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Synthesis and Diels-Alder Reactions of Prop-1-ene-1,3-sultone, and Chemical Transformations of the Diels-Alder Adducts

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Abstract: A reliable and novel synthetic route for the preparation of prop-1-ene-1,3-sultone (**1**) has been developed. An overall yield of 34% could be achieved for this five-step synthesis. The Diels-Alder reactions of **1** with a variety of dienes were investigated for the first time and achieved with good chemical yield and excellent *endo*-selectivity. The subsequent transformations of the Diels-Alder cycloadducts were also explored.

Introduction

In a simple synthetic operation, the Diels-Alder reaction allows the formation of two new sigma bonds in a stereo- and regioselective manner at the expense of two π bonds present in the starting materials. This versatile reaction has been regarded as an indispensable synthetic tool in organic synthesis. Numerous demonstrations of the utility of this reaction were found in the total synthesis of important natural products and biologically active compounds.

For the past decades, a great number of dienes and dienophiles have been developed for the Diels-Alder reaction.[1,2] With regard to the development of new dienophiles, various sulfur-containing functional groups have been used as dienophile activators. Vinyl sulfone,[3] sulfoxide[4] and sulfonate[5] have been utilised in the Diels-Alder reactions. We are also interested in utilising sulfur-containing functionalities as activating groups in the dienophile design. Recently, the syntheses of alkynyl sulfoxides, sulfinates, sulfonates and their subsequent use in Diels-Alder reactions have been reported by us.[6] To extend our interest in this area, we report herewith the preparation of prop-1-ene-1,3-sultone and its applications in Diels-Alder reactions. In addition, building on the well known chemistry of saturated sultones, through further manipulation of the Diels-Alder cycloadducts, we demonstrated that the unsaturated sultone could serve as the synthetic equivalent to many compounds which are poor dienophiles if used directly in Diels-Alder reactions.

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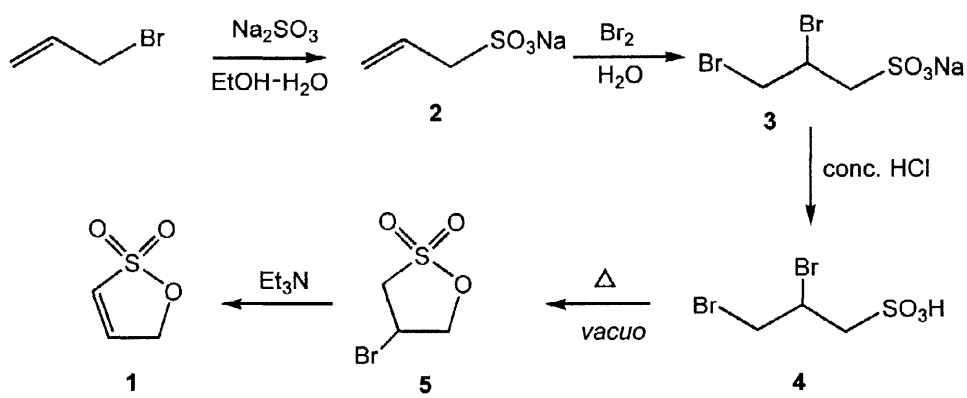
Results and Discussion

There are numerous synthetic routes documented in the literature for the preparation of saturated sultones.[7] In contrast, the syntheses of α,β-unsaturated sultones have received scarce attention in the literature. For instance, only three reports have been documented for the preparation of prop-1-ene-1,3-sultone (**1**).[8] However, all these synthetic routes are either not described in enough detail for reproduction or the starting materials are not generally ready available. In order to investigate its reactivity in the Diels-Alder reaction, the need to develop an expeditious synthesis of **1** is evident.

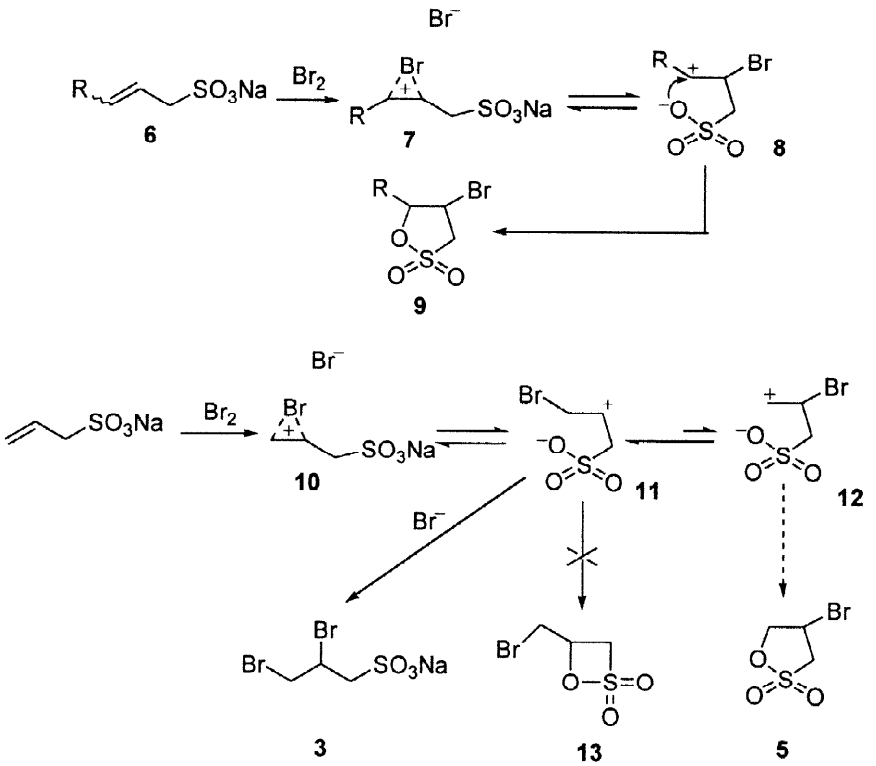
Our synthetic approach began with commercially available allyl bromide, according to the reaction sequence shown in Scheme 1.[9] Sulfonation of allyl bromide by refluxing sodium sulfite with 2 mol eq. of allyl bromide in a mixed solvent of water and ethanol for 2 h gave allyl sulfonate (**2**) in 78% yield after recrystallization twice in 95% EtOH.[10] Addition of bromine to **2** in aqueous solution at room temperature afforded quantitatively dibromosulfonate **3**. In contrast to the bromination of γ-substituted alkene sulfonates,[11] none of cyclization product was observed in this case. This may be rationalised by the relative stability of the reactive intermediates, which are produced in the course of the bromination reaction (Scheme 2).

Scheme 1



Examination of the reaction mechanism revealed that the facile transformation of 2-alkenyl sulfonates **6** into γ-substituted five-membered ring sultones **9** induced by bromine requires the generation of a fairly stable secondary carbocation **8** as the intermediate. To proceed with the same mechanism, starting from allyl sulfonate, the relative stability of secondary carbocation **11** and primary carbocation **12** would direct the mode of subsequent transformation. The low stability of **12** precluded the cyclization reaction leading to **5**, while the more stable **11** thus formed would pick up a bromine ion to give the dibromosulfonate **3** in preference to producing the cyclized product **13**.

