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ALKATRIENYL SULFOXIDES AND SULFONES. PART VI. CHELETROPIC ADDITION OF SULFUR DIOXIDE TO 1- AND 3-VINYLALLENYL SULFOXIDES AND SULFONES[1,2]

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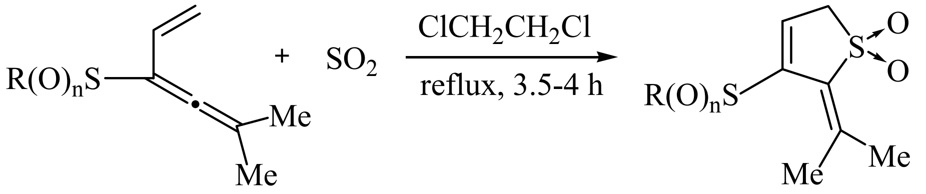
Abstract – The reaction of 1- and 3-vinylallenyl sulfoxides and sulfones with sulfur dioxide in 1,2-dichloroethane at reflux proceeds as a cheletropic addition leading to the formation of 2-isopropylidene-3-sulfinyl(sulfonyl)- or 2-sulfinyl-(sulfonyl)methylidene-substituted 2,5-dihydrothiophene 1,1-dioxides in very good yields.

Conjugated dienes are known to undergo cheletropic additions[3] with sulfur dioxide to generate the corresponding 2,5-dihydrothiophene 1,1-dioxides (sulfolenes),[4] or to generate polymers (polysulfones).[5] At low temperature and in the presence of a protic or Lewis acid catalyst, simple acyclic alkyl-substituted 1,3-dienes that can adopt the *s-cis* conformation add reversibly to SO_2 by hetero-Diels-Alder additions to generate the corresponding 3,6-dihydro-1,2-oxathiine 2-oxides (sultines).[6,7] The latter are unstable above -50 °C and undergo fast cycloreversion to liberate the starting 1,3-dienes and SO_2, which can then undergo the expected cheletropic addition at higher temperature. The competition between the hetero-Diels-Alder and the cheletropic additions of sulfur dioxide strongly depends on the nature of the substituents of the 1,3-dienes.[8] Reactions of sulfur dioxide with conjugated diallenes take place at room temperature with formation of 2,5-bis(alkylidene)-2,5-dihydrothiophene 1,1-dioxides.[9] Reactions of sulfur dioxide with vinylallenes, in particular, with vinylallenyl sulfoxides and sulfones have not been investigated to date.

During our previous works concerning electrophile-induced cyclization reactions of alkatrienyl sulfoxides and sulfones,[10a-10d] we were able to show that 1- and 3-vinylallenyl sulfoxides and sulfones are readily accessible by [2,3] sigmatropic rearrangement of the corresponding 1- and 3-vinylpropargylic sufenates and sulfinates, formed in the reactions of the corresponding α-alkynols with sulfenyl or sulfinyl chlorides.[10a-10d] In view of the advantages of vinylallenes as diene component in Diels-Alder reaction,[10e] we therefore initiated a study of their use in cheletropic addition. The results of this work are presented here.

We initiated this study with the cheletropic addition of sulfur dioxide to 5-methyl-3-(phenylsulfinyl)hexa-1,3,4-triene (**1a**). The reaction conditions have been optimized in order to obtain better yields. The reaction in benzene, toluene, xylene, CCl_4, CH_2Cl_2, and $CHCl_3$ as a solvent resulted in low product yields and mainly recovered the starting material or polymeric residue. According to results in the screening solvents, 1,2-dichloroethane was found to be the best. Thus, optimization of the reaction conditions was conducted in $ClCH_2CH_2Cl$ and finally it was found that when sulfur dioxide was bubbled through a stirred boiling solution of the vinylallene (**1a**), fast darkening of the reaction mixture took place and after 3.5 h no characteristic band for the allenic bond in the IR spectrum of the mixture was observed. The resulting 2,5-dihydrothiophene 1,1-dioxide (sulfolene) (**3a**) was isolated by preparative TLC in 78% yield. Note that at room temperature the two reactants still interacted (much more slowly) with the formation of the compound (**3a**).

