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New mechanistic aspects on the catalytic transformation of vinylthiiranes to mono and disubstituted 3,6-dihydro-1,2-dithiins by tungsten pentacarbonyl monoacetonitrile

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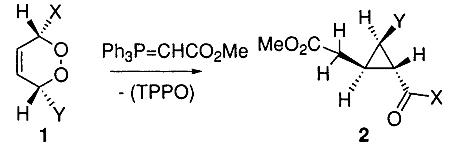
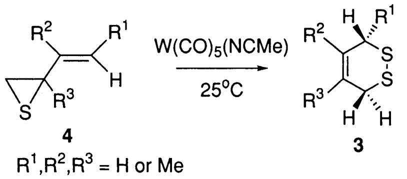
Abstract—Various alkyl and aryl mono- and disubstituted 3,6-dihydro-1,2-dithiins have been synthesised from their corresponding vinylthiiranes exploiting Adams' tungsten pentacarbonyl monoacetonitrile catalytic transformation. New conclusions pertaining to the rate determining step, the sensitivity of the process to precursor sterics and electronics, and the nature of various reaction intermediates are highlighted. © 2002 Published by Elsevier Science Ltd.

1. Introduction

In connection with our ongoing studies on the ring-opening of 3,6-disubstituted 1,2-dioxines **1** by stabilised phosphorous ylides with the final construction of highly substituted cyclopropanes **2**, we were stimulated to prepare an analogous range of 3,6-dihydro-1,2-dithiins of type **3**.[1] While there is significant interest in 1,2-dithiins of type **3** within the scientific community their preparation is not yet routine, with much of that interest residing in chemistry parallel to their synthesis. In work aimed at exploring the chemistry of singlet sulfur, the synthesis of 1,2-dithiins by Diels–Alder chemistry has been used as a model to monitor the formation of this reactive elemental form of sulfur.[2] More recently, Adams and his colleagues investigated novel methods to desulfurise petroleum feedstock which led to the synthesis of 1,2-dithiins along with other sulfur containing heterocycles such as thiiranes and thietanes.[3] Finally, the bioactivity of 1,2-dithiins has been investigated with various natural products isolated. For instance, unsaturated 1,2-dithiins as typified by thiarubin A and B display significant antiviral,[4] antibacterial[5] and antifungal[5a,6] activities. Furthermore, dihydro-1,2-dithiins have been isolated from various foods such as the garlic bush,[7] onions[8] and cooked asparagus.[9] Our interest in 1,2-dithiins lay in their possible use as synthetic building blocks and as such we were interested in an efficient route to these compounds. Although the work discussed above is not centred around synthesis, the use of singlet sulfur and also the desulfurisation of thiiranes provided possible routes to these compounds. After some preliminary work our synthetic efforts became concentrated on the use of vinyl thiiranes as precursors to 1,2-dithins as pioneered by Adams, due to the high reported yields and mild reaction conditions.



X and Y = H, alkyl and aryl.



R^1,R^2,R^3 = H or Me

The catalytic cycle proposed by Adams[3] for the conversion of vinylthiiranes **4** into 1,2-dithiins **3** initially involves the formation of the vinylthiirane W(CO)$_5$ complex **5** through the displacement of the acetonitrile ligand by **4**, step a, Scheme 1. It has been tentatively proposed that formation of zwitterionic intermediate **6**, step b, occurs via the intermediacy of **7**, and not as a direct result of a bimolecular nucleophilic addition mechanism in which the sulfur atom of the second thiirane adds to the β-carbon of complex **5**. This proposition was based on the observation that methyl substitution on the vinyl group of **4** led to acceleration of reaction rate through stabilisation of the resultant carbocation **7**. Intramolecular cyclisation of **6** with concomitant loss of the 1,3-butadiene **8**, step c, affords intermediates of type **9** which have been characterised crystallographically.[3c] Final displacement of the 1,2-dithiin from **9** by vinyl

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Keywords: vinylthiiranes; 1,2-dithiins; tungsten pentacarbonyl monoacetonitrile.

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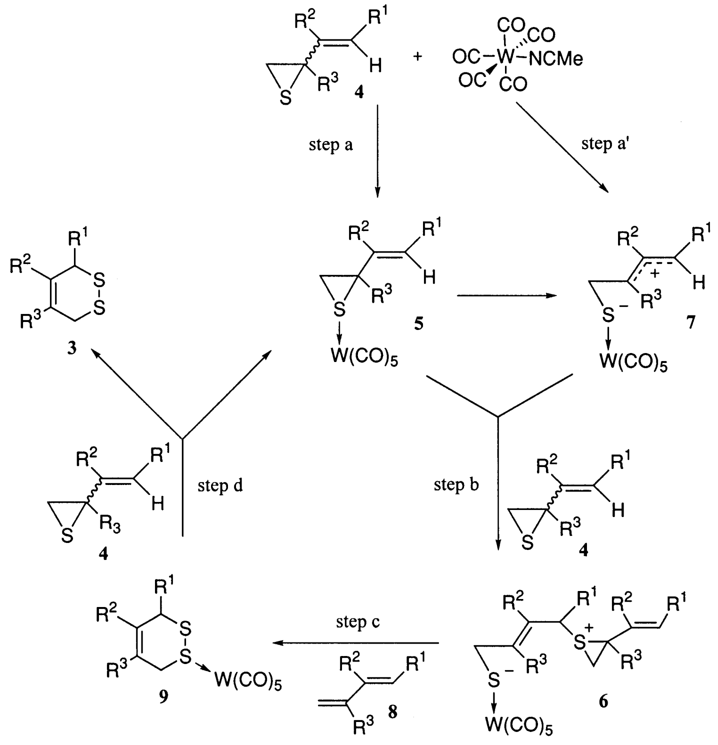


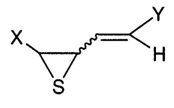
Scheme 1.

thiirane **4**, step d, completes the catalytic cycle, thus, reforming intermediate **5**. While Adams has shown that the reaction is successful for a range of H and Me-substituted vinylthiiranes **4**, the ability of the transformation to 'carry' a diverse range of substituents (H, alkyl and aryl) both in the 3- and 6-positions of the forming 1,2-dithiin is yet to be demonstrated. Furthermore, by utilising aryl substituted vinylthiiranes for the synthesis of 3- and 6-substituted 1,2-dithiins, aspects of the reaction mechanism pertaining to the formation and stability of intermediates of type **5** and **7** can be investigated. This report, therefore, highlights a range of new mechanistic findings in regard to the tungsten catalysed synthesis of mono and disubstituted 3,6-dihydro-1,2-dithiins from their respective precursor vinylthiiranes and also extends the overall synthetic scope of Adams' new catalytic transformation.

2. Results

2.1. Construction of the requisite vinylthiiranes (10a–h)

In order to accumulate significant mechanistic information whilst limiting the study to a practical size we decided to investigate Adams' catalytic 1,2-dithiin transformation utilising the eight distinctly different vinylthiiranes (**10a**–**h**) depicted below. In particular, the incorporation of various aryl substituents on the vinylthiiranes was deemed highly desirable as this should allow for conclusions pertaining to the rate determining step, the processes sensitivity to precursor sterics and electronics, and the nature of various reaction intermediates to be made. Furthermore, the preparation of various vinylthiiranes as mixtures of their *cis* and *trans* isomers was considered fortuitous as this should effectively double the mechanistic information attainable as the transformation of each individual isomer into the corresponding 1,2-dithiin should be able to be conveniently monitored by ^{1}H NMR.