Scheme 2



With dibromosulfonate **3** in hand, the synthetic challenge is reduced to initiating its cyclization to sultone **5**. According to the approach described by Manecke *et al.*,[8c] dibromosulfonate **3** was directly subjected to heating and distillation *in vacuo* to afford sultone **5**. However the reaction yield was far from satisfactory (below 10%). Attempts to facilitate the cyclization of sodium salt **3** in solvents at high temperature also failed. Thus, we turned to the functionalized sulfonic acid cyclization methodology.[8b,8c] The solid dibromo sulfonate **3** was treated with concentrated hydrochloric acid by stirring at room temperature for one day to give the desired 2,3-dibromopropane-1-sulfonic acid (**4**) after filtration and concentration. Without further purification, the sulfonic acid was subjected to heating at 150-160°C under vacuum and simultaneous distillation *in vacuo* to give the β-bromosultone **5** into 45% yield based on the sulfonate **3**. Transformation of β-bromosultone **5** to propene sultone **1** could be readily achieved by treating the sultone **5** with triethylamine in benzene at room temperature for 5 h with excellent yield (>95%). ^{1}H and ^{13}C NMR, HRMS, FTIR and elemental analysis shows that the sultone **1** possesses the assigned structure.

In summary, we have developed a reliable approach for the preparation of sultone **1** by a five-step sequence with an overall yield of 34%.

After successfully developing a convenient and direct access to prop-1-ene-1,3-sultone (**1**), we turned our attention to study its chemistry and its applications in organic synthesis. To follow our interests in using

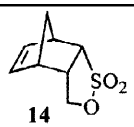
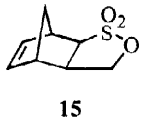
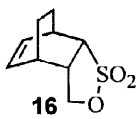
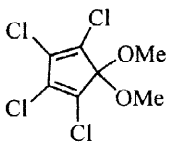
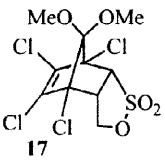
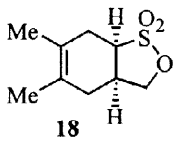
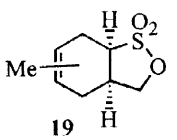
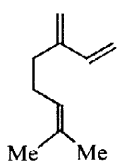
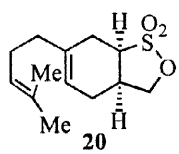
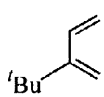
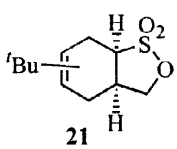
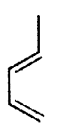
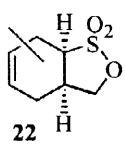
achiral and chiral unsaturated sulfur-containing compounds such as sulfoxides,[6a,6b] sulfinates[6c] and acyclic sulfonates,[6d] we hope to fully exploit sulfonate as a new dienophile in the Diels-Alder reaction. To examine its dienophilicity in the Diels-Alder reaction, **1** was allowed to react with a wide variety of dienes, including both cyclic and acyclic dienes, the results are summarised in Table 1.

Generally, good to excellent yield of the cycloadducts was obtained in all cases. The electron-withdrawing functionality allows propene sultone (**1**) to undergo a smooth Diels-Alder cycloaddition with reactive dienes like cyclopentadiene. This reaction proceeded very slowly at room temperature and took one week for completion to afford quantitative yield of tricyclic adducts and with good stereoselectivity (*endo/exo*=84:16). Raising the temperature can accelerate the reaction substantially. For instance, the reaction can be achieved within 4 h by heating at 120°C in a sealed tube with 95% yield and 73:27 *endo/exo* selectivity. For other less reactive dienes (Table 1, Entries 2 to 8), the Diels-Alder reactions occurred only at higher temperatures. To avoid side reactions of the Diels-Alder reaction occurring at elevated temperatures, a small amount of 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added as a radical scavenger.

The above results indicated that the dienophilicity of **1** is only moderate and probably comparable to that of vinyl sulfonate, vinyl sulfinate and vinyl sulfoxide. In principle, the Diels-Alder reaction of **1** with cyclic dienes would give a mixture of *endo* and *exo* stereoisomers. In practice, the Diels-Alder reaction of **1** with cyclopentadiene did give two cycloadducts whereas the reactions of **1** with the other two cyclic dienes afforded only one stereoisomer. According to the "*endo* rule" of Diels-Alder reactions, the major (or only) product of these reactions was tentatively assigned as the *endo* isomer. The relative configuration of sultone **14** and **15** (*endo/exo* isomer) was readily confirmed by a full analysis of their ^{1}H NMR spectra and the inference of decoupling experiments (Table 2).

A direct comparison of the ^{1}HNMR spectra of these two stereoisomers manifested their similarity and difference. The one to one correspondence of resonances with regard to chemical shift and multiplicity is most apparent. Because of the shielding effect of the C(8)-C(9) double bond, the chemical shifts of H(2) and H(6) of the *exo* isomer exhibited an upfield shift of 0.6 ppm as compared to the corresponding signals of the *endo* isomer. Another outstanding feature is that H(10b) of the *exo* isomer located in the proximity of the pseudo axial S=O bond resulted in a downfield shift of 0.3 ppm compared to its *endo* counterpart. Under the influence of the π-bond, to a less extent, H(10a) of the *exo* isomer also recorded a down field shift of 0.15 ppm. Systematic decoupling experiments in both *endo* and *exo* isomers further substantiate the validity of the proton assignments. Of great diagnostic value were $^4J_{HH}$ between H(2) or H(6) and one of the bridge head hydrogen H(10a). When these two protons are in W relationship (as in the *exo* isomer) $J_{10a,6}$ and $J_{10a,2}$ are relatively large (1.6-1.9 Hz). Such large strong long range coupling could not be observed for the *endo* isomer.

Table 1 Diels-Alder Reactions of Sultone **1**

Entry	Dienes	Solvent; *T*/°C; *t*/h	Adduct (% yield)
1			 **14**  **15**
		CH_2Cl_2; 20; 168	84 : 16 [c]
		Toluene; 120[a]; 4	73 : 27
2		Toluene; 150[a]; 18	 **16** *endo* only (96%)
3		Xylene; reflux; 20	 **17** *endo* only (72%)
4		Toluene; 150[a]; 18	 **18** (96%)
5		Toluene; 140[a]; 13	 **19** (84%) [b]
6		Xylene; reflux; 20	 **20** (75%) [b]
7		Benzene; 110[a]; 18	 **21** (89%) [b]
8		Toluene; 140[a]; 20	 **22** (59%) [b]

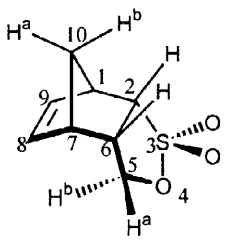
a) Reaction was carried out in a sealed tube, b) Mixtures of inseparable regioisomers were formed, c) The ratio of *endo*/*exo* isomers was determined by ^{1}H NMR spectroscopy

We were also pleased to find that a far higher *endo* selectivity was achieved for the reaction of **1** with cyclohexadiene and 2,3,4,5-tetrachloro-1,1-dimethoxycyclopentadiene (Table 1, Entries 2 and 3). Although higher temperature was required to initiate the reactions, the *endo* stereoselectivity in both cases is very high.

