SYNTHESIS, REACTIVITY AND APPLICATIONS OF 1,2-OXATHIINE 2,2-DIOXIDES

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Abstract. *The structure, synthesis, reactivity and applications of the 1,2-oxathiine 2,2-dioxide ring system are reviewed. This relatively scarcely studied heterocycle can be accessed by a variety of traditional and modern synthetic chemistry strategies and offers great potential as a building block for the construction of acyclic and heterocyclic compounds. Furthermore, the δ-sultone ring is an invaluable reagent for imparting water solubility into a variety of materials including colorants and polymers.*

Contents

1. Introduction

1,2-Oxathiine 2,2-dioxides, historically described as either 1,4-sultones, 1,4-butanesultone or δ-sultones, are the relatively scarcely studied isomers in the homologous series of sultones.[1,2,3] Indeed the 1,2-oxathiine ring is the lesser explored isomer of the six-membered heterocyclic systems which contain one sulfur and one oxygen atom.[4] The objective of this review is to present the structure, synthesis, chemistry and applications of this interesting class of heterocycle and will encompass the tetrahydro- **1** (1,2-oxathiane 2,2-dioxide), the three isomeric dihydro- **2**, **3**, **4** and the fully unsaturated **5** 1,2-oxathiine 2,2-dioxide systems which can be considered as SO_2 isosteres of the extensively studied, biologically significant, pyran-2-one system **6** (Figure 1).

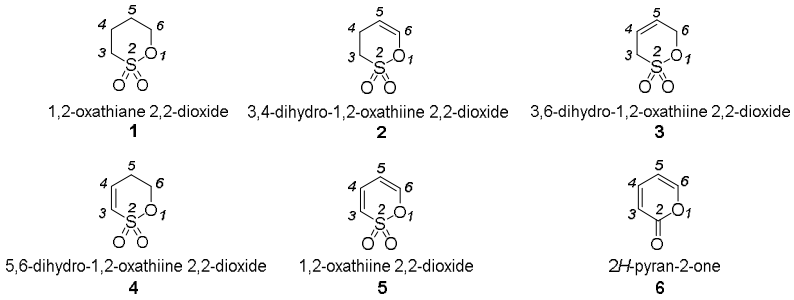


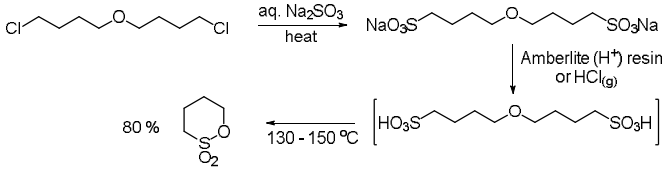
Figure 1. Structure and nomenclature.

2. Synthesis

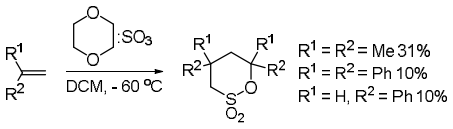
In this section, the synthesis of monocyclic ring systems is organised by degree of saturation, commencing with the fully saturated 1,2-oxathiane 2,2-dioxides and progressing through the three isomeric dihydro derivatives leading to the fully unsaturated 1,2-oxathiine 2,2-dioxides. It should be noted that for organisational purposes the transformation of, for example, a dihydro isomer into the fully unsaturated analogue, is included in the synthesis section rather than in the discussion of reactivity.

2.1. 1,2-Oxathiane 2,2-dioxides

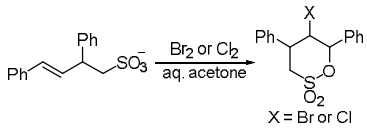
Historical routes to 1,2-oxathiane 2,2-dioxides (saturated δ-sultones) **1**, which have been reviewed in the mid-1950s[5] and late 1980s,[2] include the vacuum distillation of δ-halogeno and δ-hydroxy sulfonic acids.[6] The process has been extended to the thermal cyclisation of δ-acyloxysulfonic acids[7] and of 4,4'-oxybis(butane-1-sulfonic acid) (Scheme 1).[8] The sulfonation, dimerization of simple terminal alkenes with dioxane:sulfur trioxide complex, was extensively studied by Bordwell *et al.*, and several examples of 4,6-disubstituted 1,2-oxathiane 2,2-dioxides were described (Scheme 2).[9] Barium 2,4-diphenylbut-3-ene-1-sulfonate, derived from the ring-opening and thermolysis of 4,6-diphenyl-1,2-oxathiane 2,2-dioxide, underwent halosultonisation upon treatment with either bromine or chlorine (Scheme 3).[10] The electrophilic cyclisation of 2-allylphenol to 3-ethyl-6-(2-hydroxyphenyl)-1,2-oxathiane 2,2-dioxide was accomplished in 61% yield upon reaction with butyl sulfurochloridate generated *in situ* from SO_3 and butyl chloride at low temperature in CCl_4.[11] Sulfonation of internal olefins such as 9-octadecene using SO_3 and a falling film reactor afforded low yields of *trans*-3,6-dialkyl δ-sultones.[12] Progress on the synthesis of δ-sultones was reviewed by Gaunersdorfer *et al.*, in 2018.[13]



Scheme 1. Thermal cyclisation of 4,4'-oxybis(butane-1-sulfonic acid).

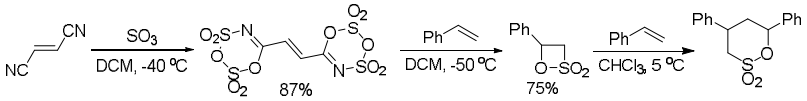


Scheme 2. Sulfonation, dimerization of simple alkenes.



Scheme 3. Halosultonisation reaction.

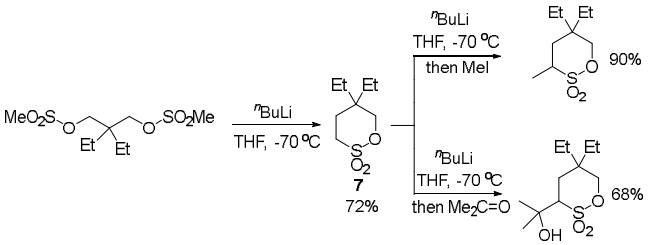
Fumaronitrile reacts with SO_3 in dichloromethane (DCM) at -40 °C to afford the tetra-SO_3 adduct, (*E*)-6,6'-(ethene-1,2-diyl)bis(1,3,2,4,5-dioxadithiazine 2,2,4,4-tetraoxide), in 87% yield. Subsequent sulfonation of styrene in pyridine at low temperature forms an initial β-sultone which reacts with further styrene upon warming to afford 4,6-diphenyl-1,2-oxathiane 2,2-dioxide (Scheme 4).[14]



Scheme 4. Sulfonation of styrene with fumaronitrile tetra-SO_3 adduct.

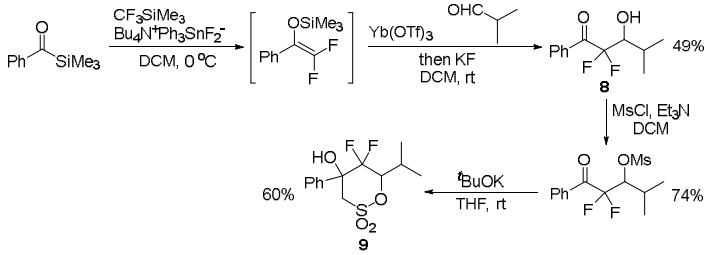
Following from the initial study by Durst and Tin, who described the anion-mediated cyclisation of 1,3-alkanedisulfonate esters in good to excellent yields,[15] this strategy has been employed to obtain 5,5-diethyl-1,2-oxathiane 2,2-dioxide **7** in 72% yield. Reaction of **7** with ^{n}BuLi at low temperature and

quenching with either methyl iodide or acetone gave 3-substituted derivatives in good yield (Scheme 5).[16] Intramolecular cyclisation of the sulfur stabilised carbanion from 2,2-dimethyl-3-oxobutyl methanesulfonate afforded 4-hydroxy-4,5,5-trimethyl-1,2-oxathiane 2,2-dioxide in 49% yield; X-ray crystallography was employed to firmly establish the structure.[17]



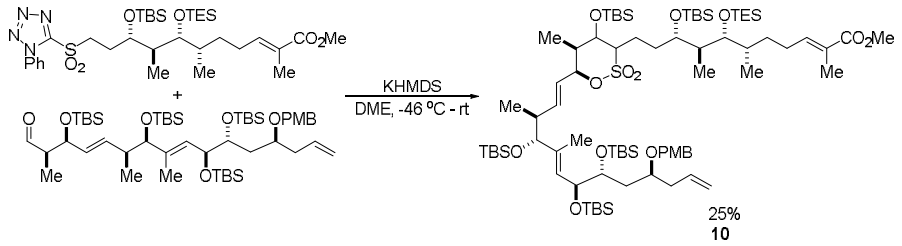
Scheme 5. Anion mediated cyclisation of 1,3-methanedisulfonate esters.

The ytterbium triflate-mediated aldol condensation between trifluoromethyltrimethylsilane and isobutyraldehyde afforded the difluoroaldol precursor **8** in 49% yield. *O*-Mesylation was readily accomplished in 74% with MsCl and Et_3N and subsequent deprotonation of the $MeSO_2$ function with ^{t}BuOK in THF effected the smooth cyclisation to the 1,2-oxathiane 2,2-dioxide **9** (Scheme 6).[18]



Scheme 6. Formation of difluorinated 1,2-oxathiane 2,2-dioxide.