10a X = Ph, Y = H
10b X = *p*-MeO-Ph, Y = H
10c X = *p*-Cl-Ph, Y = H
10d X = *p*-CN-Ph, Y = H
10e X = Ph, Y = Me
10f X = Me, Y = Ph
10g X = H, Y = Ph
10h X = CH=CH$_2$, Y = Ph

The most direct route to the requisite vinylthiiranes (**10a**–**h**) was from the corresponding vinyloxiranes[10] (**11a**–**h**), which were in turn prepared by the action of various sulfur ylides on the appropriate aldehyde, as summarised in Table 1. Thus, treatment of aldehydes (**12a**–**e**) with the appropriate

Table 1. Preparation of vinyloxiranes (**11a**–**h**)

Entry	Aldehyde	Sulfur ylide	Product	Yield (%)[a]	*cis*/*trans*[b]
1	**12a**	**13a**	**11a**	71	45:55
2	**12b**	**13a**	**11b**	91	25:75
3	**12c**	**13a**	**11c**	78	41:59
4	**12d**	**13a**	**11d**	81	45:55
5	**12a**	**13b**	**11e**	81	–
6	**12e**	**13d**	**11f**	75[c]	47:53
7	**12e**	**13c**	**11g**	80[c]	–
8	**12e**	**13a**	**11h**	58	29:71

See Section 5 for general procedures.

[a] Isolated yield except where noted.

[b] *cis*/*trans* ratios were determined from the coupling constants between the protons about the oxirane moiety; *cis*~4.5 Hz, *trans*~3.0 Hz.

[c] Unpurified yield; purity estimated to be ~95% by ^{1}H NMR.

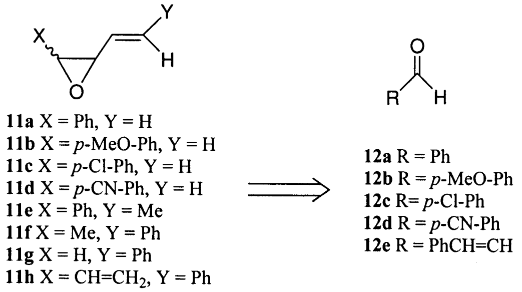
Table 2. Preparation of vinylthiiranes (**13a–h**)

Entry	Vinyloxirane	Vinylthiirane (%)[a]	Recovered oxirane (%)[a]	Diene (%)[a]
1	**11a**	**10a** (43)	20	11
2	**11b**	**10b** (40)	15	15
3	**11c**	**10c** (44)	20	12
4	**11d**	**10d** (–)	–	73
5	**11e**	**10e** (39)	15	22
6	**11f**	**10f** (65)	–	5
7	**11g**	**10g** (67)	–	–
8	**11h**	**10h** (46)	–	23

See Section 5 for general procedures.

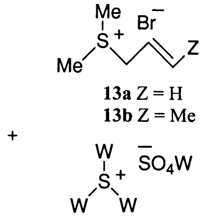
[a] Isolated yield except where noted.

sulfonium salt (**13a–d**) under basic conditions afforded vinyloxiranes (**11a–g**) in excellent yields with *cis*/*trans* ratios consistent with the literature.[11] Vinyloxiranes (**11f**, **g**) were utilised crude as attempted purification led to facile decomposition, while in the case of vinyloxirane **11h** only moderate yields were attained due to decomposition in the neat form.



11a X = Ph, Y = H
11b X = *p*-MeO-Ph, Y = H
11c X = *p*-Cl-Ph, Y = H
11d X = *p*-CN-Ph, Y = H
11e X = Ph, Y = Me
11f X = Me, Y = Ph
11g X = H, Y = Ph
11h X = CH=CH$_2$, Y = Ph

12a R = Ph
12b R = *p*-MeO-Ph
12c R= *p*-Cl-Ph
12d R = *p*-CN-Ph
12e R = PhCH=CH



13a Z = H
13b Z = Me

13c W = Me
13d W = Et

The preparation of the requisite vinylthiiranes (**10a–h**) was readily achieved by exposure of the vinyloxiranes to an aqueous inorganic thiocyanate solution Table 2.[10b–d] Isolated yields were moderate due to the extrusion of sulfur, thus, forming appreciable quantities of the corresponding diene. Vinylthiirane **10d** was too unstable to be isolated from the reaction mixture, undergoing exclusive sulfur extrusion, Table 2, entry 4. Indeed, electron withdrawing substituents have been found to facilitate the loss of sulfur from analogous vinylthiiranes.[12] Due to the instability of all vinylthiiranes it was considered desirable to quench the reaction prior to completion, thus maximising the yield of both the vinylthiirane and recovered starting material. Furthermore, in order to avoid sulfur extrusion following purification, all vinylthiiranes were stored as chloroform solutions.

Table 3. Preparation of 1,2-dithiins (**14a–g**)

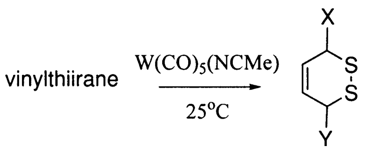
Entry	Vinylthiirane	1,2-Dithiin	Yield (%)[a]	Reaction time (h)
1	**10a**	**14a**	87	24
2	**10b**	**14b**	80	20
3	**10c**	**14c**	82	26
4	**10e**	**14d**	79	30
5	**10f**	**14d**	75	38
6	**10g**	**14a**	85	34
7	**10h**	**14e**, **14f**	40, 43	30

See Section 5 for a general procedure.

[a] Isolated yield taking into account the stoichiometry of the reaction, i.e. 2 equiv. of vinylthiirane are necessary to afford 1 equiv. of 1,2-dithiin and the corresponding butadiene.

2.2. Treatment of vinylthiiranes with tungsten pentacarbonyl monoacetonitrile

With the majority of the requisite vinylthiiranes successfully prepared, it was now time to verify whether tungsten pentacarbonyl monoacetonitrile would catalyse conversion to the appropriate 1,2-dithiin. The data collated within Table 3 indicates that all vinylthiiranes undergo smooth conversion into the 1,2-dithiins with excellent yields attainable. Vinylthiiranes **10a** and **10g** (entries 1, 6) as well as **10e** and **10f** (entries 4, 5) afford the same 1,2-dithiins, **14a** and **14d**, respectively, in approximately the same yields indicating flexibility in the position of the thiirane moiety with respect to the vinyl grouping. In addition, vinylthiirane **10h** affords two 1,2-dithiins (**14e** and **14f**) due to the precursor vinylthiirane containing two inequivalent vinyl groupings, entry 7.