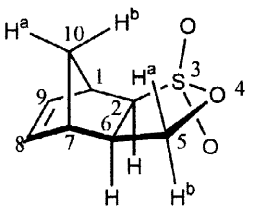
The improvement in *endo* stereoselectivity of these reactions could be explained by examining transition states which are leading to the formation of *exo* products (Scheme 3).

It should be noticed that the stereoselectivity towards the formation of *endo* adducts in Diels-Alder reactions is favoured by the secondary orbital interactions in the transition state. It becomes apparent that the steric hindrance of transition state **B** is greater than that of **A** (R = H). This is because the two allylic methylene groups of cyclohexadiene are just located on the top of the "-SO_2-" and "-CH_2-" groups of the dienophile while the methylene group of cyclopentadiene is on the top of the centre of the five-member ring of propene sultone. When the methylene protons of cyclopentadiene are replaced by two bulky methoxy groups (in **A**, R = OCH_3), the steric hindrance arose greatly and prevented the formation of *exo* product.

Table 2 ^{1}H NMR Data of *endo* Sultone **14** and *exo* Sultone **15** and Selected Decoupling Experiments



endo-**14**



exo-**15**

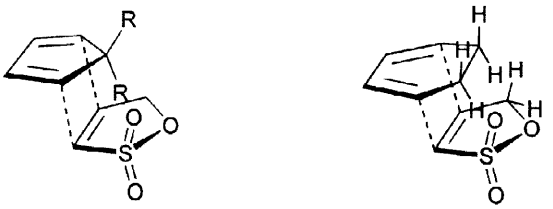
Proton	*Endo*-**14**	Protons with reduced multiplicity [a]	*Exo*-**15**	Protons with reduced multiplicity [a]
1	3.15, br.s	H_9, H_2	3.0, br.s	H_9, H_2
2	3.9, ddd	H_6	3.25	H_6
5a	4.3, dd	H_{5b}, H_6	4.2, d	
5b	4.0, d		4.5, dd	
6	3.4, t	H_2	2.8, t	H_{5b}, H_2
7	3.42, br.s	H_8, H_6	3.4, br.s	H_8
8	6.4, dd	H_7	6.4, dd	
9	6.3, dd	H_1	6.3, dd	
10a	1.45, d	H_{10b}	1.6, dd	
10b	1.70, d		2.0, dd	

[a] irradiated at the proton of the left column in the decoupling experiments

To define the scope of Diels-Alder reactions of **1**, we have to establish the regiochemistry of the cycloadducts. When the diene and dienophile are both unsymmetrical, the Diels-Alder reaction gives a

mixture of regioisomers. The regiochemical outcome of the reaction in many cases is directed by the *ortho, para* rule. Our investigation of sultone **1** gave, in most cases, poor regioselectivity (Table 1, Entries 5-8). The regioisomeric ratio of the adducts ranged from 1:1 to 1:1.5. The disappointed results could be ascribed to the absence of directing groups in the substituted 1,3-diene systems and the high temperature adopted in the reactions.

Scheme 3



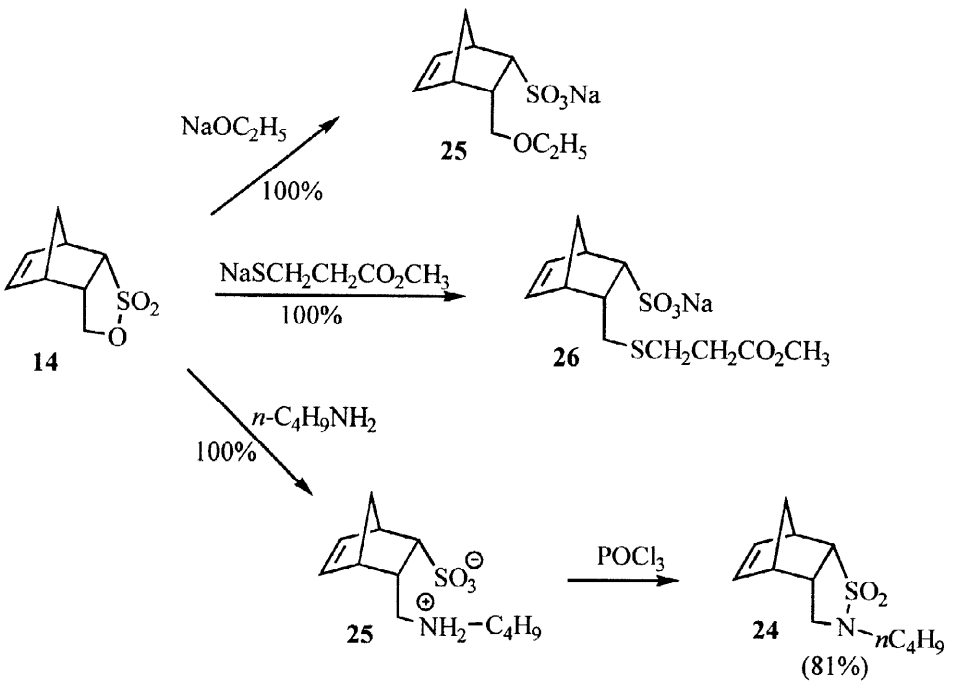
As Diels-Alder reactions of prop-1-ene-1,3-sultone (**1**) have been demonstrated successfully, a series of bicyclic and tricyclic sultones, which all are new compounds, were synthesized in our laboratory. Since saturated sultones are susceptible to nucleophilic attack, we therefore shifted our attentions to explore further chemical manipulations of these sultones. In the broad sense, sultones can be regarded as the sulfur analogues of lactones. However, they behave differently in most ring opening reactions. When reacting with nucleophiles, sultones behave as sulfoalkylating agents and cleave at alkyl-oxygen bond, while lactones behave as acylating agents and cleave at acyl-oxygen bond.

Tricyclic sultone **14** and bicyclic sultone **18** were chosen as model substrates to study the ring opening reactions with oxygen, sulfur and nitrogen nucleophiles (Schemes 4 and 5).