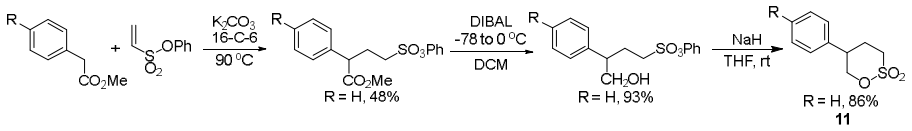
During an enantioselective synthesis of Oasomycin A, the tetrasubstituted 1,2-oxathiane 2,2-dioxide **10** was isolated as a significant by-product in up to 25% yield from the attempted Kocienski-Julia olefination. The formation of **10** was rationalised by a Brook rearrangement of the Julia intermediate followed by alkoxide attack on the sulfur atom (Scheme 7).[19]



Scheme 7. Serendipitous formation of tetrasubstituted 1,2-oxathiane 2,2-dioxide **10**.

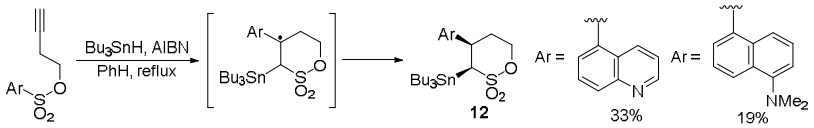
Michael addition of methyl phenylacetate anion to phenyl vinyl sulfonate provided a mixture of the mono- and bis-adducts from which the former was isolated in 48% yield. Reduction of the ester to the primary alcohol was accomplished using DIBAL in 93% yield. Generation of the alkoxide anion with NaH resulted in cyclisation to the 5-phenyl-1,2-oxathiane 2,2-dioxide **11** in 86% yield with elimination of

phenoxide. The scope of the reaction was extended to include the 4-bromo- and 4-hydroxy-phenyl analogues (Scheme 8).[20]



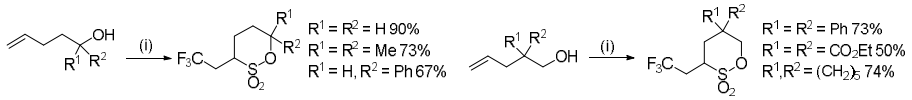
Scheme 8. Alkoxide mediated cyclisation to form a δ-sultone.

Tributyltin hydride-promoted free radical reaction of homopropargyl benzosulfonates resulted in an unexpected rearrangement to afford 3-tributylstannyl-4-aryl substituted 1,2-oxathiane 2,2-dioxides **12** in moderate yields. Crystal structures of **12** revealed a *cis*-orientation of the ring substituents which suggested that the tin hydride reduction of the intermediate radical occurred stereoselectively in a *trans* fashion (Scheme 9).[21]



Scheme 9. Free radical reaction of homopropargyl benzosulfonates.

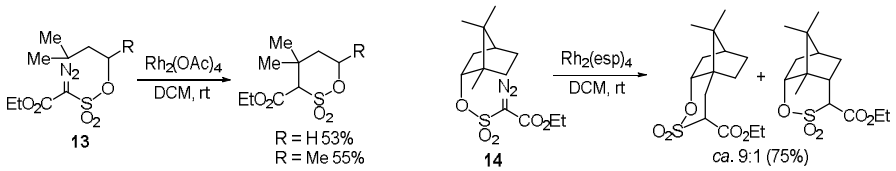
Both primary and tertiary α,ω-alkenols have been cyclised by a photo-redox-catalysed procedure to afford a diverse range of trifluoromethylated δ-sultones in excellent yields. A single-electron transfer process, mediated by the photoexcited copper catalyst, affords the trifluoromethyl radical which adds to the alkenol to generate a second radical that captures SO_2Cl from an intermediate Cu(II) complex and subsequently cyclises to the product (Scheme 10).[22]



Reagents and conditions: (i) alkenol (1.0 eq.), CF_3SO_2Cl (2.0 eq.), K_2HPO_4 (2.0 eq.), $[Cu(dap)_2]Cl$ (1 mol%), MeCN, 530 nm irradiation, *ca.* 17 h. (dap = 2,9-di(*p*-anisyl)-1,10-phenanthroline)

Scheme 10. Photo-redox-catalysed synthesis of trifluoromethyl substituted δ-sultones.

Perhaps the most recently and widely exploited approach to variously substituted 1,2-oxathiane 2,2-dioxides employs the intramolecular C-H insertion reactions of carbenoids derived from α-diazosulfonates (ethyl 2-diazo-2-(alkoxysulfonyl)acetates) **13** which were conveniently obtained from the requisite ethyl 2-(alkoxysulfonyl)acetates *via* established diazo transfer protocols. Novikov *et al*., effected the cyclisation of a series of Rh-carbenoids to afford substituted δ-sultones in good yields (Scheme 11).[23]

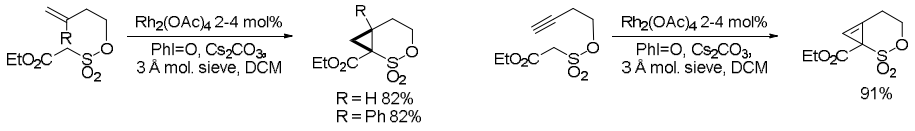


Scheme 11. Rh-carbenoid approach to substituted δ-sultones.

Extension of the foregoing methodology to the ethyl 2-(alkoxysulfonyl)acetate derived from citronellol enabled a quaternary stereocentre to be installed at C-4.[24] Application to the borneol derived diazosulfonate

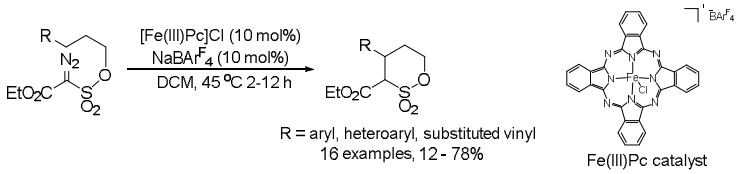
14 afforded two fused δ-sultones resulting from insertion into the C-H bond of the methyl group and the methylene bridge (Scheme 11).[25]

The foregoing rhodium carbenoid cyclisation methodology was complemented by Du Bois *et al*., who also simplified the protocol by obviating the requirement to isolate the ethyl 2-diazo-2-(alkoxysulfonyl)acetates and instead cyclised the precursor ethyl 2-(alkoxysulfonyl)acetates directly employing iodosobenzene and $Rh_2(OAc)_4$ to generate aryliodonium ylides as surrogate diazo intermediates. Interestingly, in addition to simple di-, tri- and tetra- substituted δ-sultones, strained bicyclic [4.1.0] δ-sultones were constructed by this methodology (Scheme 12).[26]



Scheme 12. Synthesis of strained bicyclic δ-sultones by $Rh_2(OAc)_4$-mediated cyclisation of *in situ* generated aryliodonium ylides.

An extensive series of 3,4-disubstituted 1,2-oxathiane 2,2-dioxides has been generated through an iron phthalocyanine-catalysed alkylation of allylic and benzylic C(sp^3)-H bonds. An electrophilic iron carbene is purported to mediate the homolytic C-H bond cleavage and subsequent C3-C4 bond formation (Scheme 13).[27]



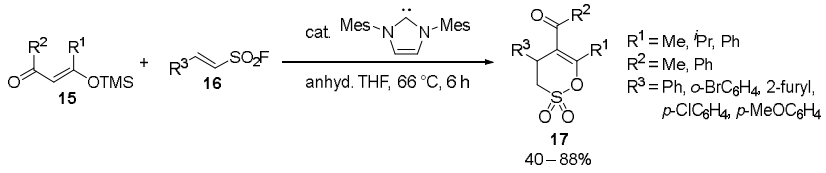
Scheme 13. Iron phthalocyanine-mediated formation of 3,4-disubstituted 1,2-oxathiane 2,2-dioxides.

The oxidation of 4-chloro-4-methyl-1,2-oxathiane 1-oxide, derived from the reaction of 3-methylbut-3-en-1-ol with $SOCl_2$, using H_2O_2 gave 4-chloro-4-methyl-1,2-oxathiane 2,2-dioxide; the route constitutes a unique heteroatom oxidation approach to the δ-sultone unit.[28]

2.2. Dihydro-1,2-Oxathiine 2,2-dioxides

2.2.1. 3,4-Dihydro-1,2-oxathiine 2,2-dioxides

Lupton *et al.*, have reported the *N*-heterocyclic carbene (NHC)-catalysed annulation of multiple trimethylsilyl enol ethers **15** with various α,β-unsaturated sulfonyl fluorides **16** to afford the corresponding 3,4-dihydro-1,2-oxathiine 2,2-dioxides **17** in moderate to very good yields (40-88%) (Scheme 14).[29]

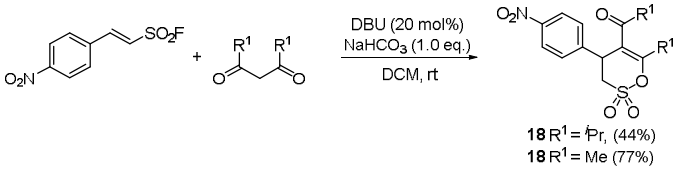


Scheme 14. NHC-catalysed annulation of trimethylsilyl enol ethers with various α,β-unsaturated sulfonylfluorides to afford 3,4-dihydro-1,2-oxathiine 2,2-dioxides.

The authors propose that the reaction progresses by the addition of the NHC to the α,β-unsaturated sulfonyl fluoride with simultaneous loss of the fluoride and desilylation of the trimethylsilyl enol ether generating a sulfonyl azolium and a desilylated enolate, respectively. The latter then undergoes a conjugate

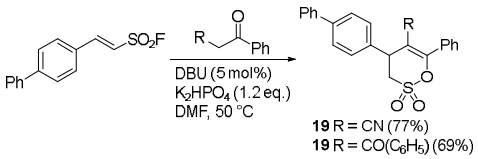
addition to the sulfonyl azolium generating a sulfonyl azolium enolate that, after proton transfer and loss of the NHC, formed the δ-sultone. The reaction conditions were sensitive to the electronic nature of the substrates as electron-deficient sulfonyl fluorides generated the corresponding 3,4-dihydro-1,2-oxathiine 2,2-dioxides in higher yields than the electron-rich analogues.