14a X = Ph, Y = H
14b X = *p*-MeO-Ph, Y = H
14c X = *p*-Cl-Ph, Y = H
14d X = Ph, Y = Me
14e X = Ph, Y = CH=CH$_2$
14f X = PhCH=CH$_2$, Y = H

Having successfully synthesised a series of new 1,2-dithiins, attempts were now made to elucidate the reaction's sensitivity to precursor sterics and electronics through an investigation of the reaction's kinetics. Rate data was obtained from ^{1}H NMR experiments in which 1.4 mol% of catalyst transformed 0.573 mmol of substrate using CDCl$_3$ (0.7 ml) as solvent, except where noted. All experiments were performed at 21°C with the consumption of thiirane calculated by comparison to hexamethylbenzene as an internal standard. Table 4 contains a summary of the rates determined for each thiirane. In the cases of vinylthiiranes **10a** and **10c**, the rate of consumption of the *cis* and *trans* isomers were conveniently monitored by

Table 4. Rate constants determined for various vinylthiiranes

Entry	Vinylthiirane	Solvent	Isomer[a]	10^5 rate (s^{-1})[b]
1	**10a**	$CDCl_3$	*cis*	7.71
2		$CDCl_3$	*trans*	11.00
3[c]		$CDCl_3$	*cis*	4.91
4[c]		$CDCl_3$	*trans*	5.92
5[c]		C_6D_6	*cis*	5.66
6[c]		C_6D_6	*trans*	6.79
7[c]		$OC(CH_3)_2$	*cis*	1.86
8[c]		$OC(CH_3)_2$	*trans*	2.31
9[c]		CD_3CN	mix	0.00
10	**10b**	$CDCl_3$	mix	20.70
11	**10c**	$CDCl_3$	*cis*	5.81
12		$CDCl_3$	*trans*	10.20
13	**10e**	$CDCl_3$	mix	3.65
14[d]	**10f**	$CDCl_3$	*cis*	0.75
15[d]		$CDCl_3$	*trans*	0.43
16[d]	**10g**	$CDCl_3$	–	2.26

See Section 5 for a general procedure.

[a] Isomers were assigned as discussed. Rates were not determined for the individual isomers of vinylthiiranes (**10b** and **10e**) and were determined for the complete mixture.

[b] Rate constants were calculated using the modulus of the slope of ln (A/′A) plotted against time and are for reactions performed with 1.4 mol% catalyst at 21°C and were determined only for the first 10% of the overall reaction.

[c] Reactions performed with dilution factor of two compared to other entries.

[d] Rate constant obtained over the entire course of the reaction.

observing the difference in peak area of the doublet at δ 4.2 ppm, corresponding to the *cis* vinylthiirane, to the multiplet at δ 3.7 ppm, corresponding to the combined *cis* and *trans* vinylthiirane concentration. Similarly, the consumption of *cis* and *trans* **10f** could be followed by observing the area of the doublet of doublets at δ 3.74 ppm, *cis* isomer only, and the pentet at δ 2.91 ppm, *trans* isomer only. In the case of vinylthiiranes **10b** and **10e**, determining the rates for the individual isomers was not possible due to overlaying precursor/product resonances, consequently the rates were determined as an average of the two isomers.

A plot of the variation in 2-phenyl-3-vinylthiirane **10a** concentration against time is shown in Fig. 1 and is typical for the systems investigated. Data manipulation[13] indicated that the reaction was only first order over the first 10% of the reaction course, Fig. 2. Therefore, all rate constants except where noted within Table 4, were calculated before 10% completion. The occurrence of first order kinetics only in the initial stages of the reaction can be contributed to catalyst inhibition by the product.[13] In order to test this hypothesis, the reaction was repeated using a stoichiometric quantity of catalyst. A plot of the variation in 2-phenyl-3-vinylthiirane **10a** concentration against time was again generated and is presented in Fig. 3, while Fig. 4 represents a plot of ln (A/′A) against time. The reaction now proceeded

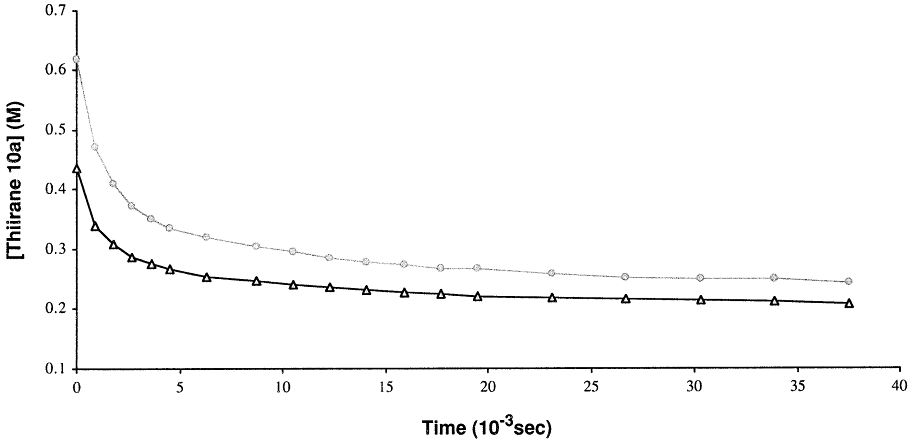


Figure 1. Consumption of *cis* (Δ) and *trans* (○) 2-phenyl-3-vinylthiirane **10a** plotted against time with 1.4 mol% $W(CO)_5(MeCN)$ in $CDCl_3$ at 21°C.

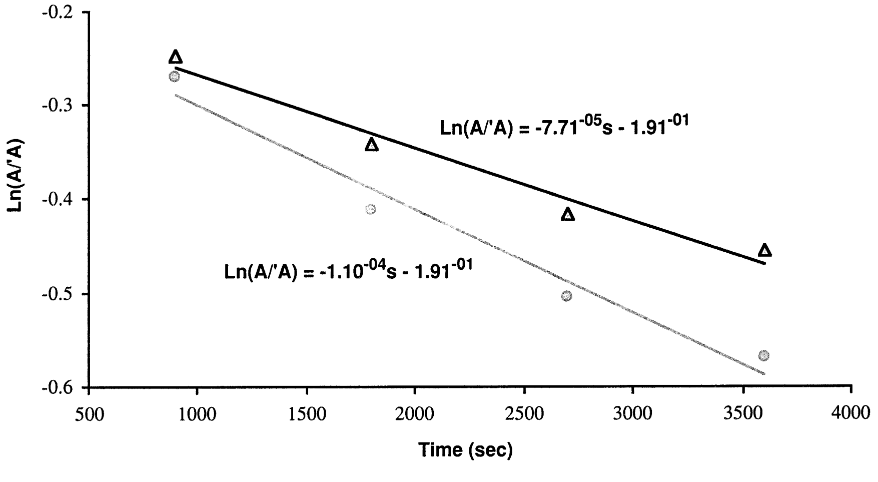


Figure 2. Plot of ln (A/′A) against time for the first 10% of the reaction of **10a** with 1.4 mol% $W(CO)_5(MeCN)$ in $CDCl_3$ at 21°C with an equation of the trendline, for the two isomers, displayed within the key.

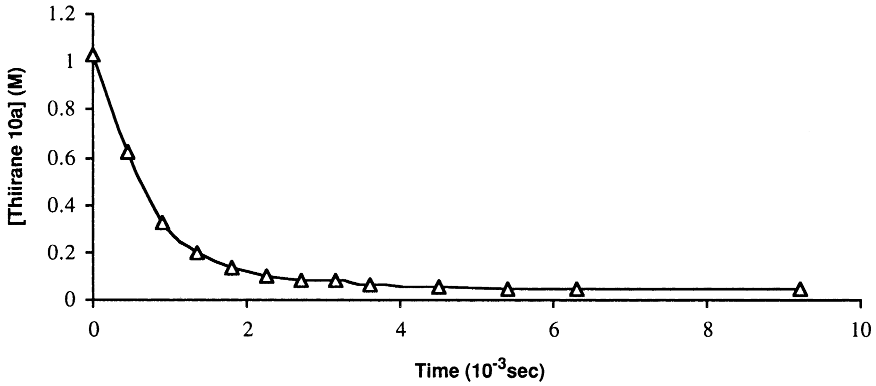


Figure 3. Consumption of 2-phenyl-3-vinylthiirane **10a** plotted against time in seconds with a stoichiometric quantity of W(CO)$_5$(MeCN) performed in CDCl$_3$ at 21°C temperature.

with first order kinetics until 85% completion after which, presumably, the 1,2-dithiin concentrations is sufficient to inhibit the catalyst.

