4e) with TsNSO–BF_3·OEt_2. Alcohol **4e** (0.4 g, 4.65 mmol) afforded the sultine **5e** as a pale yellow oil (196 mg, 32%): ν_{max} (film) 1650 (w), 1120 cm^{-1}; δ_H 5.22 (1H, bd s), 5.05 (1H, bd s), 4.59 (1H, t of d, J = 2 and 10 Hz), 4.03 (1H, d of d of m, J = 1, 7, and 7 Hz), 3.60 (1H, d, J = 14 Hz), 3.18 (1H, d, J = 14 Hz), 2.6 (1H, t of d, J = 3 and 10 Hz), and 2.36 (1H, bd, J = 10 Hz); δ_C 131.5 (s), 118.2 (t), 61.3 (t), 59.4 (t), and 34.2 (t); and the *N*-toluenesulfonamide **6e** (94 mg, 6%): mp 180–183 °C; δ_H 7.75 (2H, d, J = 8 Hz), 7.31 (2H, d, J = 8 Hz), 4.55 (1H, t of d, J = 1 and 10 Hz), 4.04 (1H, d of m, J = 10 Hz), 3.1 (1H, d, J = 15 Hz), 2.8 (1H, d, J = 15 Hz), 2.42 (3H, s), 2.25 (1H, m), 1.65 (1H, m), and 1.61 (3H, s); δ_C 143.4 (s), 140.0 (s), 129.7 (d, 2 lines), 126.6 (d, 2 lines), 58.3 (t), 58.0 (t), 52.8 (s), 36.1 (t), 26.1 (q), and 21.3 (q). Anal. Calcd for $C_{12}H_{17}NO_4S_2$: C, 47.51; H, 5.65; N, 4.62. Found: C, 47.50; H, 5.64; N, 4.62.

Reaction of 1-(2-Methylprop-2-enyl)cyclopentan-1-ol (4f) with TsNSO–BF_3·OEt_2. Alcohol **4f** gave the corresponding sultines **5f** (2–5%); discernible in the ^1H NMR spectra were the following characteristic signals for the sultine: δ_H 5.22 (1H, s), 5.15 (1H, s), 3.62 (1H, d, J = 15 Hz), and 3.20 (1H, d, J = 15 Hz).

Reaction of 1-(2-Methylprop-2-enyl)cyclohexan-1-ol (4g) with TsNSO–BF_3·OEt_2. Alcohol **4g** gave the corresponding sultines **5g** (2–5%); discernible in the ^1H NMR spectra were the following characteristic signals for the sultine: δ_H 5.15 (2H, m), 3.55 (1H, d, J = 15 Hz) and 3.10 (1H, d, J = 15 Hz).

Reaction of 1-(2-Methylprop-2-enyl)cyclododecan-1-ol (4h) with TsNSO–BF_3·OEt_2. Alcohol **4h** gave the corresponding sultines **5h** (2–5%); discernible in the ^1H NMR were the following characteristic signals for the sultine: δ_H 5.21 (2H, m), 3.63 (1H, d, J = 15 Hz), 3.15 (1H, d, J = 15 Hz), and 2.4 (2H, m).

The sultines obtained from the reactions of **14**, **15**, and **16** could not be purified sufficiently for characterization, either as the sultine or sultone. The samples readily decomposed over several hours.

