# Synthesis and Diels–Alder reactions of α,β-unsaturated γ-sultone

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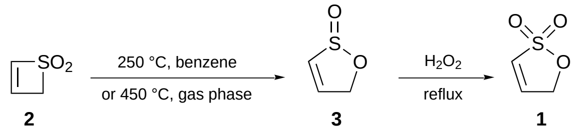
**An efficient synthesis of prop-1-ene 1,3-sultone 1 and its Diels–Alder reactions are reported; ring-opening reactions of the cycloadducts with nucleophiles and transformations to the sultams were also investigated.**

Sultones are cyclic esters of the corresponding hydroxysulfonic acid, the sulfur analogues of lactones. The preparation and chemistry of saturated sultones of 4- to 6-membered ring sizes are relatively well studied.[1] However, there is less investigation of the chemistry of the unsaturated sultones, in particular, the α,β-unsaturated γ-sultone prop-1-ene 1,3-sultone **1**. We have long been interested in the uses of sulfur-containing functional groups for the activation of acetylenic or vinyl moieties resulting in useful synthons for organic synthesis.[2] We here report a synthesis of **1**, its Diels–Alder reactions and some further transformations of the cycloadducts.

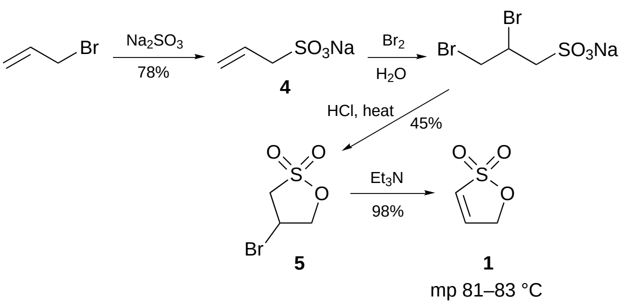
There are only limited accounts in literature for the synthesis of **1**. Thermolysis of thiete 1,1-dioxide **2** yielded sultine **3** which could be oxidized to **1** (Scheme 1).[3] It had also been reported that distillation of 3-hydroxyprop-1-ene-1-sulfonic acid, which was synthesized from prop-2-ynyl alcohol *via* free radical sulfitation, also afforded **1**.[4] These reported procedures were not efficient and practical enough for the laboratory synthesis of the compound. Our synthesis of **1** is shown in Scheme 2. Sodium prop-2-enesulfonate **4** could be prepared from allyl bromide and sodium sulfite in good yield.[5] Bromination of **4** in water gave the dibromide which was not isolated. Vacuum distillative cyclization of the dibromide under acidic conditions afforded β-bromo sultone **5** in 45% isolated yield from **4**. Treatment with amine base in benzene solution at room temperature afforded **1**† as a white crystalline solid in good yield.

The dienophilicity of unsaturated sultone **1** in the Diels–Alder reaction was investigated. Sulfonate has been used as an activating group for olefinic dienophiles, for example, vinyl sulfonates were found to be reactive dienophiles in both intermolecular[6] and intramolecular[7] Diels–Alder reactions. The results of Diels–Alder reactions of **1** towards a series of simple dienes are summarized in Table 1.‡ For a reactive diene such as cyclopentadiene, despite the slow reaction rate, reaction with **1** could take place at room temperature with moderate *endo* : *exo* selectivity. At a higher temperature, the reaction could be completed in 4 h. The *endo*-**6** and *exo*-**7** isomers could be easily separated by column chromatography. For less reactive dienes, elevated temperature or sealed tube conditions were used. In the cases of cyclohexa-1,3-diene and 2,3,4,5-tetrachloro-1,1-dimethoxycyclopentadiene, the *endo*-isomers were the only isolated products. For unsymmetrical dienes, 1 : 1 inseparable mixture of regioisomers resulted.

The sultone cycloadduct could be further manipulated by ring-opening with various nucleophiles such as alcohols, amines and thiols at the γ-position. Selected examples are depicted in Schemes 3 and 4. The alkoxide reacted smoothly with cycloadducts **6** and **8** at room temperature to afford the ring opening products **9a**,**b** in quantitative yields. Similarly, amine and thio compounds also reacted with the cycloadducts in

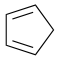
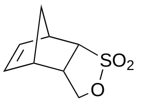
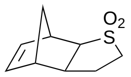
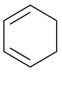
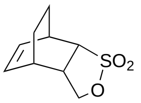
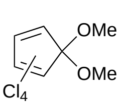
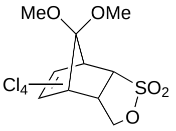
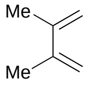
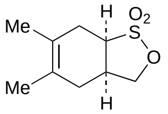
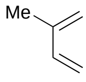
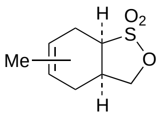
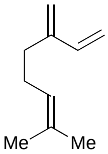
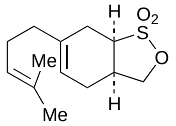
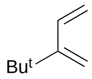
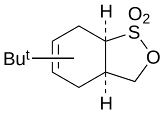