Thiiranes **10f** and **10g** did not display catalytic inhibition and were found to be first order over the entire course of the reaction, the rates being depicted within Table 4, entries 14–16. Finally, rates for the conversion of **10a** were also determined in a range of solvents under identical reaction conditions in order to probe for solvent effects, entries 3–9.

3. Discussion

3.1. Solvent and substituent effects

The effect of solvent polarity on the conversion of 2-phenyl-3-vinylthiirane **10a** into 1,2-dithiin **14a** was investigated using various deuterated solvents, Table 4 entries 3–9. No significant effect on the reaction rate was observed with change in solvent. This result concurs with the previously proposed rate determining step of co-ordination.[3] Furthermore, this result eliminates the possibility of simultaneous co-ordination and ring-opening, Scheme 1, step a′. A second observation from these experiments was the lack of reaction when employing acetonitrile as solvent. This result suggests an equilibrium between the acetonitrile bound catalyst and the vinylthiirane bound catalyst. Thus, when employing acetonitrile as the solvent, the equilibrium exists solely on the side of the acetonitrile bound catalyst and the reaction is completely inhibited. To further characterise the rate determining step, the reaction rates associated with various *p*-substituted aryl thiiranes were then considered, entries 1, 2 and 10–12, Table 4. Comparison of the σ_p value of the substituent to the log (k/k_H) indicates rate enhancement with electron donating groups and retardation with electron withdrawing groups. This trend is consistent with a rate determining step of associative coordination by the vinylthiirane in which donation of a lone pair of electrons from sulfur is promoted by electron donating aryl substituents. Although the magnitude of the slope of the plot could be used to derive conclusions as to the nature of the transition state, this was considered inappropriate at this stage due to the limitation of the data set.

3.2. Involvement of zwitterionic species

In the work of Adams the formation of a zwitterionic intermediate of type **7** prior to nucleophilic addition of a second vinylthiirane was proposed.[3c,d] This pathway is preferred due to kinetic observations pertaining to different methyl substituted thiiranes and also differences in reaction rate of alternative tungsten catalysts.[3c] In order to probe the proposed zwitterionic mechanism we believed that the synthesis of a divinylthiirane in which the alternative zwitterions would have significantly different stability, thus determining the obtained product, was warranted. To this end, vinylthiirane **10h** was synthesised and its conversion to

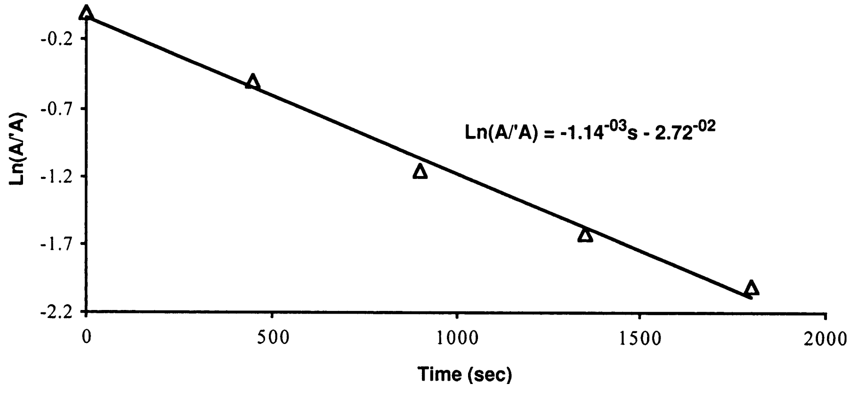
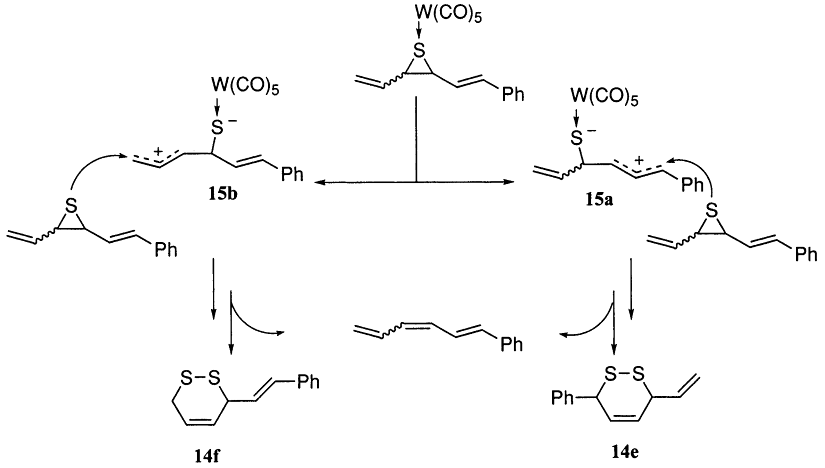


Figure 4. Plot of the ln (A/′A) against time for the first 85% of the reaction of **10a** with a stoichiometric quantity of W(CO)$_5$(MeCN) in CDCl$_3$ at 21°C with an equation of the trendline within the key.



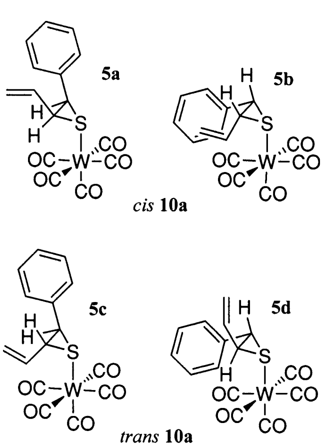
Scheme 2.

1,2-dithiins **14e** and **14f** investigated, Scheme 2. If zwitterionic species were involved in the reaction, as proposed by Adams, then benzylic stabilisation would favour intermediate **15a** over **15b**, thus, leading to 1,2-dithiin **14e** as the major product, following nucleophilic 'attack' and cyclisation. Alternatively, if neutral intermediates were involved then equivalence between 1,2-dithiins **14e** and **14f** would be expected with, perhaps, slight predominance of **14f** due to steric considerations.

Upon synthesising vinylthiirane **10h** it was transformed into 1,2-dithiins **14e** and **14f** under the usual conditions. The two isomers formed were distinguished by the resonance due to the hydrogen in the 3-position, and from their relative areas, the ratio of the 1,2-dithiins could be determined. The more prevalent 1,2-dithiin was **14f**, Table 3, entry 7, thus, indicating that the reaction was not preceeding via a charged intermediate and was slightly sensitive to steric effects. This result is in stark contrast to the aforementioned observations of Adams.[3c]

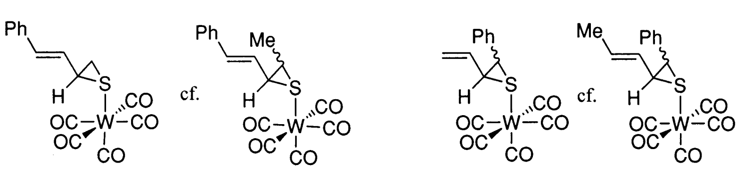
3.3. Steric effects on the rate determining step

Entries 1, 2, 11 and 12 of Table 4 demonstrate that the *trans* isomers of **10a** and **10c** reacted more rapidly than the *cis* isomers, while the *cis* isomer of thiirane **10f** reacted more quickly than the *trans*, Table 4, entries 14 and 15. These differences in rate can be attributed to differences in steric crowding around the catalyst during formation of intermediate **5**. Since the sulfur atom of the thiirane has two lone pairs of electrons through which it can coordinate, two isomeric complexes of intermediate **5** are possible, Scheme 3. These alternative isomers were observed in the work of Adams by using ^{13}C enriched NMR studies.[3c] Although coordination by the *cis* thiiranes gives the sterically more favourable intermediate **5a**, it also affords the unfavourable intermediate **5b**. The *trans* isomer on the other hand gives the two intermediates **5c** and **5d**, presumably of moderate stability. The faster reaction rate for the *trans* isomers of **10a** and **10c** implies that the increased probability of coordination, two orientations (**5c** and **5d**) compared to one (**5a**), outweighs the greater stability of **5a**. In the case of thiirane **10f** the greater stability of the equivalent isomer **5a** must outweigh the effect of an increased number of orientations through which coordination can occur.