Reaction of 3-Methyl-1-phenyl-3-buten-1-ol (4i) with TsNSO–BF_3·OEt_2. Alcohol **4i** (354 mg, 2.16 mmol) gave the sultine **5i** as a pale yellow oil (40 mg, 11%): δ_H 7.4–7.2 (5H, m, Ar H), 5.6 (1H, m), 5.31 (1H, s), 5.15 (1H, s), 3.67 (1H, d, J = 13 Hz), 3.25 (2H, d J = 13 Hz), and 2.66 (2H, m), δ_C 139.0 (s), 131.9 (t), 128.7 (d, 2 lines), 126.5 (d, 2 lines), 118.8 (s), 119.6 (t), 73.1 (d), 58.8 (t), and 41.7 (t); and *N*-toluenesulfonamide **6i** (76 mg, 11%): δ_H 7.5 (2H, d, J = 8 Hz), 7.2–7.0 (7H, m), 5.19 (1H, bd t, NH, J = 5 Hz), 4.8 (1H, m), 4.72 (1H, m), 4.48 (1H, m), 2.36 (5H, m), and 1.55 (3H, s); δ_C 143.0 (s), 140.9 (s), 129.2 (d, 2 lines), 128.5 (d, 2 lines), 128.3 (d, 2 lines), 127.3 (d), 126.2 (d, 2 lines), 115.2 (t), 55.6 (d), 46.7 (t), 30.1 (q), and 21.5 (q); m/z (EI) 313 (M, 1%); 260 (97), 155 (57), and 91 (100). The parent ion was too weak to allow an accurate HRMS measurement.

Reaction of 3-Methyl-2-phenyl-3-buten-1-ol (4j) with TsNSO–BF_3·OEt_2. Alcohol **4j** (211 mg, 1.30 mmol) gave the sultine **5j** as a 5:2 *syn:anti*-mixture, a pale yellow oil (188 mg, 69%): δ_H 7.4–7.2 (5H, m, Ar H), 5.29 (1H, s), 5.01 (1H, s), 4.83 (1H, d of d, J = 6 and 10 Hz), 4.62 (1H, d of d, J = 6 and 10 Hz), 3.90 (2H, s), and 3.75 (1H, m).

Reaction of 1,1,3-Trimethyl-3-buten-1-ol (4k) with TsNSO–BF_3·OEt_2. Alcohol **4k** (195 mg, 1.71 mmol) afforded the sultine **5k** as a pale yellow oil (19 mg, 17%): δ_H 5.18 (2H, m), 3.54 (1H, d, J = 15 Hz), 3.12 (1H, d, J = 15 Hz), 2.4 (1H, bd s), 1.5 (3H, s), and 1.34 (3H, s); and the *N*-toluenesulfonamide **6k** (121 mg, 26%): mp 104–105 °C; δ_H 7.71 (2H, d, J = 8 Hz), 7.20 (2H, d, J = 8 Hz), 4.90 (1H, m), 4.75 (1H, bd s, NH), 4.7 (1H, m), 2.35 (3H, s), 2.15 (2H, m), 1.72 (3H, s), and 1.15 (6H, s); δ_C 142.8 (s), 141.6 (s), 140.7 (s), 129.4 (d, 2 lines), 127.0 (d, 2 lines), 116.4 (t), 56.5 (s), 51.0 (t), 28.0 (q, 2 lines), 25.0 (q), and 21.5 (q). Anal. Calcd for $C_{14}H_{21}NO_2S$: C, 62.88; H, 7.91; N, 5.23. Found: C, 62.87; H, 7.85; N, 5.08.

Reaction of 2,2,3-Trimethyl-3-buten-1-ol (4l) with TsNSO–BF_3·OEt_2. Alcohol **4l** (375 mg, 3.29 mmol) afforded the sultine **5l** as a pale yellow oil (331 mg, 64%); ν_{max} (film) 1640 (w), 1140 (s) cm^{-1}; δ_H 5.2 (1H, s), 5.02 (1H, d, J = 0.9 Hz), 4.31 (1H, d, J = 10 Hz), 3.83 (1H, dt, J = 10 and 0.9 Hz), 3.48 (1H, d, J = 10 Hz), 3.30 (1H, d, J = 10 Hz), and 1.3 (3H, s), and 1.13 (3H, s); δ_C 139.4 (s), 115.9 (t), 69.6 (t), 57.1 (t), 37.0 (s), 24.0 (q), and 23.0 (q).