Qin *et al.*, have reported the DBU-catalysed annulation of (*E*)-2-(4-nitrophenyl)ethene-1-sulfonyl fluoride with 1,3-diketones to afford the condensed monocyclic 3,4-dihydro-1,2-oxathiine 2,2-dioxides **18** (Scheme 15) as part of a screening project for treatments for Alzheimer's disease.[30] The reactions were performed under mild conditions of DBU catalysis and $NaHCO_3$ in DCM at rt. The authors postulate that the reaction progressed by the conjugate addition of the enolizable 1,3-diketone to the α,β-unsaturated sulfonyl fluoride promoted by $NaHCO_3$, followed by fluoride activation by DBU and subsequent cyclisation to afford the δ-sultone.

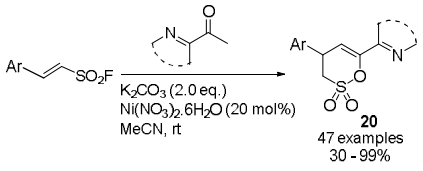


Scheme 15. DBU-catalysed annulation of a styrylsulfonyl fluoride with 1,3-diketones to afford 3,4-dihydro-1,2-oxathiine 2,2-dioxides.

The same group has reported the DBU-catalysed annulation between (*E*)-2-([1,1'-biphenyl]-4-yl)ethenesulfonyl fluoride and the enolizable ketones affording the 3,4-dihydro-1,2-oxathiine 2,2-dioxides **19** in good yields (Scheme 16).[31] Once again a catalytic amount of DBU was employed, but with a weaker base (K_2HPO_4) at a higher temperature (50 °C) in DMF. Qin *et al.*, have also prepared an extensive series of 4-(hetero)aryl-6-heteroaryl-3,4-dihydro-1,2-oxathiine 2,2-dioxides **20** from the treatment of (*E*)-(hetero)arylethenesulfonyl fluorides with a range of acyl aza-heterocycles (Scheme 17).[32] In a similar way, a $Ni(acac)_2$-catalysed annulation of 2-(*Z*)-phenylethenesulfonyl fluoride with 2-acetyl pyridine afforded 4-phenyl-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide in 69% yield. (Scheme 17).[33]

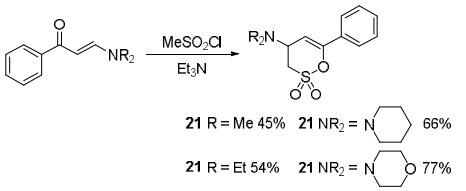


Scheme 16. DBU-catalysed annulation of a styrylsulfonyl fluoride with enolizable ketones to afford 3,4-dihydro-1,2-oxathiine 2,2-dioxides.

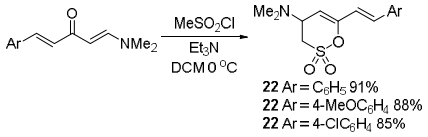


Scheme 17. Ni-mediated synthesis of 3,4-dihydro-1,2-oxathiine 2,2-dioxides from styrylsulfonyl fluorides and acyl substituted heterocycles.

Building upon early work concerning the addition of sulfenes to enaminoketones[34-36] Schenone *et al.*, have reported the synthesis of 3,4-dihydro-1,2-oxathiine 2,2-dioxides **21** by the cycloaddition of sulfene, generated *in situ* from the action of Et_3N upon methanesulfonyl chloride, to a series of enaminoketones, derived from acetophenone, in fair to good yield (45-77%) (Scheme 18).[37] The foregoing sulfene methodology was exploited by Schenone and co-workers to afford an extensive series of condensed ring systems incorporating the 3,4-dihydro-1,2-oxathiine 2,2-dioxide moiety.[38-46] Mahajan *et al.*, have prepared 6-styryl substituted 3,4-dihydro-1,2-oxathiine 2,2-dioxides **22** in excellent yield (85-91%) by reaction between enaminoketones, derived from (*E*)-4-arylbut-3-en-2-ones, and methanesulfonyl chloride in the presence of Et_3N in DCM (Scheme 19).[47]

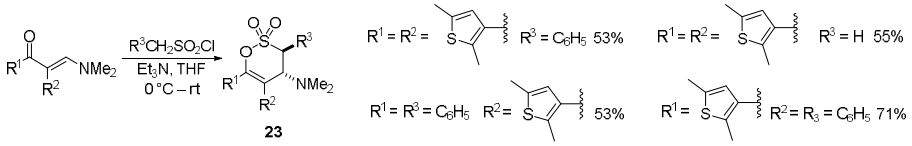


Scheme 18. Synthesis of 3,4-dihydro-1,2-oxathiines from the addition of sulfenes to aryl enaminoketones.

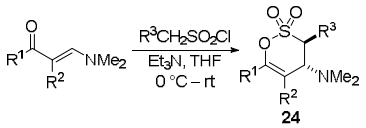


Scheme 19. Synthesis of 3,4-dihydro-1,2-oxathiines from the addition of sulfenes to styryl enaminoketones

The addition of sulfenes, generated by the action of base on a series of alkanesulfonyl chlorides, to enaminoketones has been revisited in two studies by Zonidis *et al.*, with the reported synthesis of a series of 3-thienyl substituted 3,4-dihydro-1,2-oxathiine 2,2-dioxides **23** which exhibited P-type photochromism (Scheme 20).[48] By employing an identical sulfene addition protocol diverse examples of poly-substituted 3,4-dihydro-1,2-oxathiine 2,2-dioxides **24** with different substituents at C-3, C-5 and C-6 were obtained in generally good yields (Table 1). The authors noted that the reaction progressed stereoselectively as the major products adopted a half-chair like conformation with a *trans*-diaxial arrangement of R^3 and NMe_2 as established by X-ray crystallography.[49]



Scheme 20. Application of the sulfene route to the synthesis of photochromic 3,4-dihydro-1,2-oxathiine 2,2-dioxides.



R^1	R^2	R^3	Yield (%)
C_6H_5	C_6H_5	C_6H_5	92
C_6H_5	C_6H_5	4-$CF_3C_6H_5$	60
4-$MeOC_6H_4$	4-$MeOC_6H_4$	C_6H_5	68
Bn	C_6H_5	C_6H_5	48 (*trans*), 25 (*cis*)
C_6H_5	Bz	C_6H_5	96
C_6H_5	H	C_6H_5	52
4-$MeOC_6H_4$	H	C_6H_5	83
4-$CF_3C_6H_4$	H	C_6H_5	64
4-C_5H_5N	H	C_6H_5	10
2-$NO_2C_6H_4$	H	C_6H_5	75
C_6H_5	C_6H_5	H	53
4-$MeOC_6H_4$	H	H	40
Me	2-FC_6H_5	C_6H_5	79

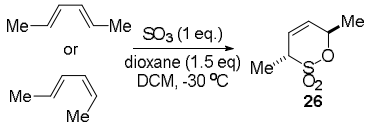
Table 1. Structural diversity of 3,4-dihydro-1,2-oxathiine 2,2-dioxides obtained from the addition of sulfenes to enaminoketones.

Lei *et al.*, describe an alternative synthesis of a styryl substituted 3,4-dihydro-1,2-oxathiine 2,2-dioxide **25** in 36% yield by sulfonation-mediated ring-closure of cinnamic acid derived ketoester using acetic anhydride and concentrated sulfuric acid (Scheme 21).[50]

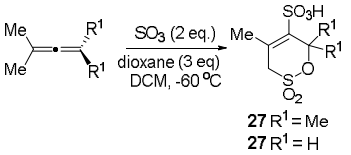
Scheme 21. Sulfonation-mediated ring closure of an enolisable ketoester.

2.2.2. 3,6-Dihydro-1,2-oxathiine 2,2-dioxides

The use of dienes features prominently in the synthesis of 3,6-dihydro-1,2-oxathiine 2,2-dioxides. Bordwell *et al.*, in 1958, examined the sulfonation (dioxane-SO_3 in 1,2-DCE) of 2,3-dimethyl-1,3-butadiene and obtained a 16% yield of 4,5-dimethyl-3,6-dihydro-1,2-oxathiine 2,2-dioxide.[51] Comparative data for the sulfonation of various 1,3-dienes with either SO_3-dioxane or SO_3-DMF has been summarised.[2] Cerfontain and co-workers studied the sulfonation of a series of 1,3-dienes using dioxane-SO_3 at -30 °C -rt in DCM and obtained the requisite 3,6-dihydro-1,2-oxathiine 2,2-dioxides in low to moderate yields. Of note was the reaction of (2*Z*,4*E*)- and (2*E*,4*E*)- hexa-2,4-dienes which led to the same oxathiine **26** (Scheme 22).[52] Mechanistically the reaction was thought to proceed *via* a fast [2+2]-cycloaddition to the diene to afford an initial β-sultone followed by a rapid ring cleavage-recyclisation process to the δ-sultone. In the same work, sulfonation of substituted allenes afforded oxathiine sulfonic acids **27** (Scheme 23). Further examples of diene sulfonation with SO_3-dioxane have been reported by Semenovskii *et al.*[53]



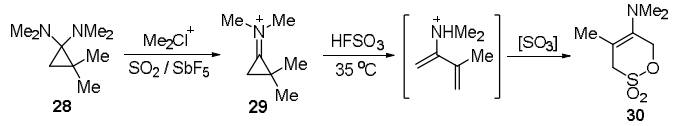
Scheme 22. Sulfonation of 1,3-dienes to afford 3,6-dihydro-1,2-oxathiine 2,2-dioxides.