To establish the generality of this method, the cheletropic addition of SO_2 to the corresponding 1-vinylallenyl sulfone (**1b**) was examined under the optimized conditions and 3-(methylsulfonyl)-2,5-dihydrothiophene 1,1-dioxide (**4b**) was isolated in 79% yield after bubbling with SO_2 and heating at reflux for 4 h (Scheme 1).

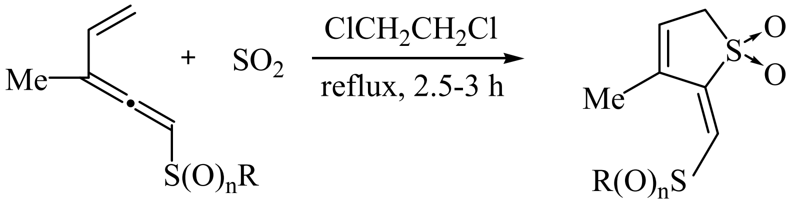


1a,b

3a, R = Ph, n = 1, 3.5 h, 78 %
3b, R = Me, n = 2, 4 h, 79 %

Scheme 1

Interestingly, this protocol can also be successfully applied to the corresponding cheletropic addition of SO_2 to the 3-vinylallenic starting materials. We have carried out the reaction of the 1-phenylsulfinyl- and 1-methylsulfonyl-substituted penta-1,2,4-trienes (**2a**) and (**2b**) with sulfur dioxide leading to (*E*)-2-phenylsulfinyl- or (*E*)-2-methylsulfonyl-methylidene-2,5-dihydrothiophene 1,1-dioxides (**4a**) and (**4b**) (Scheme 2). Although it was anticipated that the olefinic proton of the (*E*)-isomer would be observed



2a,b

4a, R = Ph, n = 1, 2.5 h, 72 %
4b, R = Me, n = 2, 3 h, 76 %

Scheme 2

downfield from the corresponding proton of the (*Z*)-isomer,[13] with the chemical shift value[12] (δ = 7.32 ppm for **4a** and 7.35 ppm for **4b**) alone we cannot determine whether dihydrothiophenes **4** is the (*E*)- or (*Z*)-isomer. On the other hand, in the ^{13}C NMR spectra the chemical shift value of the two carbon atoms of the exocyclic double bond of the (*E*)-isomer would be observed upfield from the corresponding carbons of the (*Z*)-isomer.[13] The obtained chemical shift value[12] for these carbons (δ = 136.2 and 155.5 ppm for **4a** and 137.3 and 149.2 ppm for **4b**) suggests that the olefinic proton is situated *cis* to the sulfonic group in the ring. Thus, the structure of **4** was determined to be (*E*).

Reaction times longer than 4 hours decrease the yields due to polymerization of the starting vinylallenic materials or decomposition of the products. The only product obtained in each case was the 2,5-dihydrothiophene 1,1-dioxides (**3a,b**) and (**4a,b**) – in all cases no traces of the corresponding 3,6-dihydro-1,2-oxathiine 2-oxides (sultines) as products of the hetero-Diels-Alder reaction or any other products were detected. Structural assignments of the new dihydrothiophenic compounds (**3**) and (**4**) are based on ^{1}H and ^{13}C NMR spectral data, IR spectra as well as elemental analyses.[11,12] In particular, on one hand, the protons on C-5 of the ring in ^{1}H NMR spectra resonate at δ = 3.79-4.18 ppm as two double doublets and the proton on C-4 appears as triplet, thus accounting for the depicted regiochemistry of the cycloaddition. On the other hand, the ^{13}C NMR spectra of these products (**3**) and (**4**) also showed a complex signals of the sp^2 carbons (δ = 120.7-155.5 ppm) and the sp^3 C-5 (δ = 47.2-48.4 ppm), characteristic for newly-formed 2,5-dihydrothiophenes.

In conclusion, we have developed an efficient synthesis of 2- and 3-sulfinyl(sulfonyl)-substituted 2,5-dihydrothiophene 1,1-dioxides by cheletropic addition of sulfur dioxide to 1- and 3-vinylallenyl sulfoxides and sulfones. This study reveals the potential of the cycloaddition reactions of vinylallenyl sulfoxides and sulfones to selectively construct exocyclic double bond on six-[2] or five-membered rings. Further expansion and applications of this methodology are in progress and will be reported in due course.