Reaction of 2-Methyl-2-propen-1-ol (4m) with TsNSO–BF_3·OEt_2. Alcohol **4m** (300 mg, 4.16 mmol) in benzene afforded the sulfonamide **6m** (328 mg, 26%) as a white solid: mp 123–124.5 °C; ν_{max} (KBr disc) 3300 (bd), 1590 (w), and 1310 cm^{-1}; δ_H 7.70 (2H, d, J = 8 Hz), 7.4–7.2 (7H, m, ArH), 4.5 (1H, bd s, NH), 2.87 (2H, s), 2.40 (3H, s), and 1.15 (6H, s); δ_C 142.9 (s), 140.6 (s), 136.6 (s), 130.8 (d, 2 lines), 129.4 (d, 2 lines), 128.3 (d, 2 lines), 126.9 (d, 2 lines), 126.8 (d), 56.9 (s), 49.0 (t), 27.4 (q, 2 lines), and 21.5 (q); m/z (CI) 325 (M + 18, 8%), 303 (M^+, 22), 286 (12), 261 (22), 222 (15), and 211 (100). Anal. Calcd for $C_{17}H_{21}NSO_2$: C, 67.30; H, 6.98; N, 4.62. Found: C, 67.15; H, 6.89; N, 4.59.

When the reaction was performed using dichloromethane as the solvent, the *N*-toluenesulfonamide **6n** (230 mg, 25%) was isolated as a viscous oil: ν_{max} 3300 (bd), 1660 (w), 1260 (bd s), and 1160 (bd s) cm^{-1}; δ_H 7.75 (2H, d, J = 8 Hz), 7.32 (2H, d, J = 8 Hz), 4.85 (2H, m), 4.4 (1H, bd t, J = 6 Hz), 3.46 (2H, d, J = 6 Hz), 2.42 (3H, s), and 1.70 (3H, s); δ_C 143.4 (s), 140.5 (s), 136.9 (s), 129.7 (d, 2 lines), 127.1 (d, 2 lines), 112.7 (t), 49.0 (d), 21.5 (q), and 20.1 (q); m/z (EI) 225 (M^+, 11), 155 (33), 91 (96), 70 (100), and 65 (24); HRMS calcd for $C_{11}H_{15}NSO_2$ 225.0823, found 225.0831.

Reaction of 4-Methyl-4-penten-1-ol (4o) with TsNSO–BF_3·OEt_2. Alcohol **4o** (300 mg, 3.0 mmol) afforded the sultine **5o** as a pale yellow oil (206 mg, 46%); ν_{max} (film) 1640 (w), 1140 cm^{-1}; δ_H 5.11 (1H, m), 4.97 (1H, s), 4.57 (1H, t of m, J = 10 Hz), 3.95 (1H, d of d, J = 10 and 1 Hz), 3.87 (1H, d, J = 14 Hz), 3.32 (1H, d, J = 14 Hz), 2.5–1.90 (3H, m); δ_C 135.6 (s), 119.0 (t), 66.2 (t), 62.1 (t), 35.9 (t), and 27.9 (t).

Reaction of *trans*-2-(2-Methylprop-2-enyl)cyclopentan-1-ol (4p) with TsNSO–BF_3·OEt_2. Alcohol **4p** (300 mg, 2.11 mmol) gave the sultine **5p** as a pale yellow oil (183 mg, 47%) and a 7:2 mixture of epimers at sulfur. The sultine was characterized as the sultone **7p**.

Reaction of *threo*-1,2,4-Trimethylpent-4-en-1-ol (4q) with TsNSO–BF_3·OEt_2. Alcohol **4q** (300 mg, 2.36 mmol) afforded the sultine **5q** as a colorless crystalline solid (154 mg, 38%): mp 52–56 °C; ν_{max} (KBr disc) 1640 (w), and 1270 cm^{-1}; δ_H 5.1–4.9 (3H, m), 3.88 (1H, d, J = 15 Hz), 3.32 (1H, d, J = 15 Hz), 2.4 (1H, m), 2.1 (1H, m), 1.82 (1H, m), 1.3 (3H, d, J = 6 Hz) and 0.93 (3H, d, J = 6 Hz); δ_C 133.6 (s), 119.6 (t), 71.8 (d), 67.8 (t), 44.5 (t), 34.7 (d), 20.8 (q) and 11.7 (q); m/z 174 (M^+, 1%), 109, (18), 95 (100), 81 (47), and 67 (56). Anal. Calcd for $C_8H_{14}O_2S$: C, 55.14; H, 8.14. Found: C, 55.14; H, 8.02.