Scheme 3.

The effect of steric bulk on reaction rate can also be observed by comparing the various phenyl and methyl substituted thiiranes utilised. In changing the hydrogen substitution β to the thiirane moiety into a methyl group, Table 4, entries 1, 2 and 13–16, respectively, a decrease in reaction rate is observed. This result is contrary to the observations of Adams and Perrin who noted rate enhancement with addition of a methyl group to either the position α, or β, to the thiirane. Their rate enhancement was attributed to stabilisation of charged intermediate **7** by the methyl group on the double bond. Ignoring the fact that these arguments pertained to the non rate determining ring-opening, it would seem likely, in any respect, that the stability of the allylic cation derived from methyl substitution α, or β, or on the thiirane would be similar. Similarly when thiiranes **10f** and **10g**, Table 4, entries 14–16, are compared then it is noted that methyl substitution, this time on the thiirane ring, results in retardation of the reaction rate. This latter result concurs with the work of Adams and Perrin who observed that stabilisation of the thiirane ring by methyl substituents leads to a slower reaction rate.[3c] However, their explanation once again invokes chemistry not associated with the rate determining step but rather the subsequent ring-opening.



Large decrease in rate as methyl substitution is proximal to tungsten

Smaller decrease in rate as methyl group is distal to tungsten

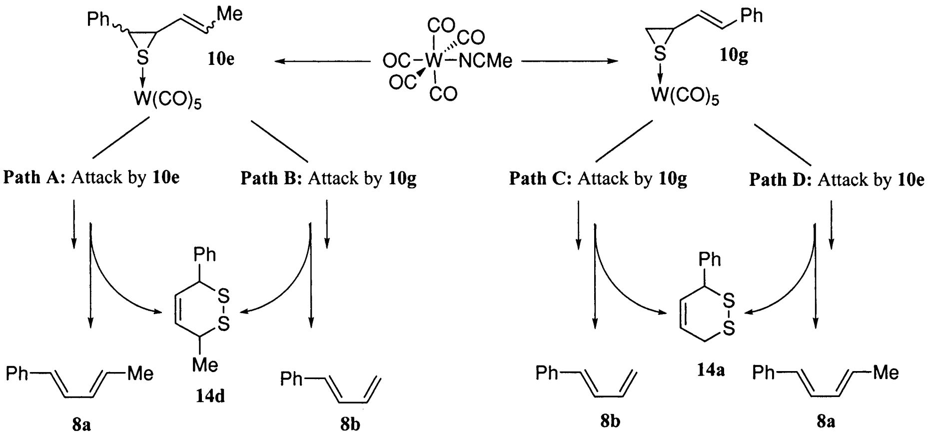
Scheme 4.

We believe that the increase in steric bulk upon substitution of a methyl group directly onto the thiirane ring, or onto the vinylic double bond, results in a decrease in the reaction rate due to unfavourable steric interactions, Scheme 4. Furthermore, the degree of change appears to correlate with the proximity of the steric bulk to the thiirane ring, namely, the rate decrease is much larger when methyl substitution occurs on the ring, 4.5 fold, compared to the more distal vinylic position, 2.5 fold. Apparently, contradicting this conclusion is the observation of faster reaction rates for thiiranes **10a** and **10e**, compared to thiiranes **10f** and **10g**, the later of which are terminal thiiranes which, presumably, you might expect to give rise to less steric crowding. However, this result appears to pertain to the stability of the formed complex rather than the kinetics of association, and is discussed below.

3.4. Catalytic inhibition

As discussed previously the reaction rates of thiiranes **10f** and **10g**, Table 4, entries 14–16, are lower than expected based on the grounds of sterics alone. Furthermore, these substrates are the only substrates to display first order kinetics over the entire reaction. In order to clarify the implications of these results, and to further characterise the nature of the rate determining step, a reaction in which a mixture of thiiranes **10e** and **10g** was transformed into 1,2-dithiins **14d** and **14a**, respectively, was undertaken. It was expected that the faster reacting thiirane **10e** would bind to the catalyst more quickly and subsequently be 'attacked' by either thiirane **10e** or **10g**, Path A or B, Scheme 5, in the Michael fashion to eventually furnish the 1,2-dithiin **14d** as the major product along with both diene **8a** and **8b**. More favourable attack by **10g**, Path B, would result in the formation of 1,2-dithiin **14d** and diene **8b** exclusively. Alternately, if Michael attack by **10e** is more favourable than **10g** then the complete conversion to 1,2-dithiin **14a** and diene **8a**, Path A, would be followed by the conversion of thiirane **10g** to 1,2-dithiin **14a** and diene **8a**, Path D, and, thus, equal quantities of 1,2-dithiins **14a** and **14d** would be observed. Similarly, the unexpected paths would yield **14a** initially followed by **14d**, Path C, or **14a** and **8a** as the only products, Path B. These scenarios are depicted within Scheme 5, and represent the extremes that may be expected.

The experiment was set up as described, and monitored by ^{1}H NMR as for the kinetic studies, although in this case over 19 h. The results of the experiment are shown in Fig. 5. As can be seen the more 'slower' reacting thiirane **10g** gives rise to the major product, **14a**, while the formation of the minor 1,2-dithiin proceeds after a lag time to give **14d** derived from the more 'rapidly' reacting thiirane **10e**. Although this result appears counter intuitive it can, however, be rationalised by considering previously discussed results. Firstly, the thiirane **10e** can be considered to be in equilibrium between the catalyst bound and unbound forms, as demonstrated by the lack of reaction in acetonitrile. Secondly, thiirane **10g** reacts after a lag time indicating that the thiirane bound catalyst has a comparatively long lifetime. Coupled to this we observe no catalytic inhibition with thiirane **10g**, thus, indicating that the 1,2-dithiin does not compete for the catalyst, therefore the thiirane binds with a higher affinity than the 1,2-dithiin. Since catalytic inhibition is observed with thiirane **10e** it is therefore possible to conclude that thiirane **10g** forms a thermodynamically more stable complex with the catalyst than does thiirane **10e**. This is presumably due to less steric bulk around the thiirane ring. Hence, although the thiirane **10e** binds more rapidly to the catalyst, it is in equilibrium with the unbound form, thus allowing the catalyst to form



Scheme 5.