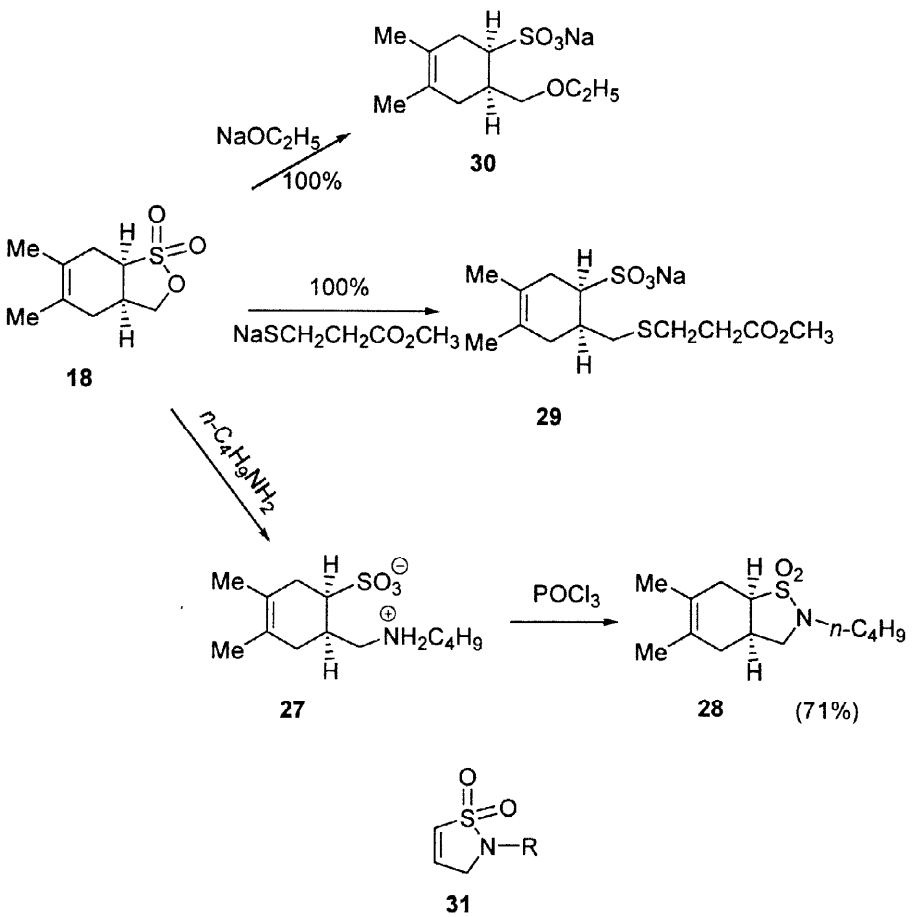
Sodium alkoxide and thiolate, generated *in situ* from sodium and the corresponding alcohol and thiol, reacted smoothly with both **14** and **18** at room temperature within a few hours to afford the clean sulfonates in near quantitative yield. In contrast, the ring opening reactions with butylamine could be carried out in refluxing THF for 1 h affording the ammonium sulfonates **23** and **27** as internal salts.

It is worthy of mention that all the ring opening products being ionic sulfonates are very hydroscopic. Therefore, the structural characterization of these ring opening products is only confined to NMR spectroscopy. Nevertheless, the purity and structures of the products **23**, **25** and **26** were established with confidence by the NMR technique. In addition, ammonium sulfonates could be characterized fully as their sultam derivatives. Thus, **23** and **27** were further cyclized to sultams **24** and **28** in good yield upon treatment with $POCl_3$ in THF. In this connection, prop-1-ene-1,3-sultone (**1**) could be viewed as the synthetic equivalent of unsaturated sultam **31** using as a dienophile in the Diels-Alder reaction. It is also this hydrophilic property that gives sultones a broad range of uses in industry, for example, uses as sulfoalkylating agent to produce wetting agents, surface active agents, water soluble polymer, antifogging agents etc.[7a, 12]

Scheme 4



Scheme 5



Several methods have been recently developed by Metz *et al.*[5, 13] for desulfurization of δ-sultones. In an effort to get rid of the sulfur moiety in the cycloadducts, we chose the *endo* sultone **14** as a model substrate to investigate the alkylation/desulfurization process (Scheme 6). Thus, lithiation of sultone **14** by *n*-butyllithium at -78°C, followed by alkylation with (iodomethyl)trimethylsilane, gave the desired alkylation product **32**, together with the butylated sultone **33** as a by-product. Apparently, in the presence of excess BuLi and (iodomethyl)trimethylsilane, BuI was generated which then reacted with the α-anion of **14** to furnish **33**. In agreement with this supposition, the formation of **33** could be suppressed by limiting the amount of *n*-butyllithium used (Table 3). The structures of both compounds were vigorously established by ^{1}H NMR, ^{13}C NMR, MS and elemental analysis. However, alkylation at above 0°C was undesirable and no product was obtained in the organic extracts after the reaction (Table 3, Entry 4). Presumably at such a high temperature, the ring opening reaction took place at the carbon centre adjacent to the sulfonate oxygen to afford water soluble ionic products. The best result could be achieved by first deprotonating of **14** with one mol equivalent of *n*-BuLi and then alkylation of the resulting carbanion with (iodomethyl)trimethylsilane at –78°C to –40°C for 0.5 h. Sultones **32** and **33** were easily separated by flash chromatography. Using Metz's recipe, it is gratifying that the fluoride-induced desulfurization of **32** to dienol **34** was readily achieved by refluxing sultone **32** with *tetra-n*-butylammonium fluoride on silica gel giving a crude yield of 73% (Scheme 6). Further purification by flash chromatography gave the pure product **34** as a colourless liquid in 30% yield. Since the dienol **34** is a formal [4+2] adduct of allene homolog with cyclopentadiene, the prop-1-ene-1,3-sultone (**1**) can serve as a synthetic equivalent of allene homologs in Diels-Alder cycloaddition.

In summary, prop-1-ene-1,3-sultone **1** has been proven to be an effective dienophile in the Diels-Alder reaction. Taking the viability of the ring opening reactions on the cycloadducts as mentioned above, **1** could be viewed as the synthetic equivalent to a variety of bifunctional olefins. The possibility of removing sulfur containing functionalities *via* Metz's or other literature known procedures[14] in principle allows us to claim **1** as dienophilic equivalents to a series of olefinic compounds, which are otherwise unreactive towards direct Diels-Alder reactions. The versatility of unsaturated sultone **1** in Diels-Alder reactions should make it a valuable tool and provide a new alternative for organic chemists when Diels-Alder reactions are called for in complex syntheses.

Scheme 6

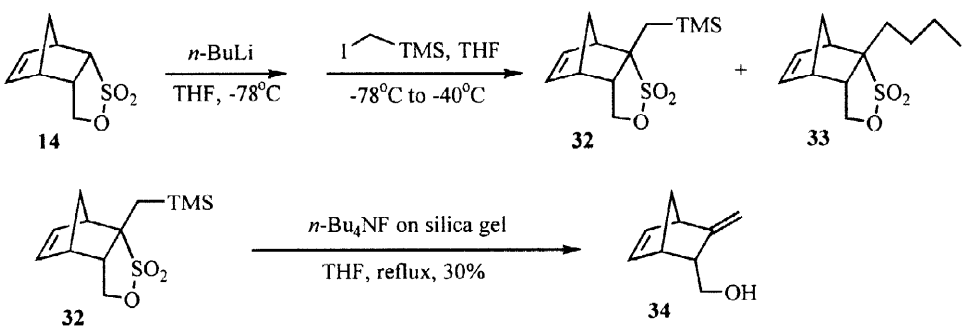


Table 3 Alkylation Reactions of Sultone **14** Under Different Conditions

Entry	*n*-BuLi (eq.)	TMS-CH_2I (eq.)	Condition (°C/h)	**32 : 33**	Total Yield(%)
1	2.0	2.0	-78/14	1 : 3	70
2	2.0	2.0	-78~rt/1	2.2 : 1	70
3	1.1	1.2	-78~rt/20min then rt/10min	4 : 1	35
4	1.0	1.05	0~rt/0.5	No product	–
5	1.0	1.25	-78~-40/0.5	18 : 1	68

Experimental

General Information. Low-resolution mass spectra (MS) were obtained at 50-70 eV by electron impact (EI) or fast atomic bomb (FAB) on a Finnigan MAT SSQ-710 mass spectrometer. High-resolution mass spectra were performed at the University of Alberta. IR spectra were recorded on a Nicolet Magna-IR550 spectrometer. NMR spectra in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard or in D_2O with were measured with a JEOL EX 270 (270 MHz for ^1H and 67.8 MHz for ^{13}C) spectrometer sodium 2,2-dimethyl-2-silapentane-5-sulfonate as the internal standard. Elemental analysis was performed at the Shanghai Institute of Organic Chemistry. Melting points were determined with a MEL-TEMP II melting point apparatus and are reported in Celsius degrees uncorrected. All chemicals used were of reagent grade and purchased from Aldrich Chemical Company or Acros Organics.