Reaction of *erythro*-1,2,4-Trimethylpent-4-en-1-ol (4r) with TsNSO–BF_3·OEt_2. Alcohol **4r** (300 mg, 2.36 mmol) gave, after chromatography, an inseparable 1:1 mixture of sultine **5r** and *N*-toluenesulfonamide **6r** as an oil (102 mg). The following characteristic peaks for the sultine were detected: δ_H 5.01 (1H, bd s), 4.88 (1H, bd s), 4.54 (2H, m), 3.80 (1H, d, J = 14 Hz), 3.21 (1H, d, J = 14 Hz), 1.22 (3H, d, J = 6 Hz), and 0.88 (3H, d, J = 6 Hz).

General Procedure for the Oxidation of Sultines to Sultones. To a solution of the sultine (100–200 mg) in

dichloromethane (5–10 mL) were added *m*-chloroperbenzoic acid (*m*-CPBA) (1.2 equiv) and sodium hydrogen carbonate (0.5 g), and the reaction was stirred for 3–16 h (completion monitored by TLC). Potassium fluoride (0.5 g) was then added and the resulting suspension filtered. The filtrate was washed with aqueous sodium hydrogen carbonate (5%, 20 mL) and dried and the solvent removed. The residue was either recrystallized from petroleum ether–dichloromethane or purified by column chromatography, to afford the sultone.

Following the procedure above, the sultine **5c** (67 mg, 0.36 mmol) was characterized by oxidation to the corresponding sultone **7c** (53 mg, 75%) following the above procedure: mp 92-94 °C; ν_{max} (KBr disc) 1660 (w), and 1360 cm^{-1}; δ_H 5.12 (1H, m), 5.0 (1H, m), 4.45 (1H, t of d, J = 4 and 10 Hz), 3.91 (1H, d, J = 15 Hz), 3.72 (1H, d, J = 15 Hz), 2.54 (1H, m), 2.1–1.3 (4H, m), 1.29 (3H, s), and 1.13 (3H, s); δ_C 136.5 (s), 114.0 (t), 85.6 (d), 56.3 (t), 47.0 (d), 43.9 (t), 37.6 (t), 34.5 (s), 32.5 (q), and 31.9 (q), m/z (CI) 234 (M + 18, 12%), 216 (3), 135 (100), 108 (22), 93 (46), 79 (15), and 67 (10). Anal. Calcd for $C_{10}H_{16}O_3S$: C, 55.53; H, 7.46. Found: C, 55.69; H, 7.59.

The sultine **5d** (122 mg, 0.61 mmol) was characterized by oxidation to the corresponding sultone **7d** (106 mg, 79%) by oxidation: mp 90-91 °C; ν_{max} (KBr disc) 1650 (w), 1360 and 1280 cm^{-1}; δ_H 5.20 (1H, m), 5.08 (1H, m), 4.88 (1H, q, J = 1 Hz), 3.82 (1H, d of m, J = 15 Hz), 3.68 (1H, d, J = 15 Hz), 2.85 (1H, m), 1.8–1.5 (4H, m), 1.12 (3H, s), and 1.05 (3H, s); δ_C 136.0 (s), 118.7 (t), 90.6 (d), 52.1 (t), 46.8 (t), 46.3 (d), 43.2 (t), 37.5 (s), 31.2 (q), and 31.1 (q); m/z (CI) 234 (M + 18, 89%), 216 (3), 135 (100), 119 (22), 108 (34), 93 (41), and 81 (18). Anal. Calcd for $C_{10}H_{16}O_3S$: C, 55.53; H, 7.46%). Found: C, 55.22; H, 7.46.