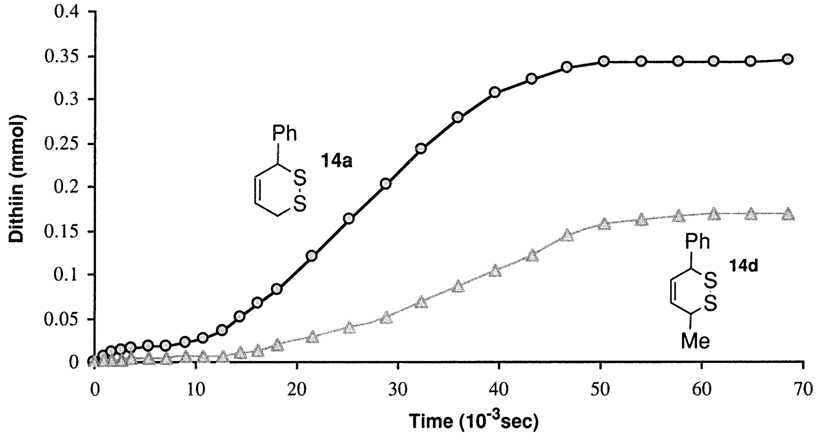


Figure 5. Plot of the conversion of vinylthiirane 10 h to 1,2-dithiins **14a** and **14d** by $W(CO)_5(NCMe)$ in $CDCl_3$ at 21°C against time.

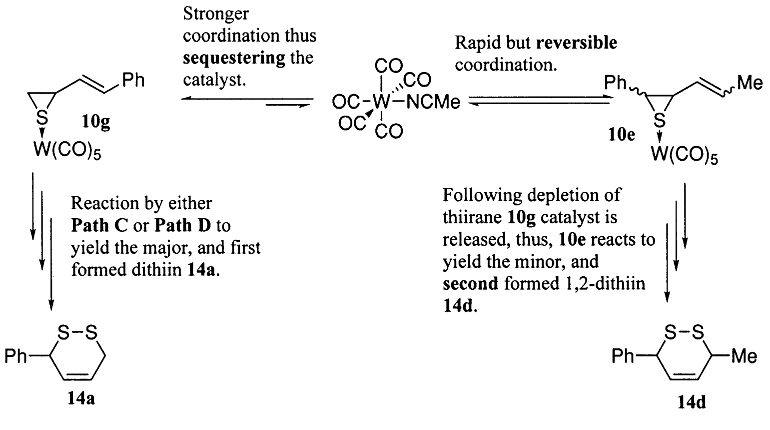
the more stable association with thiirane **10g**. As a result the catalyst is sequestered away from the rapidly reacting thiirane, resulting in the formation of 1,2-dithiin **14a** as the major product due to Michael attack by both thiiranes, Scheme 5 Paths C and D. These results are summarised in Scheme 6.

4. Conclusions

We have successfully applied the methodology of Adams to the synthesis of various alkyl and aryl mono and 3,6-disubstituted 1,2-dithiins with consistently good yields, thus, further demonstrating the robust nature of this methodology. Furthermore, through our synthetic endeavours we have been able to present findings that concur with Adams proposal of the rate determining step being the associative coordination of the thiirane moiety to tungsten, whilst noting a high degree of sensitivity to thiirane sterics as indicated by the different kinetics of the various phenyl or methyl substituted derivatives. In regard to the Michael attack on a neutral or zwitterionic intermediate we are able to report that the reaction appears to proceed via a neutral species which is then ring-opened by a second vinyl thiirane. Finally, we have observed subtle differences in the thiiranes affinity for the catalyst and there ability to sequester and thus retard the reaction of other thiiranes. This last observation could possibly be exploited in the future in the reaction of thiirane mixtures in which one thiirane provides the 'backbone' and the other the second sulfur atom, thus allowing for a more atomically efficient synthetic tool.

5. Experimental

Solvents were dried by appropriate methods wherever needed. All organic extracts were dried over anhydrous magnesium sulfate. Thin-layer chromatography (TLC) used aluminum sheets silica gel 60 F_{254} (40×80 mm^2) from Merck. Melting points were taken on a Reichert Thermovar Kofler apparatus and are uncorrected. Infrared spectra were recorded on a ATI Mattson Genesis Series FTIR spectrophotometer as nujol mulls unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Varian INOVA (600 MHz) or on a Varian Gemini 2000 instrument, TMS (0 ppm) and $CDCl_3$ (77.0 ppm) as internal standards unless otherwise specified. All yields reported refer to isolated material judged to be homogeneous by TLC and NMR spectroscopy unless otherwise specified. The following materials were purchased from Aldrich and used without further purification; Aldehydes (**12a–e**), methyl sulfide, ethyl sulfide, dimethyl sulfate, diethyl sulfate, allyl bromide.



Scheme 6.

5.1. Materials

5.1.1. Preparation of 2-phenyl-3-vinyloxiranes (11a–e). A typical procedure.[11b] A heterogeneous mixture of allyl bromide (4.84 g, 0.04 mol), methyl sulfide (2.79 g, 0.045 mol) and water (3.75 ml) was stirred vigorously for 20 h at ambient temperature. Excess methyl sulfide was removed under vacuum from the resulting brown solution and the appropriate benzaldehyde (2.65 g, 0.025 mol) in isopropanol (7.5 ml) added. To this solution, sodium hydroxide (1.6 g, 0.04 mol) in water (3.25 ml), was added dropwise over 30 min. The reaction was monitored by TLC and after 5 h was complete. The produced methyl sulfide was removed in vaccuo and the solution extracted with ether (3×30 ml) and dried ($MgSO_4$) to yield the crude product. Purification by flash chromatography (5% ethyl acetate/hexanes) yielded a *cis* and *trans* mixture of the title compound, **11a**. Refer to Table 1 for yields and *cis*/*trans* ratios of all oxiranes prepared using this methodology. Physical and spectroscopic data was consistent with the literature for all compounds prepared using this methodology. **11b**,[11b] **11c**[11b] and **11d**[11b] were prepared from *p*-methoxybenzaldehyde, *p*-chlorobenzaldehyde and *p*-cyanobenzaldehyde, respectively. **11e**[11c] was prepared from benzaldehyde and the salt of crotyl bromide and methyl sulfide using the approach for **11a**. **11h**[11d] was prepared from cinnamaldehyde using the approach for **11a**.

5.1.2. Preparation of 2-methyl-3-[(*E*)-2-phenyl-1-ethenyl]-oxiranes (11f, g and i). A typical procedure.[11a] Triethylsulfonium (sulfonatooxy)ethane (6.08 g, 25 mmol) was added to a stirred solution of cinnamaldehyde (2.64 g, 20 mmol) in dichloromethane (20 ml) followed by the addition of 50% aqueous NaOH solution (10 ml) to give a dark orange heterogeneous mixture. After 2.5 h the solution was diluted with H_2O (50 ml), the organic phase separated, and the aqueous phase extracted with ether (2×50 ml). The combined organic fractions were washed with water (2×50 ml), dried ($CaCl_2$), and the volatiles removed in vacuo to afford the title compound **11f** in sufficient purity for the next step. The title compound can be purified by chromatography (10% hexanes/dichloromethane). Refer to Table 1 for yields and *cis*/*trans* ratios of all oxiranes prepared using this methodology. All physical and spectroscopic data was consistent with the literature. **11g**[11a] was prepared from trimethylsulfonium (sulfonatooxy)methane using the approach for **11f**.