Preparation of Sodium Prop-2-ene Sulfonate (2)[9]

To a boiling solution of 3-bromopropene (14 mL, 165 mmol) in 95% ethanol (100 mL) and H_2O (30 mL) was added dropwise a solution of sodium sulfite (10 g, 79 mmol, in 42 mL of H_2O). Then the reaction mixture was continued to reflux for 2.5 h. The solvent was removed in *vacuo*. The residue was dried on a vacuum line. The crude products were purified by extracting with boiling ethanol (95%, 80 mL). After cooling to room temperature, the crystallized products were collected by filtration. The mother liquor was used for a second extraction of the residue. The total yield is 8.6 g (75%). Mp 242°C (decomposed); IR (KBr): 1640 cm^{-1}; ^1H NMR (D_2O): δ 3.55 (d, J = 7.29 Hz, 2H), 5.35–5.41 (m, 2H), 5.84–5.97 (m, 1H); ^{13}C NMR (D_2O): δ 58.0, 124.8, 130.3.

Preparation of Sodium 2,3-Dibromopropane Sulfonate (3)

To a solution of sodium prop-2-ene sulfonate (**2**) (4.0 g, 27.8 mmol) in water (16 mL) was added bromine (about 1.5 mL) dropwise with stirring until the solution turned pale brown. The solution was stirred at room temperature for 2 h. A very little amount of Na_2SO_3 was added to destroy the excess bromine. The solvent was then removed in *vacuo* and a white solid was obtained. The solid was purified by extraction with absolute ethanol (2 × 80 mL) under reflux for 15 min. On cooling, the solution was filtered and the solid product was washed with absolute ethanol and dried on a vacuum line, to produce a white crystal (quantitative). Mp 197°C (decomposed); IR (KBr): 1620, 1202 cm^{-1}; ^1H NMR (D_2O): δ 3.43–3.51 (m, 1H), 3.67–3.75 (m, 1H), 3.89–3.95 (m, 1H), 4.04–4.09 (m, 1H), 4.60 (m, 1H); ^{13}C NMR (D_2O): δ 40.1, 47.1, 58.8; Anal. Calcd. for $C_3H_5O_3Br_2SNa$: C, 11.86; H, 1.66. Found: C, 11.58; H, 1.74.

Preparation of 2-Bromopropane-1,3-sultone (5)

To a solution of concentrated hydrochloric acid (16 mL) was added sodium 2,3-dibromopropane sulfonate (**3**) (8.44 g, 28.0 mmol). The mixture was then stirred vigorously at room temperature for one day. The precipitate (NaCl) was filtered out and the liquid solution was concentrated to give quantitative yield of the crude product as a slightly yellow liquid. Without further purification, the liquid was subjected to vacuum distillation. A colorless liquid was obtained (2.53 g, 125–130°C/3-4 mmHg, 45% over two steps). IR (neat): 3024, 1643 cm^{-1}; MS-EI *m/z* 201 (M^+); ^1H NMR ($CDCl_3$): δ 3.52 (dd, J = 7.0, 14.0 Hz, 1H), 3.88 (dd, J = 7.8, 14.0 Hz, 1H), 4.49–4.56 (m,1H), 4.70–4.82 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 35.7, 53.2, 74.4; Anal. Calcd. for $C_3H_5O_3BrS$: C, 17.92; H, 2.51. Found: C, 17.79; H, 2.77.

Preparation of Prop-1-ene-1,3-sultone (1)

A solution of 2-bromopropane-1,3-sultone (**5**) (2.93 g, 14.7 mmol) and triethylamine (3.2 mL, 23.0 mmol) in benzene (130 mL) was stirred at room temperature for 4 h. After filtration of triethylamine hydrobromide and concentration of the solution, a white solid was obtained (1.77 g, 97%). Recrystallization from chloroform gave **1** as needle crystals. Mp 81–83°C (Lit 81–83°C)[9]; IR (KBr): 3214, 3115, 3095, 1610 cm^{-1}; ^1H NMR ($CDCl_3$):δ 5.12 (dd, J = 1.89, 2.43 Hz, 1H), 6.83 (dt, J = 2.43, 6.62 Hz, 1H), 7.08 (dt, J = 1.89, 6.62 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 72.5, 123.9, 137.3; MS-EI *m/z* 120 (M^+); HRMS Calcd. for $C_3H_4O_3S$ (M^+): 119.9881. Found: 119.9893; Anal. Calcd. for $C_3H_4O_3S$: C, 30.00; H, 3.36. Found: C, 30.08; H, 3.39.

(±)-*endo*-4,3-Oxathiatricyclo[5.2.1.$0^{2,6}$]deca-8-ene 3,3-dioxide (14):

A mixture of propene sultone (**1**) (120 mg, 1.0 mmol), cyclopentadiene (about 470 mg, 0.6 mL, 7 mmol) and BHA (5 mg) in toluene (3 mL) placed in a sealed tube was heated at 120°C for 4 h. On cooling, flash chromatography of the solution over silica gel, using ethyl acetate-petroleum ether (4:6) as eluent, gave a

endo/exo mixture (176 mg, 96%, *endo:exo* = 73:27). Further purification by column chromatography on silica gel using ethyl acetate-petroleum ether (3:7) as eluent afforded pure *endo*-sultone **14** and *exo*-sultone **15**.

***endo*-Sultone 14:** as a white solid, mp 104.5–106.5°C; IR (KBr): 3073, 1655 cm^{-1}; MS-EI *m/z* 186 (M^+); ^1H NMR ($CDCl_3$): δ 1.45 (d, J = 8.91 Hz, 1H), 1.66 (d, J = 8.91 Hz, 1H), 3.15 (br.s , 1H), 3.35-3.42 (m, 2H), 3.89 (dd, J = 3.92, 8.75 Hz, 1H), 3.97 (dd, J = 1.62, 9.72 Hz, 1H), 4.29 (dd, J = 7.15, 9.72 Hz, 1H), 6.35 (dd, J = 3.37, 5.60 Hz, 1H), 6.42 (dd, J = 2.70, 5.60 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 44.8, 46.0, 46.1, 50.8, 61.5, 69.1, 133.7, 135.9; Anal. Calcd. for $C_8H_{10}O_3S$: C, 51.60; H, 5.41. Found: C, 51.17; H, 5.24.