The sultine **5e** (64 mg, 0.48 mmol) was characterized by oxidation to the sultone **7e** (51 mg, 72%), a pale yellow oil: δ_H 5.25 (1H, s), 5.20 (1H, s), 4.51 (2H, t, J = 4 Hz), 3.85 (2H, s), and 2.51 (2H, t, J = 4 Hz); HRMS calcd for $C_5H_8O_3S$ 148.0194, found 148.0189.

The sultine **5j** (188 mg, 0.90 mmol) was characterized by oxidation to the corresponding sultone **7j** (163 mg, 77%): mp 121–124 °C; ν_{max} (KBr disc) 1650 (w), 1350 (s), and 1180 cm^{-1}; δ_H 7.4–7.2 (5H, Ar H), 5.29 (1H, s), 5.01 (1H, s), 4.83 (1H, d of d, J = 6 and 10 Hz), 4.62 (1H, d of d, J = 6 and 10 Hz), 3.90 (2H, s), and 3.75 (1H, m); δ_C 137.8 (s), 135.4 (t), 129.1 (d, 2 lines), 128.3 (d, 2 lines), 128.1 (d), 119.6 (t), 74.2 (t), 56.0 (t), and 46.3 (d); m/z (CI) 224 (M^+, 10%), 159 (18), 143 (63), 129 (100), 115 (62), 91 (17), 64 (10), and 51 (17). Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39. Found: C, 58.80; H, 5.33.

The sultine **5l** (81 mg, 0.51 mmol) was characterized by oxidation to the corresponding sultone **7l** (68 mg, 74%): δ_H 5.15 (1H, m), 5.09 (1H, m), 4.15 (2H, s), 3.81 (2H, s), and 1.22 (6H, s); HRMS calcd for $C_7H_{12}O_3S$ 176.0500, found 176.0507.

The sultine **5o** (138 mg, 0.95 mmol) was oxidized to afford the corresponding sultone **7o** (121 mg, 77%) as a pale yellow oil: δ_H 5.24 (1H, m), 5.20 (1H, m), 4.41 (2H, t, J = 4 Hz), 4.02 (2H, m, J = 0.5 Hz), 2.51 (2H, d of t, J = 4 and 0.5 Hz), and 2.05 (2H, quintet); HRMS calcd for $C_6H_{10}O_3S$ 162.0351, found 162.0341.

The sultine **5p** (183 mg, 0.97 mmol) was characterized by oxidation to the corresponding sultone **7p** (147 mg, 74%): mp 49–51 °C; ν_{max} (KBr disc) 1650 (w) and 1340 (s) cm^{-1}; δ_H 5.22 (2H, m), 4.51 (1H, q, J = 6 Hz), 4.05 (2H, d of m, J = 15 Hz), 2.75 (1H, d of m, J = 15 Hz), 2.5–1.2 (8H, m); δ_C 134.9 (s), 121.9 (t), 86.3 (d), 59.2 (t), 45.0 (d), 39.0 (t), 31.1 (t), 30.9 (t), and 21.0 (t); m/z (CI) 203 (M + 1, 15%), 138 (8), 121 (100), and 105 (12). Anal. Calcd for $C_9H_{14}O_3S$: C, 53.44; H, 6.97. Found: C, 53.65; H, 6.93.

Reaction of Sulfonamides 6c–e with BF_3·Et_2O. Procedure illustrated for **6c**. To a solution of sulfonamide **6c** (41 mg, 0.108 mmol) in dichloromethane (5 mL) was added BF_3.Et_2O (0.03 mL, 0.22 mmol). The reaction was stirred for 15 h and then washed with water (3 mL) and dried, and the solvent was removed to leave the crude material (38 mg, 96% recovery). Analysis of the ^1H NMR of this material showed the presence of only the sultine **5c** and $TsNH_2$. Similarly, sulfonamides **6d** and **6e** were converted (96% recovery) into the respective sultines **5d** and **5e**.

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