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11. (a) *3-Phenylsulfinyl-2-isopropylidene-2,5-dihydrothiophene 1,1-dioxide* (**3a**): Yellow oil, 78 % yield. TLC: ethyl acetate : hexane = 1 : 1. *Anal.* Calcd for $C_{13}H_{14}O_3S_2$: C 55.29, H 5.00, S 22.71; Found, C 55.47, H 4.94, S 22.63. IR (film): 1046, 1143, 1288, 1599-1640. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 2.07$ (s, 3H, Me_a), 2.21 (s, 3H, Me_b), 3.72, 3.87 (2xdd, $^3J_{HH}$ 2.9 Hz, $^2J_{HH}$ 12.0 Hz, 2H, CH_2), 7.2 (t, $^3J_{HH}$ 2.9 Hz, 1H, =C-H), 7.53-8.21 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 18.4$, 20.9, 47.3, 126.1, 129.5, 130.4, 136.2, 142.9, 145.8, 146.5, 153.3. (b) *3-Methylsulfonyl-2-isopropylidene-2,5-dihydrothiophene 1,1-dioxide* (**3b**): Yellow oil, 79 % yield. TLC: ethyl acetate : heptane = 1 : 2. *Anal.* Calcd for $C_8H_{12}O_4S_2$: C 40.66, H 5.12, S 27.14; Found, C 40.61, H 5.03, S 26.98. IR (film): 1141, 1326, 1600-1648. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 2.02$ (s, 3H, Me_a), 2.10 (s, 3H, Me_b), 3.07 (s, 3H, SO_2Me), 3.77, 3.98 (2xdd, $^3J_{HH}$ 2.9 Hz, $^2J_{HH}$ 12.1 Hz, 2H, CH_2), 7.23 (t, $^3J_{HH}$ 2.9 Hz, 1H, =C-H). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 22.2$, 24.4, 36.7, 47.7, 126.3, 130.4, 141.6, 153.8.
12. (a) *(E)-2-Phenylsulfinylmethylidene-3-methyl-2,5-dihydrothiophene 1,1-dioxide* (**4a**): Yellow oil, 72 % yield. TLC: ethyl acetate : heptane = 1 : 1. *Anal.* Calcd for $C_{12}H_{12}O_3S_2$: C 53.71, H 4.51, S 23.90; Found, C 53.83, H 4.48, S 24.08. IR (film): 1038 (S=O), 1122 (ν SO_2), 1306 (ν SO_2), 1581-1684 (C=C). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 2.24$ (s, 3H, Me), 4.11, 4.24 (2xdd, $^3J_{HH}$ 3.1 Hz, $^2J_{HH}$ 12.7 Hz, 2H, CH_2), 6.18 (t, $^3J_{HH}$ 3.1 Hz, 1H, =C^4-H), 7.32 (s, 1H, =C-H), 7.51-8.45 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 21.5$, 47.2, 120.7, 125.3, 127.6, 130.1, 136.2, 139.8, 150.0, 155.5. (b) *(E)-2-Methylsulfonylmethylidene-3-methyl-2,5-dihydrothiophene 1,1-dioxide* (**4b**): Yellow oil, 76 % yield. TLC: ethyl acetate : heptane = 5 : 1. *Anal.* Calcd for $C_7H_{10}O_4S_2$: C 37.82, C 4.53, S 28.85; Found, C 37.73, H 4.59, S 28.67. IR (film): 1126 (ν SO_2), 1297 (ν SO_2), 1590-1640 (C=C). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 2.27$ (s, 3H, Me), 2.75 (s, 3H, SO_2Me), 3.93, 4.13 (2xdd, $^3J_{HH}$ 3.2 Hz, $^2J_{HH}$ 11.9 Hz, 2H, CH_2), 6.01 (t, $^3J_{HH}$ 3.2 Hz, 1H, =C^4-H), 7.35 (s, 1H, =C-H). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 21.2$, 43.7, 48.4, 129.9, 137.3, 143.8, 149.2.
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