5.1.3. Preparation of 2-phenyl-3-vinylthiiranes (10a–c). A typical procedure.[10e] To a stirred solution of oxirane **11a** (1.0 g, 6.85 mmol) in dioxane (1.3 ml) potassium thiocyanate (0.75 g, 7.53 mmol) and tetrabutyl ammonium bromide (22 mg, 6.85 mol) in water (1.5 ml) was added. The solution was stirred for 6 h at which time the aqueous layer was removed and replaced with a solution of potassium thiocyanate (0.75 g, 7.53 mmol) in water (1.5 ml). The heterogeneous solution was stirred for a further 10 h at which time diene formation was observed by TLC. Water (5 ml) was added and the solution extracted with ether (3×10 ml). The organic fractions were dried ($MgSO_4$) and solvent removed in vacuo. Thiirane was separated from starting oxirane and diene by flash chromatography (6% dichloromethane/hexanes). Refer to Table 2 for yields of all thiiranes prepared using this methodology. All physical and spectroscopic data were consistent with the literature. **10b**[10e] and **10c**[10e] where prepared from oxirane **11b** and **11c**, respectively. **11d** was treated as above, however, the only isolatable product was 4-[(*E*/*Z*)-1,3-butadienyl]benzonitrile[14] as a result of desulfurisation.

5.1.4. 2-Phenyl-3-[(*E*/*Z*)-1-propenyl]thiirane (10e). The title compound was prepared as a colourless oil from oxirane **11e** using the approach for thiirane **10a**. R_f 0.35 (5% dichloromethane/hexane); IR 1684, 1602, 1493 cm^{-1}; (*cis E*-**10e**); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.60 (dd, J=1.8, 6.6 Hz, 3H), 3.80 (dd, J=7.2, 9.6 Hz, 1H), 4.21 (d, J=7.2 Hz, 1H), 5.15–4.84 (m, 1H), 5.94–5.88 (m, 1H), 7.39–7.21 (m, 5H); (*trans E*-**10e**); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.73 (dd, J=1.8, 6.6 Hz, 3H), 3.54 (dd, J=5.4, 9.0 Hz, 1H), 3.71 (d, J=5.4 Hz, 1H), 5.26 (ddq, J=1.8, 9.0, 15.6 Hz, 1H), 5.94–5.88 (m, 1H), 7.39–7.21 (m, 5H); (*cis Z*-**10e**); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.82 (m, 3H), 4.02 (ddd, J=1.2, 7.2, 10.2 Hz, 1H), 4.26 (d, J=7.2 Hz, 1H), 5.16 (tq, J=2.4, 10.2 Hz, 1H), 5.62 (ddq, J=1.2, 6.6, 10.2 Hz, 1H), 7.39–7.21 (m, 5H); (*trans Z*-**10e**); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.82 (m, 3H), 3.73 (d, J=5.4 Hz, 1H), 3.77 (ddd, J=0.6, 5.4, 9.6 Hz, 1H), 5.15–4.84 (m, 1H), 5.71 (ddq, J=0.6, 7.2, 10.2, 1H), 7.39–7.21 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.29, 13.36, 17.82, 18.01, 38.15, 40.88, 42.50, 42.99, 43.32, 44.13, 45.91, 52.59, 126.37, 126.88, 126.93, 127.34, 127.39, 127.53, 127.97, 128.47, 128.59, 129.16, 129.23, 129.73, 130.34, 131.10, 131.18, 131.95, 135.48, 135.59, 138.62. The titled mixture has unstable and decomposed over several days. Consequently **10e** was used immediately.

5.1.5. 2-Methyl-3-[(*E*)-2-phenyl-1-ethenyl]thiirane (10f). The title compound was prepared as a colourless oil from oxirane **11f** using the approach for thiirane **10a**. R_f 0.30 (10% dichloromethane/hexanes); IR 1678, 1599, 1495 cm^{-1}; (*cis* **10f**); ^{1}H NMR ($CDCl_3$) δ 1.55 (d, J=7.0 Hz, 3H), 3.19 (p, 7.0 Hz, 1H), 3.74 (dd, J=7.0, 9.2 Hz, 1H), 6.05 (dd, J=9.2, 15.4 Hz, 1H), 6.79 (d, J=15.4 Hz, 1H), 7.35–7.22 (m, 5H); (*trans* **10f**); ^{1}H NMR ($CDCl_3$) δ 1.58 (d, J=5.4 Hz, 3H), 2.91 (p, J=5.4 Hz, 1H), 3.33 (dd, J=5.4, 9.2 Hz, 1H), 5.79 (dd, J=9.2, 15.4 Hz, 1H), 6.71 (d, J=15.4 Hz, 1H), 7.35–7.22 (m, 5H); ^{13}C NMR ($CDCl_3$) d 16.92, 21.24, 36.03, 37.74, 43.61, 46.24, 125.96, 126.08, 126.16, 126.76, 127.60, 127.66, 128.50, 130.03, 132.44, 134.41, 136.37, 136.53. The titled mixture has unstable and decomposed over several days. Consequently **10f** was used immediately.

5.1.6. Preparation of 2-[(*E*)-2-phenyl-1-ethenyl]thiirane (10g).[10d] **A typical procedure.** Oxirane **11g** (2.18 g, 14.93 mmol) was added dropwise to a stirred solution of potassium thiocyanate (1.66 g, 17.12 mmol) in water (1.8 ml) over 2.5 h. After an hour the aqueous phase was removed and fresh potassium thiocyanate (0.83 g, 8.55 mmol) in water (1.8 ml) added. The reaction was monitored by ^{1}H NMR and after 48 h was complete. Dichloromethane (50 ml) and water (50 ml) where then added, the organic phase decanted, dried ($CaCl_2$), and solvent removed in vacuo. Crude thiirane was purified by flash chromatography (45% hexane/dichloromethane) to afford **10g** as an oil. See Table 2 for the yields of all thiiranes prepared using this methodology. **10i**^{10b,c} was prepared from oxirane **11i** in an identical fashion.

5.1.7. 2-[(*E*)-2-Phenyl-1-ethenyl]-3-vinylthiirane (10h). The title compound was prepared as a colourless oil from oxirane **11h** using the approach for thiirane **10a**. R_f 0.31 (10% dichloromethane/hexane); IR 1634, 1597, 1491 cm^{-1}; (*cis* **10h**); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 3.71 (dd, J=6.9, 8.8 Hz, 1H), 3.83 (dd, J=6.9, 9.3 Hz, 1H), 5.54 (m, 3H), 6.01 (dd, J=9.3, 15.5 Hz, 1H), 6.78 (d, J=15.5 Hz, 1H), 7.39–7.21 (m, 5H); (*trans* **10h**); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 3.43 (dd, J=5.0, 8.4 Hz, 1H), 3.51 (dd, J=5.0, 8.9 Hz, 1H), 5.54 (m, 3H), 5.81 (dd, J=9.1, 15.7 Hz, 1H), 6.74 (d, J=15.7 Hz, 1H), 7.39–7.21 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 42.55, 42.78, 43.78, 44.05, 117.68, 119.48, 125.78, 126.10, 126.17, 126.40, 127.67, 128.17, 128.46, 128.85, 132.68, 132.87, 134.41, 136.15, 136.27, 137.47; MS *m*/*z* (%): 188 (M$^+$, 30), 173 (20), 156 (75), 155 (100); HRMS of (**10h**), $C_{12}H_{12}S$: calcd, 188.0677; found, 188.0665.