Scheme 23. Sulfonation of allenes to afford 3,6-dihydro-1,2-oxathiine

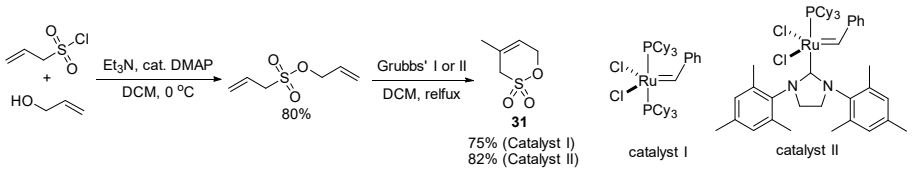
Kawanisi *et al.*, have reported the synthesis of 3,6-dihydro-1,2-oxathiine 2,2-dioxide in 48% yield by reaction of isoprene with SO_3-DMF complex.[54] The reaction of hexafluorobutadiene with SO_3 in a sealed ampule at 80 °C for 20 h gave a complex mixture of adducts which contained between 15-25 mol% of 3,3,4,5,6,6-hexafluoro-3,6-dihydro-1,2-oxathiine 2,2-dioxide which was characterized by ^{19}F NMR spectroscopy.[55]

Treatment of the tetrasubstituted cyclopropane **28** with dimethylchloronium ion in liquid SO_2 at -78 °C affords the iminium ion **29**, which when warmed to 35 °C in fluorosulfonic acid undergoes ring-opening, sulfonation and cyclisation to the 3,6-dihydro-1,2-oxathiine 2,2-dioxide **30** (Scheme 24).[56]



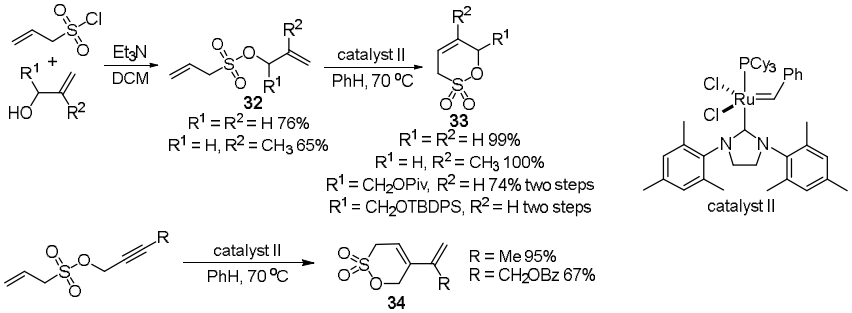
Scheme 24. Ring-opening of a *N*-cyclopropylidene-*N*-methylmethanaminium to afford a 3,6-dihydro-1,2-oxathiine 2,2-dioxide upon sulfonation.

Ring-closing metathesis of vinyl sulfonates, constructed by the base-mediated esterification of allylsulfonyl chloride with vinyl alcohols, was accomplished employing Grubbs' ruthenium catalysts and has proved to be an efficient and convenient strategy to access 3,6-dihydro-1,2-oxathiine 2,2-dioxides.[57, 58] Metz *et al.*, demonstrated the concept with the synthesis of δ-sultone **31** in good yield using Grubbs' generation I and II catalysts (Scheme 25).[59]



Scheme 25. Tethered diene metathesis route to a 3,6-dihydro-1,2-oxathiine 2,2-dioxide.

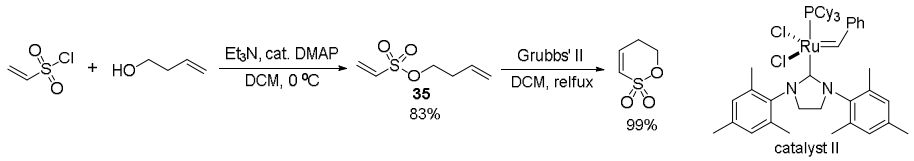
Later, Cossy *et al.*, expanded this strategy and prepared multiple 3,6-dihydro-1,2-oxathiine 2,2-dioxides **33** in good to quantitative yields (65-100%) from the olefin metathesis of sulfonates **32**, derived from the condensation reaction between the vinyl sulfonyl chlorides and primary alkenols (Scheme 26). In this same work, the metathesis protocol was extended to encompass the synthesis of the 3,6-dihydro-1,2-oxathiine 2,2-dioxides **34** from the ring-closing metathesis of but-2-yn-1-yl prop-2-ene-1-sulfonates (Scheme 26).[60]



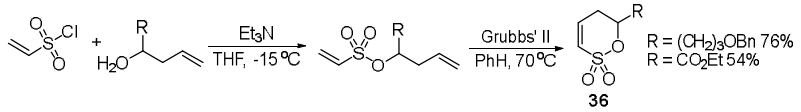
Scheme 26. Ring-closing metathesis approach to 3,6-dihydro-1,2-oxathiine 2,2-dioxides.

2.2.3. 5,6-Dihydro-1,2-oxathiine 2,2-dioxides

Ring-closing metathesis utilizing Grubbs' catalyst II has also been employed to access the unsubstituted 5,6-dihydro-1,2-oxathiine 2,2-dioxide ring by cyclisation of sulfonate **35** which was derived by the esterification of ethenesulfonyl chloride with but-3-en-1-ol (Scheme 27).[59] Two 6-substituted 5,6-dihydro-1,2-oxathiine 2,2-dioxides **36** have been obtained by a similar protocol albeit in lower yield (Scheme 28).[60]



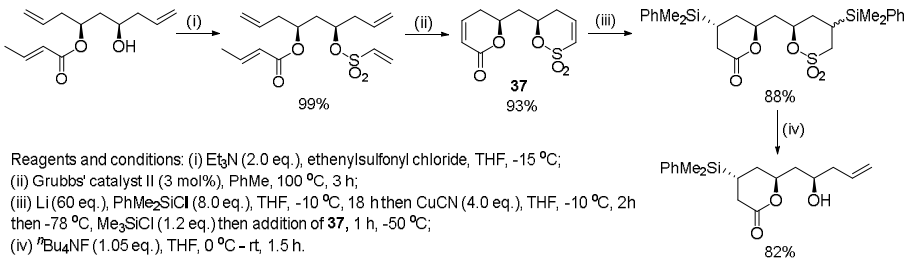
Scheme 27. Synthesis of 5,6-dihydro-1,2-oxathiine 2,2-dioxide by an RCM reaction.



Scheme 28. Extension of the RCM approach to substituted 5,6-dihydro-1,2-oxathiine 2,2-dioxides.

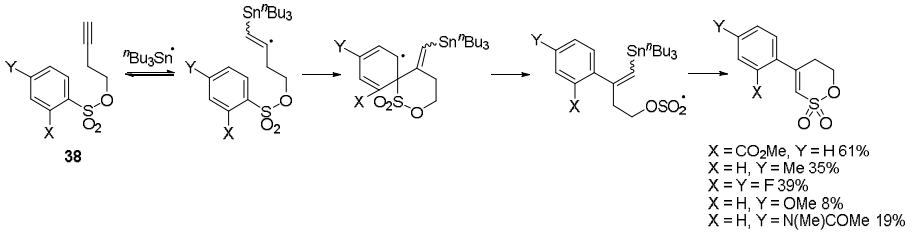
A ring-closing metathesis reaction has been used to simultaneously construct both pyran-2-one and 5,6-dihydro-1,2-oxathiine 2,2-dioxide rings **37** in high yield. The oxathiine ring served as a homoallyic alcohol protecting group through the Cu-promoted 1,4-addition of $PhMe_2SiCl$ which was subsequently

removed by fluoride ion with concomitant cleavage of the oxathiine ring regenerating the homoallylic alcohol. The protection strategy formed a key step in the synthesis of fragments of the unnatural enantiomers of the polyene polyol antibiotics Filipin III and Pentamycin (Scheme 29).[61]



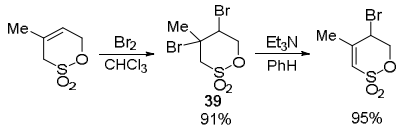
Scheme 29. Simultaneous RCM to construct a pyran-2-one ring and a 5,6-dihydro-1,2-oxathiine 2,2-dioxide ring.

A series of novel 4-aryl-5,6-dihydro-1,2-oxathiine 2,2-dioxides were obtained by Motherwell *et al.*, from the addition of a tri-*n*butylstannyl radical to arenesulfonate esters of the homopropargyl alcohol **38**. The reaction proceeds *via ipso*-substitution and a subsequent 6-*endo* addition-elimination protocol (Scheme 30).[62] Further examples from this route were reported by Zhang *et al.*, who also isolated 3-tributylstannyl substituted δ-sultones.[21]

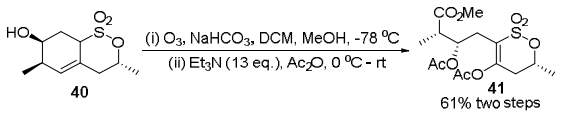


Scheme 30. Radical-mediated cyclisation route to 5,6-dihydro-1,2-oxathiine 2,2-dioxides.

The bromination of 4-methyl-3,6-dihydro-1,2-oxathiine 2,2-dioxide with molecular bromine in chloroform generated the expected dibromo adduct **39** in 91% yield. Base-promoted dehydrohalogenation afforded the 5-bromo-4-methyl-5,6-dihydro-1,2-oxathiine 2,2-dioxide in excellent yield (95%) (Scheme 31).[54] The bicyclic δ-sultone **40** was transformed into the diacetate **41** upon ozonolysis and trapping of the intermediate with a large excess of Et_3N in acetic anhydride (Scheme 32).[63]

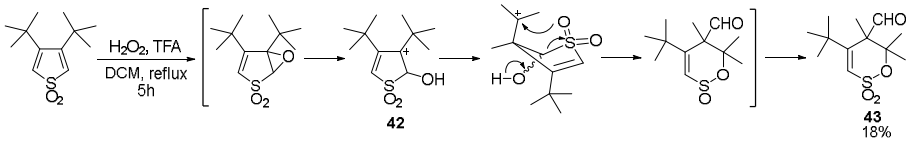


Scheme 31. Double bond migration to afford a 5,6-dihydro-1,2-oxathiine 2,2-dioxide.