(±)-*exo*-4,3-Oxathiatricyclo[5.2.1.$0^{2,6}$]deca-8-ene 3,3-dioxide (15)

***exo*–Sultone 15:** as a white solid, mp 45.5–47.5°C; IR (KBr): 3068, 1609 cm^{-1}; MS-EI *m/z*186 (M^+); ^1H NMR ($CDCl_3$): δ 1.60 (d, J =9.85 Hz, 1H), 2.02 (d, J = 9.85 Hz, 1H), 2.83 (dd, J = 7.29, 7.56 Hz, 1H), 2.96 (m,1H), 3.23 (d, J = 7.56 Hz, 1H), 3.40 (m, 1H), 4.16 (dd, J = 1.62, 9.99 Hz, 1H), 4.48 (dd, J = 7.29, 9.99 Hz, 1H), 6.23 (dd, J = 2.97, 5.54 Hz, 1H), 6.33 (dd, J = 2.97, 5.54 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 43.5, 44.9, 46.0, 48.0, 60.5, 70.5, 136.5, 140,0; Anal. Calcd. for $C_8H_{10}O_3S$: C, 51.60; H, 5.41. Found: C, 51.65; H, 5.33.

(±)-*endo*-4,3-Oxathiatricyclo[5.2.2.$0^{2,6}$]undeca-8-ene 3,3-dioxide (16)

A mixture of propene sultone (**1**) (60 mg, 0.5 mmol), cyclohexadiene (0.3 mL, about 250 mg, 3.1 mmol) and BHA (3 mg) in toluene (1.5 mL) in a sealed tube was heated at 150°C for 18 h. The reaction mixture was then chromatographied on silica gel using ethyl acetate/petroleum ether (gradient 1:9 to 6:4) as eluent. 17.3 mg of starting material was recovered and 69.2 mg of pure *endo*-sultone **16** (96% of isolated yield) was obtained as a pale yellow solid, mp 119–120°C; IR (KBr): 3016, 3060, 1662 cm^{-1}; MS-EI *m/z* 200 (M^+); ^1H NMR ($CDCl_3$): δ 1.31-1.63 (m, 4H), 2.77 (m, 1H), 2.97-3.05 (m, 1H), 3.17 (m, 1H), 3.48 (dd, J = 2.70, 9.45 Hz, 1H), 3.96 (dd, J = 3.51, 9.45 Hz, 1H), 4.30 (dd, J = 7.95, 9.45 Hz, 1H), 6.32 (dd, J = 7.02, 7.29 Hz, 1H), 6.41 (dd, J = 6.75, 7.02 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 22.5, 23.3, 30.6, 33.5, 42.3, 59.5, 70.7, 131.0, 133.0; Anal. Calcd. for $C_9H_{12}O_3S$: C, 53.98; H, 6.04. Found: C, 54.08; H, 6.00.

(±)-*endo*-10,10-Dimethoxy-1,7,8,9-tetrachloro-4,3-Oxathiatricyclo[5.2.1.$0^{2,6}$]deca-8-ene 3,3-dioxide (17)

A mixture of propene sultone (**1**) (40 mg, 0.333 mmol), 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (436 mg, 1.65 mmol), BHA (3 mg) and *p*-xylene (1.2 mL) was heated to reflux for 20 h. The mixture was then purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether (1:3), to afford sultone (**17**) as a white solid (96 mg, 75%, *endo* only). Mp 176–178°C; ^1H NMR ($CDCl_3$): δ 3.57 (s, 3H), 3.63 (s, 3H), 3.70 (m, 1H), 4.25 (d, J = 8.37 Hz, 1H), 4.30 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 51.4, 52.2, 53.0, 64.5, 65.0, 74.7, 75.4, 115.1, 128.2, 129.1; IR (KBr): 1616 cm^{-1}; MS-EI *m/z* 384 (M^+); Anal. Calcd. for $C_{10}H_{10}O_5Cl_4S$: C, 31.27; H, 2.62. Found: C, 31.12; H, 2.47.

(±)-5,6-Dimethyl-3a,4,7,7a-tetrahydro-2,1-oxathiaindene 1,1-dioxide (18)

A mixture of propene sultone (**1**) (90 mg, 0.75 mmol), 2,3-dimethyl-1,3-butadiene (0.5 mL, 4.4 mmol), BHA (3 mg) and toluene (1.5 mL) in a sealed tube was heated at 150°C for 18 h. The mixture was then purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether (1:3) to produce bicyclic sultone (**18**) as a solid (129 mg, 96%) and recovered starting material (10.0 mg). Mp 75–76°C; MS-EI *m/z* 203 (M^+); IR (KBr): 2909 and 1329 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.68 (s, 1H), 1.71 (s, 3H), 1.93-1.99 (m, 1H), 2.36-2.43 (m, 3H), 3.30 (m, 1H), 3.48 (q, J = 7.60 Hz, 1H), 4.02 (t, J = 8.50 Hz, 1H), 4.46 (dd, J = 7.26, 8.50Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 18.9, 19.0, 26.9, 30.6, 33.9, 52.7, 72.2, 12.6, 123.1; Anal. Calcd. for $C_9H_{14}O_3S$: C, 53.44; H, 6.98. Found: C, 53.49; H, 7.04.

Mixture of (±)-5-Methyl-3a,4,7,7a-tetrahydro-2,1-oxathiaindene 1,1-dioxide and (±)-6-Methyl-3a,4,7,7a-tetrahydro-2,1-oxathiaindene 1,1-dioxide (19)

A mixture of propene sultone (**1**) (60 mg, 0.5 mmol), 2-methyl-1,3-butadiene (0.3 mL, 204 mg, 3.0 mmol), BHA (5 mg), and toluene (1.5 mL) in a sealed tube was heated at 140°C for 13 h. The mixture was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether (from 1:4 to 1:1), to give the bicyclic sultone **19** as a liquid (56.3 mg, 84%) (mixture of regioisomers) and recovered the starting material (17.2 mg). ^1H NMR ($CDCl_3$): δ 1.73 (s), 1.76 (s), 1.92-2.09 (m), 2.3-2.52 (m), 3.28 (m), 3.39-3.55 (m), 4.06 (m), 4.80 (m), 5.38 (m); ^{13}C NMR ($CDCl_3$): δ 21.0, 23.2, 23.3, 24.2, 25.2, 28.6, 32.5, 33.7, 51.4, 52.4, 72.3, 72.4, 116.9, 117.6, 130.6, 131.2; IR (KBr): 1681 cm^{-1}; MS-EI *m/z* 189 (M^+).

Mixture of (±)-5-(4'-Methylpenta-3'-en-1'-yl)-3a,4,7,7a-tetrahydro-2,1-oxathiaindene 1,1-dioxide and (±)-6-(4'-Methylpenta-3'-en-1'-yl)-3a,4,7,7a-tetrahydro-2,1-oxathiaindene 1,1-dioxide (20)

A mixture of propene sultone (**1**) (60 mg, 0.5 mmol), myrcene (368 mg, 2.7 mmol), BHA (3 mg) and *p*-xylene (1.2 mL) was heated to reflux for 20 h. The mixture was then purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether (3:7), to give the bicyclic sultone **20** (a mixture of regioisomers) as an oil (91.5 mg, 72%). IR (KBr): 3060 and 1676 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.60 (s), 1.68 (s), 1.96–2.54 (m), 2.40 (m), 2.46 (m), 4.04 (m), 4.47 (m), 4.66-4.72 (m), 5.06 (m), 5.46-5.50 (m). ^{13}C NMR ($CDCl_3$): δ 17.7, 21.1, 22.3, 23.9, 24.2, 25.6, 25.9, 26.0, 27.2, 32.9, 33.8, 36.7, 37.1, 51.7, 52.5, 72.17, 72.22, 110.1, 116.8, 117.3, 123.3, 123.4, 132.04, 132.11, 134.6, 135.1; HRMS Calcd. for $C_{13}H_{20}O_3S$ (M^+): 256.1133. Found: 256.1134.