**Scheme 1**

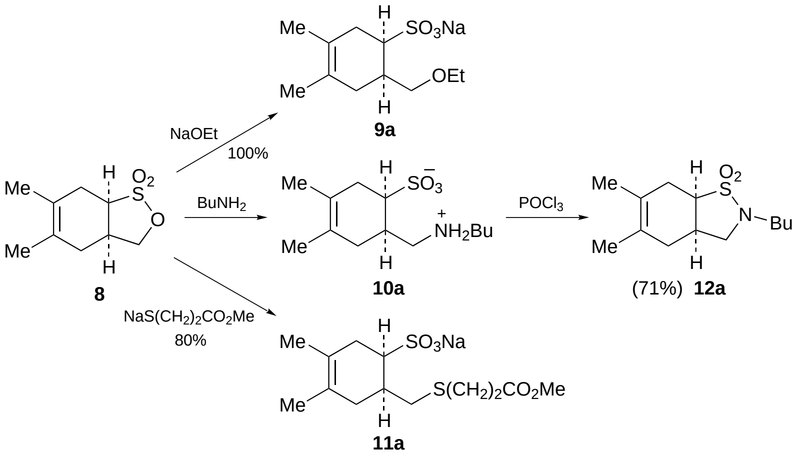


**Scheme 2**

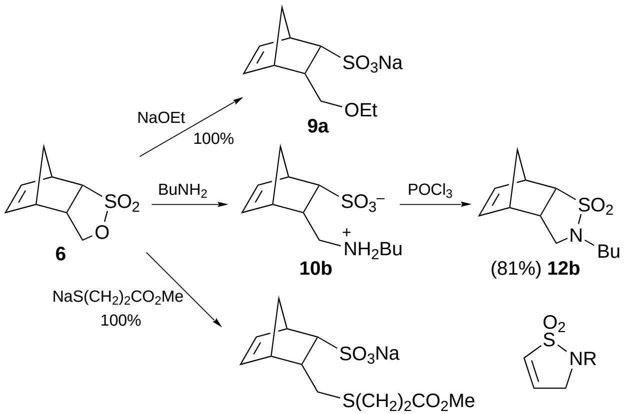
**Table 1** Diels–Alder reactions of α,β-unsaturated γ-sultone

| Dienes | Solvent; $T$/°C; $t$/h | Adduct (% yield) | | |
|---|---|---|---|---|
|  | | <br>**6** | | <br>**7** |
| | $CH_2Cl_2$; 20; 168 | 84 | : | 16 (quant) |
| | Toluene; 120$^a$; 4 | 73 | : | 27 (96%) |
|  | Toluene; 150$^a$; 18 |  | | *endo* only<br>(96%) |
|  | Xylene; reflux; 20 |  | | *endo* only<br>(72%) |
|  | Toluene; 150$^a$; 18 | <br>**8** | | (96%) |
|  | Toluene; 140$^a$; 13 |  | | (84%)$^b$ |
|  | Xylene; reflux; 20 |  | | (75%)$^b$ |
|  | Benzene; 110$^a$; 18 |  | | (89%)$^b$ |

$^a$ Sealed tube. $^b$ Mixture of regioisomers.



**Scheme 3**



**Scheme 4**

methanol solution to afford the ring-opening products **10** and **11**, respectively. Compounds **10a** and **10b** were further cyclized to sultams **12a** and **12b** in good yield upon treatment with $POCl_3$ in THF. In this regard, unsaturated sultone **1** could be viewed as the synthetic equivalent of unsaturated sultam **13**[8] as dienophile in the Diels–Alder reaction.

Financial support from the Research Grant Council (HKBC 136/94P) is gratefully acknowledged.

## Footnotes

† Prop-1-ene 1,3-sultone **1**: mp 81–83 °C; $^1$H NMR ($CDCl_3$, 270 MHz) δ 5.12 (dd, 2 H, $J$ = 2.43, 1.89 Hz), 6.83 (dt, 1 H, $J$ = 6.62, 2.43 Hz), 7.08 (dt, 1 H, $J$ = 6.62, 1.89 Hz); $^{13}$C NMR δ 72.5, 123.9, 137.3; IR (KBr) ν/cm$^{-1}$ 3214, 3115, 3095, 1610, 1323, 1179; MS *m/z* (relative intensity), 120 ($M^+$, 65), 91 (38), 66 (100), 56 (17); Analysis for $C_3H_4O_3S$. Found: C, 30.08%, H, 3.39%. Calculated C, 30.00%, H, 3.36%.

‡ All new compounds are characterized by spectroscopic methods [IR, $^1$H (270 MHz) and $^{13}$C NMR, HRMS and/or elemental analysis].

## References

1 Recent reviews: D. W. Roberts and D. L. Williams, *Tetrahedron*, 1987, **43**, 1027; A. J. Buglass and J. G. Tillett, in *The Chemistry of Sulphonic Acids, Esters and their Derivatives*, ed. S. Patai and Z. Rappoport, Wiley, New York, 1991, pp. 789.
2 A. W. M. Lee and W. H. Chan, *Top. Curr. Chem.*, in the press.
3 J. F. King, P. de Mayo, C. L. McIntosh, K. Piers and D. J. H. Smith, *Can. J. Chem.*, 1970, **48**, 3704.
4 J. H. Hellberger and G. Muller, *Ger.*, 1963, **1**, 146, 870; *Chem. Abstr.*, 1963, **59**, 11259d.
5 F. Püschel and C. Kaiser, *Chem. Ber.*, 1964, **97**, 2926.
6 L. L. Klein and T. M. Deeb, *Tetrahedron Lett.*, 1985, **26**, 3935.
7 P. Metz, M. Fleischr and R. Fröhlich, *Tetrahedron*, 1995, **51**, 711.
8 Recently, the use of sulfonamide as an activator for vinyl dieneophiles in intramolecular Diels–Alder reactions was reported: P. Metz, D. Seng, R. Fröhlick and B. Wibbeling, *Synlett*, 1996, 741.

*Received in Cambridge, UK, 29th January 1997; Com. 7/00656J*