Scheme 32. Ozonolysis induced ring cleavage to afford monocyclic dihydro oxathiine **41**.

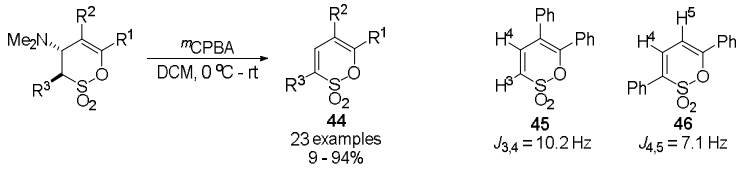
The oxidation of 3,4-di-*t*butylthiophene 1,1-dioxide with H_2O_2 in TFA induced a ring expansion to afford the penta-substituted 5,6-dihydro-1,2-oxathiine 2,2-dioxide **43** in low yield (18%). The initial step of the transformation is thought to involve epoxidation of the 2,3-bond and acid-catalysed ring-opening to afford the carbocation **42**. Methyl group migration and capture of the new tertiary carbocationic centre affords the six-membered ring and *S*-oxidation completes the sequence (Scheme 33).[64]



Scheme 33. Oxidative ring-expansion of a thiophene 1,1-dioxide to generate a 5,6-dihydro-1,2-oxathiine 2,2-dioxide.

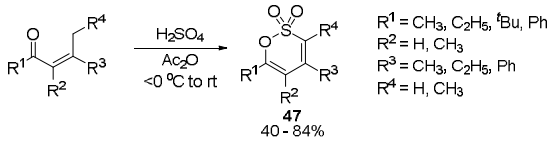
2.3. 1,2-Oxathiine 2,2-dioxides

Structural studies of the 1,2-oxathiine 2,2-dioxide ring are rare and are typically confined to articles concerning synthesis and reactivity studies. However, Barnett *et al.*, reported the X-ray crystal structure of 6-(4-bromophenyl)-1,2-oxathiine 2,2-dioxide and concluded that the ring was a non-aromatic 6π-electron system. Whilst the O1-C6=C5-C4=C3 unit is essentially planar the sulfur function escapes this plane by 0.58 Å. Furthermore, there is bond alternation with C4-C5 exhibiting appreciable single bond character (1.443 Å) with the C5-C6 (1.320 Å) and C3-C4 (1.341 Å) showing only minor deviation from the typical C=C bondlength.[65] The bond alternation and deviation from planarity was also noted for the crystal structure of 3,5,6-triaryl-1,2-oxathiine 2,2-dioxide which was obtained in a recent study by Zonidis *et al.*, concerning the synthesis of an extensive series of 3,5,6-triaryl-, 3,6-diaryl-, 3,5-diaryl- and 5,6-diaryl- 1,2-oxathiine 2,2-dioxides.[48,49] In the latter study, a facile Cope elimination of the 4-dimethylamino unit from the 3,4-dihydro-1,2-oxathiine 2,2-dioxide precursor was essential to introduce the 3,4-double bond into **44** as a consequence of the *anti-peri*-planar orientation of the dimethylamino group and the C-3 substituent (Scheme 34). Additional evidence from this study which is suggestive of the bond alternation of the diene unit of **44** was garnered from coupling constants $J_{3,4}$=10.2 Hz and $J_{4,5}$=7.1 Hz for the 5,6-diphenyl- **45** and 3,6-diphenyl **46** substituted 1,2-oxathiine 2,2-dioxides.



Scheme 34. Facile Cope elimination route to afford oxathiine 2,2-dioxides.

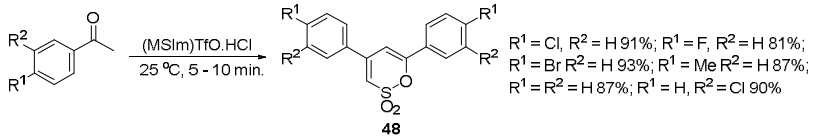
The unsaturated 1,2-oxathiine 2,2-dioxide system was first prepared by Morel and Verkade by the sulfonation of α,β- or β,γ- unsaturated ketones with concd. H_2SO_4 in Ac_2O; moderate to good yields were noted for this first small library of 1,2-oxathiine 2,2-dioxide derivatives **47** (Scheme 35).[66] Additional examples of this sulfonation-cyclisation methodology using concd. H_2SO_4 in Ac_2O were reported by Klebert *et al.*[67] In a variation of this protocol, the reaction of mesityl oxide with chlorosulfonic acid in Ac_2O gave 4,6-dimethyl-1,2-oxathiine 2,2-dioxide in 41% yield.[68]



Scheme 35. Sulfonation-mediated ring-closure of γ-methylene ketones.

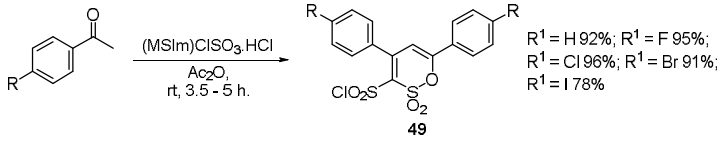
Further variations of the foregoing strategy include the use of the active ionic liquids such as methylsulfonylimidazolium triflate hydrochloride [(MSIm)TfO HCl] to effect the efficient condensation and sulfonation-cyclisation of acetophenones to afford 4,6-diaryl-1,2-oxathiine 2,2-dioxides **48** in excellent yield (Scheme 36).[69] Comparable results were obtained using *N*-methyl-2-pyrrolidonium chlorosulfonate, [NMP-$ClSO_3H$] albeit at higher reaction temperatures.[70] Unfortunately, the scope of the foregoing protocol

is limited to the introduction of identical aryl groups, derived from the acetophenone, at the 4- and 6-positions of the oxathiine moiety.



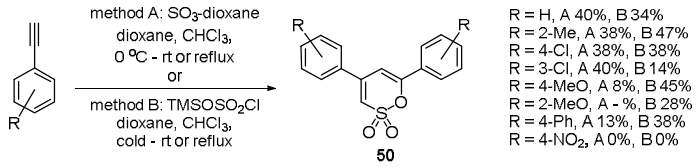
Scheme 36. Condensation and sulfonation-cyclisation of acetophenones to afford 4,6-diaryl-1,2-oxathiine 2,2-dioxides.

Methylsulfonylimidazolium chlorosulfonate hydrochloride [(MSIm)$ClSO_3$ HCl] in conjunction with TFAA effected the smooth conversion of a series of 4-substituted acetophenones into 3-chlorosulfonyl substituted oxathiines **49** (Scheme 37).[71]



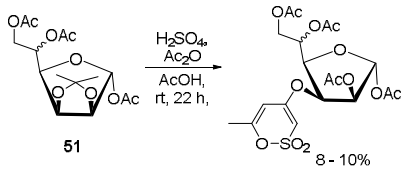
Scheme 37. Condensation and sulfonation-cyclisation of acetophenones to afford 3-chlorosulfonylated 4,6-diaryl-1,2-oxathiine 2,2-dioxides.

The sulfonation of a series of ethynylbenzenes with either SO_3-dioxane or trimethylsilylchlorosulfonate ($TMSOSO_2Cl$) provides a useful, if low yielding, alternative to the sulfonation-cyclisation of acetophenones, to afford **50**. However, this protocol also suffers from the same disadvantage of affording identical 4,6-diaryl substituents in the oxathiine ring (Scheme 38).[72]

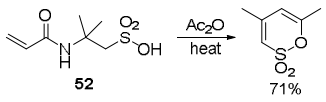


Scheme 38. Tandem sulfonylation-condensation of ethynylbenzenes.

A serendipitous formation of an oxathiine 2,2-dioxide in 8-10% yield was noted by Craig and co-worker during the H_2SO_4-Ac_2O mediated deprotection of the acetonide function on the furanose ring **51** (Scheme 39).[73] Heating a solution of 2-acrylamido-2-methylpropane sulfonic acid **52** in Ac_2O also unexpectedly afforded an oxathiine 2,2-dioxide (Scheme 40).[74]



Scheme 39. Serendipitous formation of an oxathiine 2,2-dioxide.

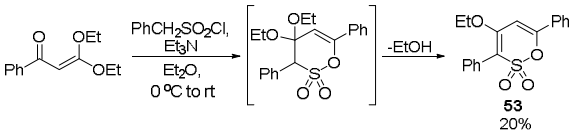


Scheme 40. Ac_2O-mediated cyclisation of **52** to afford an oxathiine 2,2-dioxide.

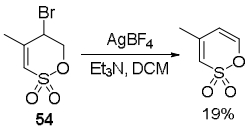
Phenylsulfene, generated *in situ* from the action of Et_3N on phenylmethanesulfonyl chloride, underwent a hetero Diels-Alder cycloaddition with the benzoyl ketene acetal to afford the 3,4,6-trisubstituted

oxathiine 2,2-dioxide **53** directly as a consequence of the facile elimination of ethanol from the initial adduct (Scheme 41).[35]

Kawanisi *et al.*, have demonstrated that a fully unsaturated 1,2-oxathiine derivative can be obtained, albeit in a low yield, *via* an $AgBF_4$-assisted dehydrobromination reaction of the 5,6-dihydro precursor **54** (Scheme 42).[54]



Scheme 41. Sulfene addition to a benzoyl ketene acetal.