Mixture of (±)-5-*t*-Butyl-3a,4,7,7a-tetrahydro-2,1-oxathiaindene 1,1-dioxide and (±)-6-*t*-Butyl-3a,4,7,7a-tetrahydro-2,1-oxathiaindene 1,1-dioxide (21)

A mixture of propene sultone (**1**) (80 mg, 0.67 mmol), 2-*tert*-butyl-1,3-butadiene (0.2 mL, 160 mg, 1.14 mmol), BHA (4 mg) and benzene (1.5 mL) in a sealed tube was heated at 110°C for 18 h. The mixture was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether (15%), to give the bicyclic sultone **21** as a solid (mixture of regioisomers) (107 mg, 89%) and recovered the starting material (17 mg). Mp 47–49°C; IR (KBr): 3066 and 1662 cm ^{1}; ^{1}H NMR ($CDCl_3$): δ 1.04 (s), 1.07 (s), 2.07 (m), 2.36-2.65 (m), 3.15 (m), 3.44 (m), 4.02 (m), 4.47 (m), 5.58 (m). ^{13}C NMR ($CDCl_3$): δ 21.2, 21.8, 24.6, 25.2, 28.4, 28.5, 33.7, 35.3, 35.5, 35.6, 52.6, 53.7, 71.9, 72.1, 114.6, 115.1, 143.9, 144.6; MS-EI *m/z* 231 (M^+); Anal. Calcd. for $C_{11}H_{18}O_3S$: C, 57.36; H, 7.88. Found: C, 57.50; H, 8.24.

Mixture of (±)-4-Methyl-3a,4,7,7a-tetrahydro-2,1-oxathiaindene 1,1-dioxide and (±)-7-Methyl-3a,4,7,7a-tetrahydro-2,1-oxathiaindene 1,1-dioxide (22)

The preparative method is the same as **19.** The bicyclic sultone **22** was obtained as a colourless liquid in 59% yield. IR (KBr): 3062 and 1654 cm^{-1}; ^{1}H NMR ($CDCl_3$): (mixture of isomers) δ 1.03 (d, J = 7.56 Hz), 1.16 (d, J = 7.02 Hz), 1.30 (d, J = 7.02 Hz), 1.99-2.06 (m), 2.23 (m), 2.47-2.54 (m), 2.68-2.85 (m), 3.04 (m), 3.21-3.39 (m), 3.47-3.56 (m), 4.04-4.17 (m), 4.40-4.53 (m), 5.52-5.80 (m); ^{13}C NMR ($CDCl_3$): δ 16.3, 20.6, 20.7, 20.9, 21.3, 23.7, 26.5, 28.5, 29.1, 33.0, 38.2, 40.2, 50.4, 51.9, 59.0, 69.9, 71.9, 72.1, 121.6, 122.5, 123.0, 129.4, 130.0, 130.1; Anal. Calcd. for $C_8H_{12}O_3S$: C, 51.05; H, 6.43. Found: C, 50.74; H, 6.52.

Ring Opening with Ethoxide:

To a solution of absolute ethanol (2 mL) was added pieces of sodium (about 1 mmol) and stirred for 15 min at room temperature. After sodium reacted completely, the same molarity of sultone (1 mmol) was added to the ethanol solution and stirred at room temperature for about 4 h. Then, the solvent was removed and the resulting solid products were washed with diethyl ether. After drying on a vacuum line, a hygroscopic white powder was obtained quantitatively.

Sodium 3-Ethoxymethylbicyclo[2.2.1]hept-5-ene-2-sulfonate (25)

IR (KBr): 1655 cm^{-1}; ^{1}H NMR (D_2O): δ 1.18 (t, J = 7.2 Hz, 3H), 1.39 (d, J = 8.5 Hz, 1H), 1.53 (d, J = 8.5 Hz, 1H), 2.91 (t, J = 7.7 Hz, 1H), 3.05 (s, 1H), 3.19 (s, 1H), 3.30 (m, 1H), 3.57 (m, 2H), 3.67 (dd, J = 3.1 Hz, 10.0, 1H), 3.80 (dd, J = 4.2, 10.0, 1H), 6.26 (s, 1H); ^{13}C NMR (D_2O): δ 16.8, 44.5, 47.7, 49.2, 51.1, 65.9, 69.1, 72.7, 137.5, 138.1.

Sodium 3,4-Dimethyl-6-ethoxymethyl-3-cyclohexene-1-sulfonate (30)

IR (KBr): 2910 and 1330 cm^{-1}; ^{1}HNMR (D_2O): δ 1.15 (t, J = 6.9 Hz, 3H), 1.62 (s, 3H), 1.65 (s, 3H), 2.17 (br.s, 2H), 2.26 (m, 2H), 2.50 (m, 1H), 3.19 (m, 1H), 3.32-3.61 (m, 3H), 3.88 (dd, J = 3.65, 9.80 Hz, 1H); ^{13}C NMR (D_2O): δ 16.7, 20.6, 20.9, 31.8, 35.7, 35.9, 60.6, 68.9, 70.4, 125.8, 126.0.

Ring Opening with Thioxide

To a solution of methanol (0.6 mL) was introduced a piece of sodium (0.5 mmol). After stirring at room temperature for 15 min, the methyl 3-mercaptopropionate (0.56 mL) was added and stirred for 2 h at room temperature. Then, to the mixture was added sultone (0.5 mmol). The mixture was stirred another 2 h at room temperature. The solvent (methanol) was removed. The crude product was washed with diethyl ether and petroleum ether successively, dried on a vacuum line to give sodium salt as a white powder (quantitative, very hydroscopic).

***Endo*-26:** Followed the above procedure, 89 mg of sultone **14** was converted to 162 mg of the sodium salt **26** (quantitative). IR (KBr): 3069, 1738, 1654 cm^{-1}; ^{1}H NMR (D_2O): δ 1.38 (d, J = 8.78 Hz, 1H), 1.52 (d, J = 8.78 Hz, 1H), 2.42 (t, J = 12.42 Hz, 1H), 2.65-2.74 (m, 3H), 2.81-2.89 (m, 2H), 3.00 (dd, J = 3.38, 12.42 Hz, 1H), 3.12 (br.s., 1H), 3.19 (br.s, 1H), 3.64 (dd, J = 2.97, 9.72 Hz, 1H), 3.71 (s, 3H), 6.23-6.30 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 29.2, 34.6, 36.9, 44.6, 48.3, 49.3, 50.9, 55.0, 66.8, 136.9, 138.5, 177.8.

29: Follow the above procedure, 70 mg (0.348 mmol) of the sultone **18** was converted to sodium salt **29** (114 mg, 95%). IR (KBr): 1738 cm^{-1}; ^{1}H NMR (CD_3OD): δ 1.62 (s, 3H), 1.65 (s, 3H), 2.19-2.48 (m,6H), 2.60-2.81 (m, 4H), 3.10 (m, 1H), 3.28 (m, H), 3.67 (s, 3H). ^{13}C NMR (CD_3OD): δ 18.9, 19.2, 27.9, 30.3, 30.4, 35.4, 35.6, 52.1, 60.6, 124.2, 174.5.