5.1.8. 3-Phenyl-3,6-dihydro-1,2-dithiine (14a). A typical procedure for the synthesis of 1,2-dithiins (14a–f). Either vinylthiirane **10a** or **10g** (0.66 g, 4.07 mmol) and tungsten pentacarbonyl monoacetonitrile (15 mg, 0.06 mmol) in deuterated chloroform (0.5 ml) were shaken in an NMR tube and allowed to react over 24 h after which time all starting material had been consumed. The reaction mixture was then concentrated in vacuo and separated by flash chromatography (5% ethyl acetate/hexane) to afford pure 1,2-dithiin as a colourless oil. Refer to Table 3 for yields and reaction times for 1,2-dithiins prepared using this methodology. R_f 0.45; IR 1641, 1597, 1492, 1451 cm^{-1}; ^{1}H NMR (CDCl$_3$, 600 MHz) δ 3.22 (ddt, J=2.2, 4.8, 17.4 Hz, 1H), 3.47 (ddt, J=2.2, 3.8, 17.4 Hz, 1H), 4.67 (p, J=2.2 Hz, 1H), 6.04 (ddt, J=2.2, 3.8, 11.7 Hz, 1H), 6.17 (dddd, J=2.2, 3.8, 4.8, 11.7 Hz, 1H), 7.39–7.28 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 27.97, 44.44, 126.45, 127.85, 128.28, 128.50, 129.61, 139.77; MS *m*/*z* (%), 194 (M$^+$, 10), 33 (8), 130 (100), 115 (45); HRMS of (**14a**), $C_{10}H_{10}S_2$: calcd, 194.0258; found, 194.0225.

5.1.9. 3-(4-Methoxyphenyl)-3,6-dihydro-1,2-dithiine (14b). The title compound was prepared as a colourless oil from **10b** using the approach for the synthesis of **14a**. R_f 0.35 (3% ethyl acetate/hexane); IR 1643, 1609, 1510 cm^{-1}; ^{1}H NMR (CDCl$_3$, 600 MHz) δ 3.18 (ddt, J=2.4, 4.8, 17.4 Hz, 1H), 3.47 (ddt, J=2.4, 3.6, 17.4 Hz, 1H), 3.79 (s, 3H), 4.65 (p, J=2.4 Hz, 1H), 6.01 (ddt, J=2.4, 3.6, 11.4 Hz, 1H), 6.14 (dddd, J=2.4, 3.6, 4.8, 11.4 Hz, 1H), 7.17–7.10 (m, 2H), 7.31–7.20 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 28.00, 44.03, 55.29, 114.01, 129.48, 126.36, 130.07, 131.81, 159.37; MS *m*/*z* (%): 224 (M$^+$, 10), 191 (67), 160 (100); HRMS of (**14b**), $C_{11}H_{12}S_2O$: calcd, 224.0363; found, 224.0333.

5.1.10. 3-(4-Chlorophenyl)-3,6-dihydro-1,2-dithiine (14c). The title compound was prepared as a colourless oil from **10c** using the approach for the synthesis of **14a**. R_f0.35 (7.5% dichloromethane/hexane); IR 1648, 1593, 1489 cm^{-1}; ^{1}H NMR (CDCl$_3$, 600 MHz) δ 3.26 (ddt, 2.2, 4.2, 17.6 Hz, 1H), 3.40 (ddt, J=2.2, 4.2, 17.6 Hz, 1H), 4.59 (m, 1H), 5.98 (ddt, J=2.2, 3.7, 11.7 Hz, 1H), 6.18 (ddt, J=2.2, 4.2, 11.7 Hz, 1H), 7.32–7.25 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 28.02, 43.47, 126.91, 128.66, 129.03, 129.63, 133.72, 138.46; MS *m*/*z* (%): 230 (M$^+$ ^{37}Cl, 2%), 228 (M$^+$ ^{35}Cl, 8), 195 (50), 164 (35), 129 (100); HRMS of (**14c**), $C_{10}H_9S_2Cl$: calcd, 227.9868, found, 227.9837.

5.1.11. 3-Methyl-6-phenyl-3,6-dihydro-1,2-dithiine (14d). The title compound was prepared as a colourless oil from **10e** or **10f** using the approach for the synthesis of **14a**. IR 1644, 1597, 1489 cm^{-1}; ^{1}H NMR (CDCl$_3$, 600 MHz) δ 1.5 (d, J=7.2 Hz, 3H), 3.42 (m, 1H), 4.58 (m, 1H), 5.95 (ddd, J=1.9, 3.2, 11.6 Hz, 1H), 6.02 (ddd, J=2.2, 4.3, 11.6 Hz, 1H), 7.37–7.27 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 20.90, 34.68, 44.37, 127.85, 128.28, 128.53, 128.92, 133.12, 139.86; MS *m*/*z* (%): 208 (M$^+$, 5), 164 (7), 144 (70), 129 (100); HRMS of (**14d**), $C_{11}H_{12}S_2$: calcd, 208.0414; found, 208.0379.

5.1.12. Preparation of 3-phenyl-6-vinyl-3,6-dihydro-1,2-dithiine (14e) and 3-[(*E*)-2-phenyl-1-ethenyl]-3,6-dihydro-1,2-dithiine (14f). The title compounds were prepared as colourless oils from **10h** using the approach for the synthesis of **14a**. R_f0.31 (2% ethyl acetate/hexane); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 3.86 (m, 1H), 4.70 (q, J=1.8, 1H), 5.29 (ddt, J=0.6, 1.2, 10.2 Hz, 1H), 5.32 (dt, J=1.2, 17.4 Hz, 1H), 6.01 (ddd, J=1.8, 4.8, 11.4 Hz, 1H), 6.12–6.06 (m, 2H), 7.39–7.25 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 27.78, 38.00, 40.88, 45.00, 117.48, 125.69, 126.13, 127.46, 128.09, 128.34, 128.48, 128.63, 128.69, 128.72, 129.14, 129.63, 130.78, 131.70, 135.83, 139.26; MS *m*/*z* (%): 220 (M$^+$, 10), 187 (40), 156 (100); HRMS of (**14e**), $C_{12}H_{12}S_2$: calcd, 220.0414, found, 220.0378.

14f: R_f 0.35 (2% ethyl acetate/hexane); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 3.14 (ddt, J=2.4, 4.2, 18.0 Hz, 1H), 3.33 (ddt, J=2.4, 4.2, 15.6 Hz, 1H), 4.05 (m, 1H), 5.92 (ddt, J=2.4, 4.2, 12.0 Hz, 1H), 6.07 (m, 1H), 6.29 (dd, J=7.8, 15.6 Hz, 1H), 6.55 (d, J=15.6 Hz, 1H), 7.39–7.21 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 27.86, 28.91, 41.13, 48.41, 126.19, 126.33, 126.81, 127.03, 127.13, 127.56, 128.16, 128.22, 128.34, 132.65, 133.85, 135.21, 136.36, 140.45; MS *m*/*z* (%) 219 (M$^+$, 4), 187 (30), 156 (100); HRMS of (**14f**), $C_{11}H_{12}S_2$: calcd, 220.0414, found, 220.0381.

5.2. General procedure for kinetic studies

Thiirane **10a** (93 mg, 0.573 mmol) and hexamethylbenzene (13 mg, 8.02 μmol) in CDCl$_3$ (0.7 ml) were mixed in a 5 mm NMR tube and an initial ^{1}H NMR spectra taken. Tungsten pentacarbonyl acetonitrile (5.5 mg, 15 mmol) was then added and the solution shaken. Spectra were then obtained periodically (4×15, 8×30 min then 6×60 min) on a Varian-Gemini-200 instrument utilising the preacquisition delay (PAD) function. The reaction rate was determined by comparing the area of the thiirane doublet at δ 4.2 ppm and the doublet of doublets at δ 3.52 to the area of the hexamethyl benzene signal.

Acknowledgements

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