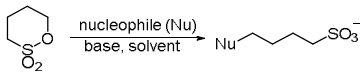
Scheme 42. 1,3-Oxathiine 2,2-dioxide by elimination of HBr using $AgBF_4$.

3. Reactivity and applications

In this section, the reactivity of the various 1,2-oxathiine 2,2-dioxide rings is presented wherein a reaction is a transformation that does not lead to another 1,2-oxathiine ring. Where there is an application associated with the target product this has been discussed.

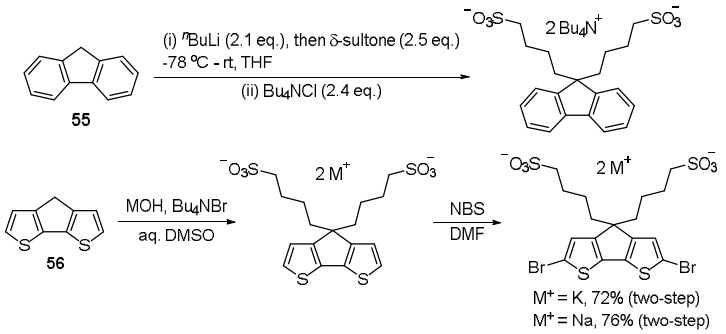
3.1. 1,2-Oxathiane 2,2-dioxides

The chemistry of the 1,2-oxathiane 2,2-dioxide unit is dominated by its propensity to undergo ring-opening upon the addition of nucleophiles to C-6 to afford new entities bearing a sulfobutyl chain (Scheme 43). The foregoing chemistry is particularly attractive as it enables water solubility to be imparted into a wide variety of molecules and polymers under relatively mild conditions.



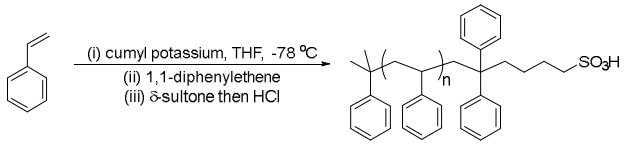
Scheme 43. Generic nucleophilic ring-opening of the 1,2-oxathiane 2,2-dioxide unit.

The reaction of δ-sultone with carbon-based nucleophiles, derived from acidic methylene compounds, has been widely applied to fluorene derivatives *e.g.* **55**[75,76] and 'heterocyclic fluorenes', such as **56**, for the formation of conjugated polymers for modern material applications (Scheme 44).[77-79]



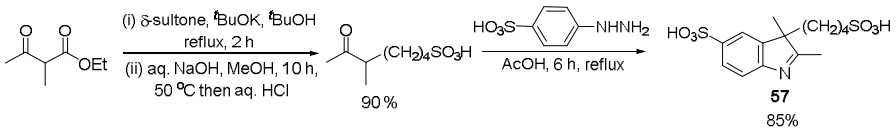
Scheme 44. Sulfobutylation of fluorene derivatives.

The living anionic polymerisation of styrene was terminated through the addition of δ-sultone to afford a poly(styrene) which was end modified with a sulfonic acid residue and which possessed a polydispersity index of 1.03 and a M_n of 1.9×10^4 (Scheme 45).[80]



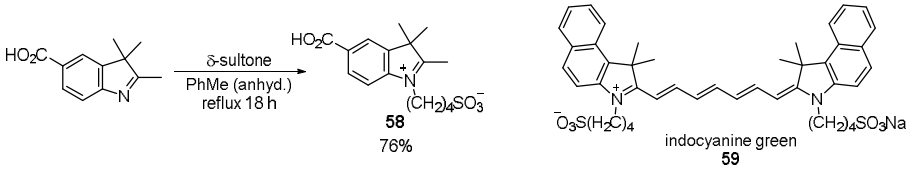
Scheme 45. δ-Sultone termination of a living anionic polymerisation.

The C-2 alkylation of ethyl 2-methyl-3-oxobutanoate has been extensively studied as the derived 5-(ethoxycarbonyl)-5-methyl-6-oxoheptane-1-sulfonic acid is essential for the preparation of water soluble 3*H*-indoles *e.g.* **57**,[81] that are key intermediates for the preparation of water soluble cyanine dyes which are extensively used in biomedical imaging applications (Scheme 46).[82-84]



Scheme 46. Preparation of 5-(ethoxycarbonyl)-5-methyl-6-oxoheptane-1-sulfonic acid.

Moving to nitrogen-based nucleophiles, the sp^2 hybridised *N*-atom of a variety of nitrogen containing heterocycles have been sulfoalkylated upon reaction with δ-sultone. Of great significance is the reaction of 3*H*-indoles to afford derivatives such as **58**, which are required for NIR absorbing and emitting cyanine colourants (Scheme 47).[85] Perhaps the best known of these colorants is indocyanine green **59** and together with a significant number of derivatives.[86]



Scheme 47. Synthesis of *N*-sulfoalkylated 3*H*-indole **58**.

Extensive use has been made of δ-sultone to *N*-sulfoalkylate azoles (imidazoles and 1,2,3-triazoles) for the preparation of task specific ionic liquids. Typically, the synthesis involves heating the *N*-alkyl imidazole in either neat δ-sultone or in an inert solvent with δ-sultone often followed by a subsequent acidification step. Examples of representative structures of the azoles are presented in Figure 2.[87-93]

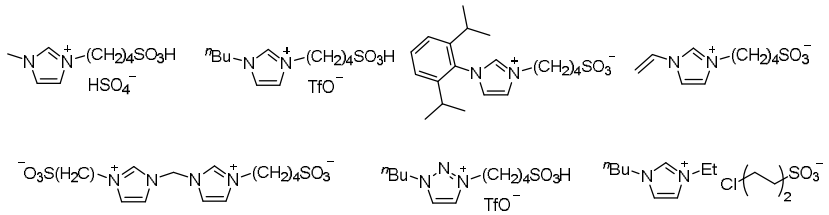


Figure 2. Representative ionic liquids prepared from δ-sultone.

Of note in Figure 2 is the example 1-butyl-3-ethyl-1*H*-imidazol-3-ium 4-chlorobutylsulfonate which was obtained by the nucleophilic ring-opening of δ-sultone by the chloride counter ion of the imidazolium ionic liquid upon stirring at 40 °C.[94]

In a similar manner to azoles, substituted pyridine,[95] bipyridine[96] and quinoline[97], *N*-atoms also effect nucleophilic ring-opening of the δ-sultone unit upon heating either neat or in a solvent to afford water soluble zwitterions (Figure 3).

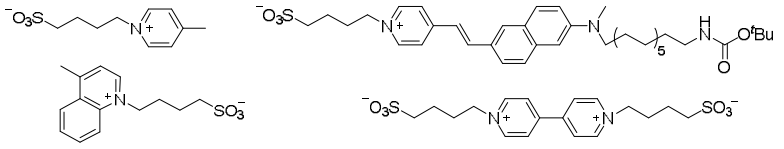
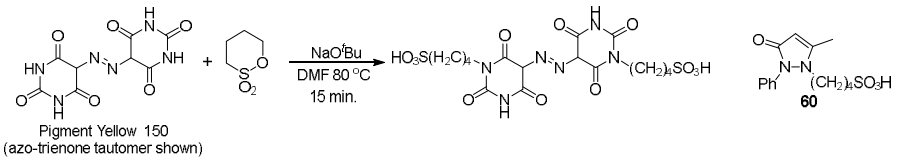


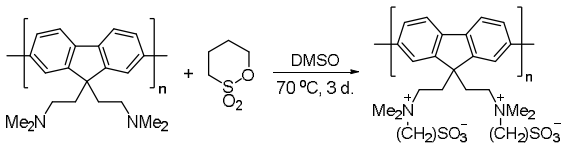
Figure 3. Selected sulfobutylated pyridinium salts.

The water solubility of the organic azo-pigment (C.I. Pigment Yellow 150) for ink-jet applications has been improved by reaction of the amide like *N*-atoms of the pyrimidinone rings with δ-sultone (Scheme 48).[98] 5-Methyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one afforded the sulfobutyl derivative **60** upon reaction with δ-sultone.[99]



Scheme 48. Modification of C.I. Pigment Yellow 150 with δ-sultone.

The nucleophilicity of terminal trialkylamine functions in a wide range of polymers, co-polymers and dendrimer-like hyperbranched polymers has been exploited in order to ring-open δ-sultone in a post polymerisation modification to impart either water solubility, surfactant or gelation properties into the resulting zwitterionic materials (Scheme 49).[100-103]

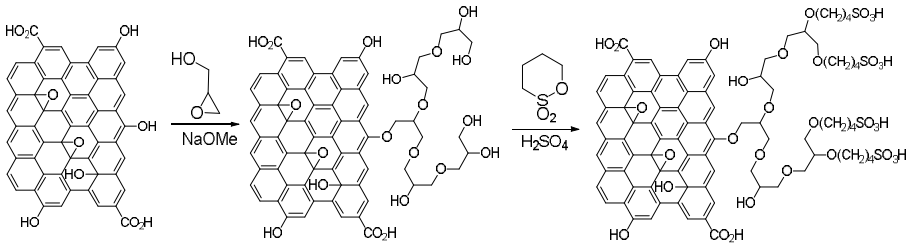


Scheme 49. Preparation of a zwitterionic, conjugated polymeric fluorescent hydrogel.[100]

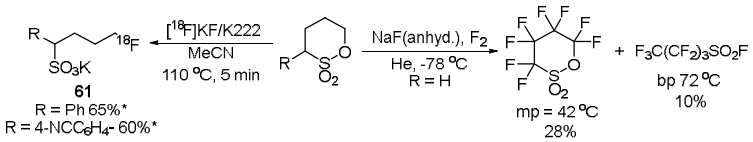
In a similar manner to the modification of polymers containing pendant trialkylamine functions, polymers comprising of phenolic units [substituted poly(aryl ether sulfones)[104] and poly(aryl ether ketones)[105]] or aliphatic hydroxyl functions *e.g.* poly(cyclodextrins)[106] have been successfully modified upon reaction with δ-sultone in the presence of a base.