Ring Opening with Amine and Sultam Synthesis:

(±)-*N*-Butyl-*endo*-3,4-thiazatricyclo[5.2.1.$0^{2,6}$]deca-8-ene 3,3-dioxide (24)

To a solution of *endo*-sultone **14** (86 mg, 0.46 mmol) in THF (2 mL) was added butylamine (80 mg, 1.1 mmol). The mixture was stirred under nitrogen at room temperature for 21 h. Then, $POCl_3$ (0.2 mL, 2.2 mmol) was added. After refluxing for 3 h, the reaction was quenched by adding a few drops of water and the solvent-THF was removed on rotarvapor. To the residue was added 10mL of H_2O and extracted with chloroform (3 x 10 mL). The extracts were combined and washed with brine, dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether (1:4) to give sultam **24** as a colourless liquid (90 mg, 81% overall yield). IR (neat): 3069, 1638 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.90 (t, J = 7.1 Hz, 3H), 1.30-1.45 (m, 5H), 1.59 (d, J = 8.91 Hz, 1H),

2.66 (m, 1H), 2.82 (d, J = 8.37 Hz, 1H), 2.95-3.09 (m, 4H), 3.38 (br.s, 1H), 3.73 (dd, J = 3.92, 8.37 Hz, 1H), 6.21 (m, 1H), 6.32 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 13.5, 19.9, 29.5, 38.9, 42.8, 46.1, 46.5, 47.6, 50.4, 62.6, 133.2, 135.8; MS-EI *m/z* 241 (M^+); Anal. Calcd. for $C_{12}H_{19}NO_2S$: C, 59.72; H, 7.93; N, 5.80. Found: C, 59.68; H, 7.80; N, 5.65.

(±)-*N*-Butyl-5,6-dimethyl-3a,4,7,7a-tetrahydro-2,1-azathiaindene 1,1-dioxide (28)

Starting from **18** (122 mg, 0.603 mmol), **28** was obtained as a colourless liquid (118 mg, 71% overall yield) using the above procedure. IR (neat): 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.96 (t, J = 7.0, 3H), 1.42-1.60 (m, 4H), 1.68 (s, 3H), 1.71 (s, 3H), 1.90-2.32 (m, 4H), 2.80-3.40 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 13.50, 18.76, 18.89, 19.77, 27.06, 29.67, 30.08, 32.10, 44.87, 50.94, 54.23, 122.34, 123.31; Anal. Calcd. for $C_{13}H_{23}OS$: C, 68.67; H, 10.20. Found: C, 68.38; H, 10.32.

Alkylation of Sultone:

To a solution of *endo*-sultone **14** (100 mg, 0.537 mmol) in dried THF (2 mL) at –78°C under nitrogen was added dropwise butyllithium (0.74 mL, 1.181 mmol, 1.6 M solution in hexane). After the mixture was stirred for 30 min at –78°C, (iodomethyl)trimethylsilane (253 mg, 0.18 mL) was added at –78°C. Then, the reaction mixture was allowed to warm up to –40°C in 0.5 h. Then, a few drops of H_2O was added. After most of THF was removed in *vacuo*, 15 mL of H_2O was added and the aqueous mixture was extracted with dichloromethane. The combined extracted layers were washed with saturated NH_4Cl and brine, dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether (1:3), to produce the TMS-sultone **32** (73 mg, 50%) and the *n*-butylsultone **33** (8 mg) (by-product).

(±)-*endo*-2-(Trimethylsilylmethyl)-4,3-Oxathiatricyclo[5.2.1.0^{2,6}]deca-8-ene 3,3-dioxide (32)

As a white solid, mp 76–78°C; IR (KBr): 3076, 1683 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.16 (s, 3H), 0.18 (s, 3H), 0.19 (s, 3H), 1.28 (d, J = 15.5 Hz, 1H), 1.69-1.80 (m, 2H), 1.83 (d, J = 15.50 Hz, 1H), 2.78 (m, 1H), 3.06 (br.s, 1H), 3.20 (br.s, 1H), 3.83 (d, J = 9.57 Hz, 1H), 4.26 (dd, J = 6.60, 9.57 Hz, 1H), 6.31 (dd, J = 3.12, 5.76 Hz, 1H), 6.50 (dd, J = 3.12, 5.76 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ .236, 25.77, 46.70, 50.10, 52.33, 55.85, 67.35, 71.70, 133.57, 138.37; MS-EI *m/z* 273 (M^+); Anal. Calcd. for $C_{12}H_{20}O_3SiS$: C, 52.91; H, 7.40. Found: C, 52.78; H, 7.64.

(±)-*endo*-2-*n*-Butyl-4,3-Oxathiatricyclo[5.2.1.0^{2,6}]deca-8-ene 3,3-dioxide (33)

As a pale yellow solid, mp 87–88°C; IR (KBr): 1625 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.95 (t, J = 7.26Hz, 3H), 1.33-1.44 (m, 2H), 1.57-1.87 (m, 5H), 2.35 (m, 1H), 2.74 (m, 1H), 3.06 (br.s, 1H), 3.30 (br.s, 1H), 3.71 (d, J = 9.90Hz, 1H), 4.23 (dd, J = 6.60, 9.90Hz, 1H), 6.33 (dd, J = 2.97, 5.60Hz, 1H), 6.47 (dd, J = 3.13, 5.60Hz, 1H);

^{13}C NMR ($CDCl_3$): δ 13.7, 23.0, 27.7, 35.9, 46.3, 49.2, 49.8, 52.1, 67.7, 73.0, 133.9, 138.0; MS-EI *m/z* 243 (M^++1). Anal. Calcd. for $C_{12}H_{18}O_3S$: C, 59.48; H, 7.49. Found: C, 59.80; H, 7.28.

Desulfurization

(±)-2-Hydroxymethyl-3-methenylbicyclo[2.2.1]hept-5-ene (34)

To a solution of TMS-sultone **32** (203 mg, 0.745 mmol) in dry THF (6 mL) was added excess of (n-Bu)$_4$NF (about 5 eq., on silica gel, 1.1 mmol, F^-/g resin). The mixture was refluxed for 2 h under nitrogen and with fast stirring. On cooling down to room temperature, a few drops of H_2O were added. The silica gel was removed by filtration and washed with diethyl ether. The solution was concentrated to give a colorless liquid (74.2 mg, 73% crude yield). Further purification by flash chromatography silica gel using ethyl acetate/petroleum ether (2:8) as eluent gave alcohol **34** (30 mg, 30%) as a colorless liquid. IR (KBr): 3438, 3067, 1653 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.48 (d, J = 8.41 Hz, 1H), 1.67 (d, J = 8.41 Hz, 1H), 2.73 (m, 1H), 3.07 (br.s, 1H), 3.17 (br.s, 1H), 3.23 (d, J = 10.71 Hz, 1H), 3.61 (dd, J = 5.44, 10.71 Hz, 1H), 4.68 (m, 1H), 4.98 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 43.97, 47.57, 49.85, 51.79, 66.38, 103.92, 13.60, 135.18, 151.54; MS-EI *m/z* 136 (M^+).

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