Nanospheres have been obtained from sulfobutylated poly(vinyl alcohol)-graft-poly(lactide-co-glycolide)s[107] and proton-conducting composite membranes incorporating surface-modified sulfobutylated montmorillonite have been described.[108] Hyperbranched poly(glycerol) functionalised graphene oxide has been prepared *via* an acid-catalysed sulfobutylation process (Scheme 50) and employed as a catalyst for the synthesis of a variety of condensed heterocycles.[109]

In addition to the ionic liquid-mediated chloride induced ring-opening of δ-sultone[94], the nucleophilic ring-opening of 3-benzyl-1,2-oxathiane 2,2-dioxides with [^{18}F]fluoride afforded the [^{18}F]-labelled fluorosolfonates **61**, in good radiochemical yields, which were developed for PET imaging (Scheme 51).[110] The direct fluorination of δ-sultone itself has been accomplished with elemental fluorine at low temperature and affords a mixture of the perfluoro-δ-sultone and the ring-opened perfluorobutane sulfonyl fluoride (Scheme 51).[111]

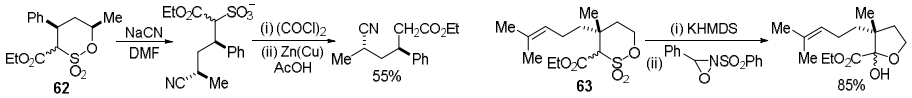


Scheme 50. Modification of functionalised graphene oxide with δ-sultone.



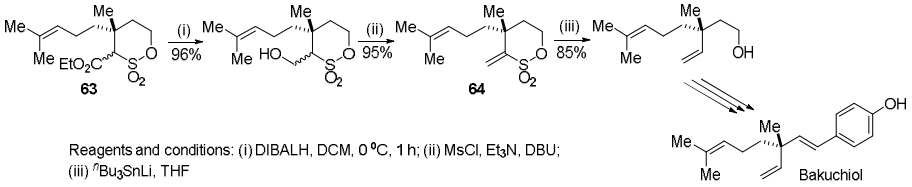
Scheme 51. Fluorination reactions of 1,2-oxathiane 2,2-dioxides.

Cyanide ion-induced ring-opening of the trisubstituted 1,2-oxathiane 2,2-dioxide **62** with subsequent Zn(Cu) couple removal of the sulfonyl chloride gave the δ-cyano ester in 55% over three-steps. In the same study, treatment of the enolate derived from **63** with Davis' oxaziridine in THF gave the lactol in 85% yield (Scheme 52).[26]



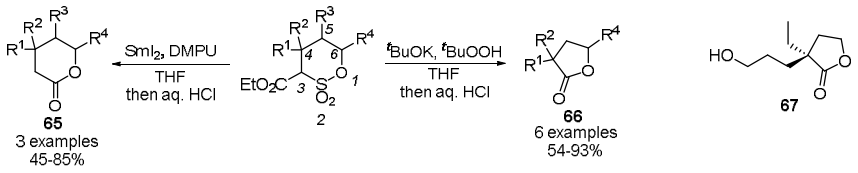
Scheme 52. Versatility of substituted 1,2-oxathiane 2,2-dioxides in synthesis.

The oxathiane **63** proved to be a useful starting material for the synthesis of Bakuchiol. Reduction and elimination provided the exomethylene derivative **64** which was desulfonated using $^{n}Bu_3SnLi$ to afford the dienol intermediate *en-route* to Bakuchiol (Scheme 53).[112]



Scheme 53. Synthesis of Bakuchiol.

The acidity of the 3-proton in 4,4-dimethyl-3-ethoxycarbonyl-1,2-oxathiane 2,2-dioxide has also been employed to introduce a 3-allyl substituent in 85% yield by classical anion chemistry. Additionally, in this work, a short series of δ-lactones **65** were obtained from substituted 3-ethoxycarbonyl-1,2-oxathiane 2,2-dioxides upon treatment with SmI_2 in the presence of DMPU (Scheme 54).[113] A related series of γ-lactones **66** were constructed in good to excellent yields by treatment of the anion derived from substituted 3-ethoxycarbonyl-1,2-oxathiane 2,2-dioxides with ^{t}BuOOH (Scheme 54). The route provided straightforward access to a key lactone intermediate **67** for the preparation of (-)-eburnamonin.[114]



Scheme 54. Conversion of 3-ethoxycarbonyl-1,2-oxathiane 2,2-dioxides into lactones.

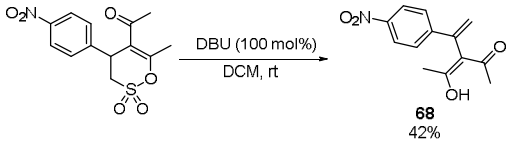
Reduction of substituted 1,2-oxathiane 2,2-dioxides with $LiAlH_4$ in either refluxing Et_2O or refluxing 1,4-dioxane effected ring cleavage to afford moderate to low yields of 4-mercaptobutanols often together with 1,4-dihydroxybutanes.[16] Treatment of 4,6-dimethyl-1,2-oxathiine 2,2-dioxide with $NaBH_4$ in aq. NaOH and subsequent hydrogenation over PtO_2 with acidification and recyclisation upon heating under vacuum gave the 4,6-dimethyl-1,2-oxathiane 2,2-dioxide.[115]

In addition to the foregoing reactions and applications of 1,2-oxathiane 2,2-dioxides, a significant number of patents have claimed variously substituted δ-sultones as non-aqueous solvents, electrolytes and additives in Li-ion batteries.[116-123]

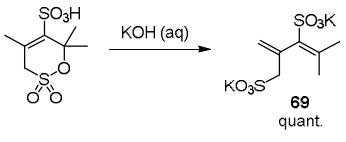
3.2. Dihydro-1,2-oxathiine 2,2-dioxides

In comparison to the 1,2-oxathiane 2,2-dioxides (δ-sultones) there is relatively little published on the reactivity of the three isomeric dihydro-1,2-oxathiine 2,2-dioxides.

Qin *et al.*, have shown that by employing a stoichiometric amount of DBU, decomposition of 3,4-dihydro-1,2-oxathiine 2,2-dioxide takes place, *via* loss of SO_2, generating the β-hydroxyketone **68** in 42% yield (Scheme 55).[30] The hydrolysis of the sulfonic acid with aq. KOH solution affords the dipotassium 4-methyl-2-(sulfomethyl)-1,3-pentadiene-3-sulfonate **69** in quantitative fashion (Scheme 56).[52]



Scheme 55. Base-mediated ring-opening of an acyl-3,4-dihydro 1,2-oxathiine 2,2-dioxide.



Scheme 56. Preparation of the disulfonate **69**.

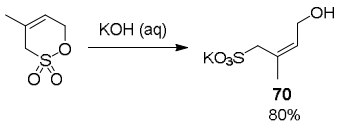
Semenovsky *et al.*, have also explored the base-mediated ring-opening of 3,6-dihydro-1,2-oxathiine 2,2-dioxides; the (*Z*)-4-hydroxy-2-methylbut-2-ene-1-sulfonate potassium salt **70** was isolated in 80% yield upon treatment of the requisite δ-sultone with a 0.1 N aq. KOH solution (Scheme 57).[124]

The electron deficient double bond of the 5,6-dihydro-1,2-oxathiine 2,2-dioxide unit has been utilised as a dienophile in Diels-Alder cycloadditions. Metz *et al.*, have shown that cyclohexa-1,3-diene undergoes a [4+2]-cycloaddition to **71** (n=1) in good yield using 2,6-di-*t*butyl-4-methylphenol (BHT) as a catalyst, albeit under forced conditions (Scheme 58).[57] Interestingly, the reaction was found to selectively afford the *endo* product, which may indicate strong secondary orbital interactions between the diene and the 1,2-oxathiine system. Considering the increased reaction time as compared with the corresponding 5-membered sultone **71** (n=0) (6 d versus 27 h), it can be suggested that the conformation and bond angles of the 5,6-dihydro-1,2-oxathiine 2,2-dioxide ring have a detrimental effect on the rate of the reaction (Scheme 58).

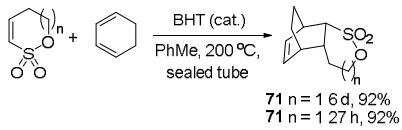
The 4-hydroxy-5,5-dimethyl derivative **72** has been employed in a three-component one-pot reaction to afford podophyllotoxin-based heterolignans, which are examples of condensed [1,2]oxathiino[4,3-*b*]quinoline 1,1-dioxides, **73** (Scheme 59).[125] The tetracycles **73** exhibited mild insecticidal activity against mustard beetle pest (*Phaedon cochleariae*) during a broad SAR study of potential insecticidal agents through inhibition of tubulin polymerization.

Several simple alkyl substituted 5,6-dihydro-1,2-oxathiine 2,2-dioxides[126-128] have been incorporated in electrolytes in lithium batteries as have (poly)fluorinated derivatives[129] and substituted

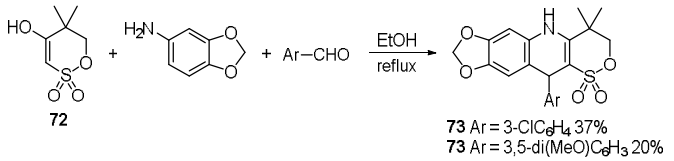
5,6-dihydro-1,2-oxathiin-6-one 1,1-dioxides.[130,131] 3,6-Dihydro-1,2-oxathiine 2,2-dioxides have also been employed as additives in the positive electrode film in energy storage devices.[132]



Scheme 57. Hydrolysis of 4-methyl-3,6-dihydro-1,2-oxathiine 2,2-dioxide.



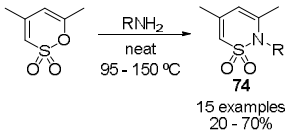
Scheme 58. 5,6-Dihydro-1,2-oxathiine 2,2-dioxide unit as a dienophile.



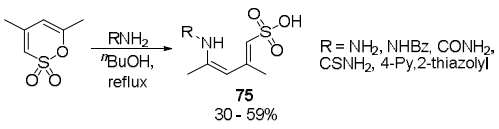
Scheme 59. Assembly of condensed [1,2]oxathiino[4,3-*b*]quinoline 1,1-dioxides *via* a multi-component reaction.

3.3. 1,2-Oxathiine 2,2-dioxides

Among the reactions that have been reported for the unsaturated 1,2-oxathiine 2,2-dioxides, the most exhaustively explored is the substitution of the *O*-atom of the 6-membered ring with a substituted *N*-atom, *via* an ANRORC (Addition of Nucleophile-Ring-Opening-Ring-Closing) reaction to afford a sultam. An extensive range of substituted anilines, benzidines and benzylamine have been employed to afford sultams **74** and the reaction typically requires heating over 100 °C either neat[133-134] or in a solvent *e.g.* anisole at reflux[135] to effect completion in moderate to good yields (Scheme 60). The presence of a 3-bromine atom on the oxathiine ring is tolerated and bromo sultams have been isolated.[136] Interestingly, the use of ^{n}BuOH as the solvent resulted in the formation of δ-aminosulfonic acids **75** with hydrazine, benzamide, urea, thiourea and electron deficient amino-substituted heterocycles (Scheme 61).[137]



Scheme 60. Transformation of a δ-sultone into a sultam.



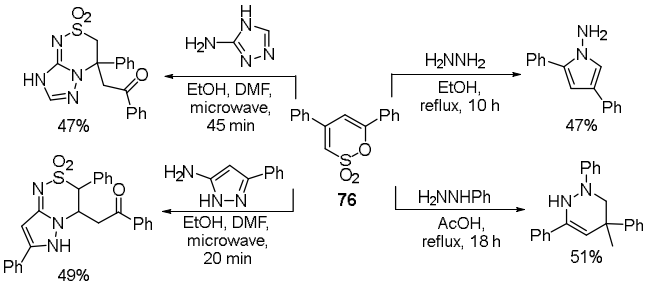
Scheme 61. Nucleophilic ring-opening of 1,2-oxathiine 2,2-dioxides.

Elaborating on the reactivity of 4,6-substituted 1,2-oxathiine 2,2-dioxides with amines and hydrazines (Scheme 60 and 61), Ali, Jäger and Metz presented a range of different addition reactions where reaction with *N*-containing bi-nucleophiles led to new heterocyclic products in moderate yields from 4,6-diphenyl oxathiine **76** (Scheme 62).[138]

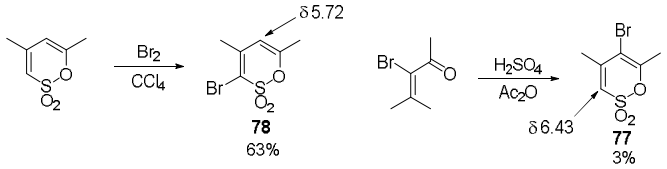
The bromination of unsaturated 1,2-oxathiines is also of significant interest, as it provides brominated precursors for further manipulation. Eastman and Gallup first attempted the bromination of the 4,6-dimethyl 1,2-oxathiine 2,2-dioxide using Br_2 in CCl_4 and claimed that the product was the 5-bromo analogue **77**.[68] The latter finding was disputed by Barnett and McCormack, who repeated the reaction and showed that the product was in fact the 3-bromo-4,6-dimethyl-1,2-oxathiine 2,2-dioxide isomer **78** (63%) by both NMR spectroscopy and the unequivocal synthesis of the 5-bromo isomer by cyclisation of 3-bromomesityl oxide (Scheme 63).[139]

Bromination of a series of 4,6-diaryl substituted 1,2-oxathiine 2,2-dioxides was unequivocally established by X-ray crystallography to afford the 3-bromo derivatives **79** in excellent yields. The bromine

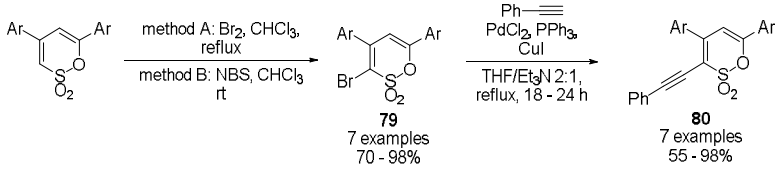
atom was subsequently replaced in a high yielding Sonogashira reaction with ethynylbenzene to afford **80** (Scheme 64).[72]



Scheme 62. Transformation of oxathiine **76** into other heterocyclic ring systems.

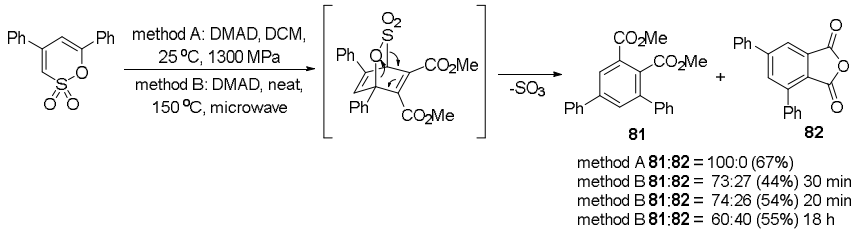


Scheme 63. Synthesis of 3- and 5- bromo-1,2-oxathiine 2,2-dioxides.



Scheme 64. Preparation of 3-phenylethynyl-1,2-oxathiine 2,2-dioxides.

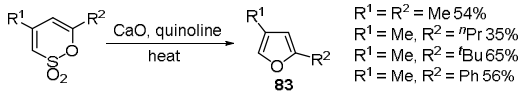
The exploration of 4,6-diphenyl-1,2-oxathiine 2,2-dioxide as the diene in cycloaddition reactions with DMAD met with success to afford a mixture of terphenylene **81** and anhydride **82** through a Diels-Alder–retro Diels-Alder sequence with additional cyclisation of the proximal ester groups to afford the anhydride unit of **82** (Scheme 65).[140] This methodology was subsequently extended by the same group to encompass symmetrical 4,6-diaryl-1,2-oxathiine 2,2-dioxides and a selection of dienophiles to afford an extended series of substituted 1,3-terphenyls.[141]



Scheme 65. Synthesis of terphenyls by a Diels-Alder-retro Diels-Alder reaction sequence.

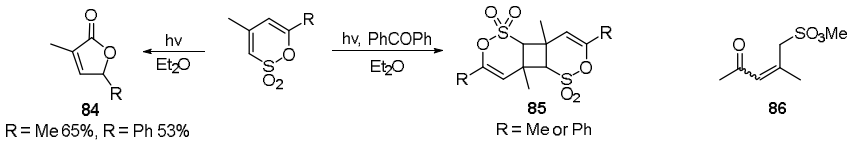
Reflecting on the reactivity of the sulfonyl moiety of the sultone ring, ring contraction reactions have been attempted under either thermal or photochemical conditions. Morel and Verkade have shown that heating various 4,6-disubstituted-1,2-oxathiine 2,2-dioxides in quinoline in the presence of CaO,

2,4-disubstituted furans **83** can be obtained in moderate to good yields (Scheme 66).[142] The thermal SO_2 extrusion process constitutes a useful approach to these relatively inaccessible substituted furans of which 2,4-dimethylfuran is a useful building block for long chain polypropionates[143] and the A and C ring subunits of taxol.[144]



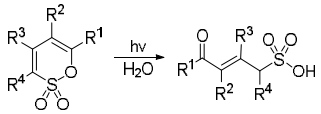
Scheme 66. Thermal extrusion of SO_2 from oxathiines to afford substituted furans.

Ether solutions of 4,6-di-substituted 1,2-oxathiine 2,2-dioxides can lose a sulfur monoxide fragment to afford the corresponding furanones **84** upon irradiation. Interestingly, when the photochemical reaction was sensitized by the addition of benzophenone, [2+2]-dimers **85** of the starting oxathiines were isolated (Scheme 67).[145]



Scheme 67. Photolysis of 1,2-oxathiine 2,2-dioxides.

Photolysis of 2,4-dimethyl-1,2-oxathiine 2,2-dioxide in the presence of MeOH results in the formation of the acyclic sulfone ester **86** in an unspecified yield through interception of an intermediate resulting from an electrocyclic ring-opening of the oxathiine moiety.[146] The propensity of 1,2-oxathiine 2,2-dioxides to ring open upon irradiation has been utilised in the development commercial photoresists (photo-acid generators) by Masaaki *et al.*, (Scheme 68).[147] 1,2-Oxathiine 2,2-dioxides have also been incorporated in lithographic printing systems, as key components in the IR photosensitive mixtures that are applied to the printing plate.[148]



Scheme 68. 1,2-Oxathiine 2,2-dioxide photoresists.

Similar to their perhydro and dihydro counterparts, the unsaturated 1,2-oxathiine 2,2-dioxide analogues have found use in lithium secondary battery technologies.[149-151]

4. Concluding remarks

The various 1,2-oxathiine 2,2-dioxides are readily accessible by employing established chemistry in generally good to excellent yields from commercially available starting materials. Their varied reactivity, which can be harnessed to obtain a multitude of interesting compounds including sulfonic acids, carbocycles and numerous heterocycles should ensure sustained interest in the years to come. Moreover, their appearance in modern technological applications such as printing, energy storage and photochromism continues to grow.

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