

A Convenient Method for the Extrusion of Sulfur Dioxide from 2,2,5,5-Tetrasubstituted 3-Sulfolenes

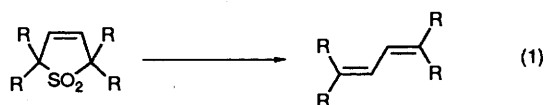
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The extrusion of SO₂ from 2,2,5,5-tetrasubstituted 3-sulfolenes to give the corresponding 1,3-dienes can be achieved by treatment with ultrasonically dispersed potassium in the presence of a proton source at room temperature. Such a transformation of functionality is difficult to achieve by other methods.

It has been well-established that substituted 3-sulfolenes† are masked 1,3-dienes.¹ For synthetic purpose, a 3-sulfolene can be functionalized by various methods to yield a substituted 3-sulfolene from which the SO₂ is ultimately removed to generate the corresponding 1,3-diene. The extrusion of SO₂ can be accomplished by thermolysis at 100–150 °C (within 2 h),² or by treatment with LiAlH₄ at below 50 °C (within 30 min),³ or with ultrasonically dispersed potassium (UDP) below room temperature (within 1 min).⁴ The thermolytic method has been used most extensively. Nevertheless, there are cases where the use of LiAlH₄ or UDP is preferred.⁵ Photolysis of 3-sulfolenes is not a practical synthetic method because of the low conversion rate and poor stereoselectivity.⁶ Whereas the aforementioned methods can conveniently remove SO₂ from mono-, di- or tri-substituted 3-sulfolenes, they are not applicable to 2,2,5,5-tetrasubstituted 3-sulfolenes. For example, 2,2,5,5-tetraethyl-3-sulfolene **1** remained intact after being heated at 220 °C for 6 h, treated with LiAlH₄ at 60 °C for 6 h, or treated with UDP at 40 °C for more than 2 h. A much higher temperature (350 °C) was used to extrude SO₂ from the tetrasubstituted 3-sulfolene **4**.⁷ It is thus desirable to develop milder reaction conditions for the conversion of tetrasubstituted 3-sulfolenes to the corresponding 1,3-dienes.



Recently we reported that a controlled amount of proton source would accelerate the UDP-induced carbon–sulfur bond cleavage reaction of saturated cyclic sulfones.⁸ We were therefore interested to test whether a proton source could also facilitate the UDP-induced SO₂ extrusion reaction from 3-sulfolenes, especially 2,2,5,5-tetrasubstituted 3-sulfolenes. When a water–THF (tetrahydrofuran) solution (3 equiv.) was added dropwise to a mixture of compound **1** and UDP in toluene, the reaction was complete immediately and the corresponding conjugated diene **6** was obtained in 64% yield (entry 2, Table 1). Similarly tetrabutyl-3-sulfolene **2** was converted to the diene **7** in 49% yield (entry 3). These reactions illustrate that the introduction of water can dramatically facilitate the UDP-induced SO₂ extrusion from a 3-sulfolene at room temperature. These reactions are very convenient and require no complex equipment but only a laboratory ultrasonic cleaning bath. When Bu'OH was used instead of water as the proton source, the reactions proceeded equally and the yields were substantially improved (entries 4 and 5). We therefore carried out the UDP-induced SO₂ extrusion reactions using Bu'OH as the

Table 1 UDP-Induced SO₂ extrusion reactions of 2,2,5,5-tetrasubstituted 3-sulfolenes

Entry	3-Sulfolenes	Proton source ^a	Products and yields (%) ^{b,c}
1	1 R = Et	none	no reaction
2	1 R = Et	H ₂ O	6 (64)
3	2 R = Bu	H ₂ O	7 (49)
4	1 R = Et	Bu'OH	6 (92)
5	2 R = Bu	Bu'OH	7 (70)
6	3 R = pentyl	Bu'OH	8 (79) ^d
7	4 R,R = -(CH ₂) ₅ -	Bu'OH	9 (70)
8	5 R,R = -(CH ₂) ₄ -	Bu'OH	10 (90)

^a The molar ratio of sulfolene–UDP–proton source was kept at 1:3:3 for all entries. ^b These are isolated yields after purification by HPLC. ^c All new compounds give satisfactory spectral (NMR, IR, MS) and analytical data. ^d This yield is based on the consumed starting material. Compound **3** was recovered in 46% yield in this reaction.

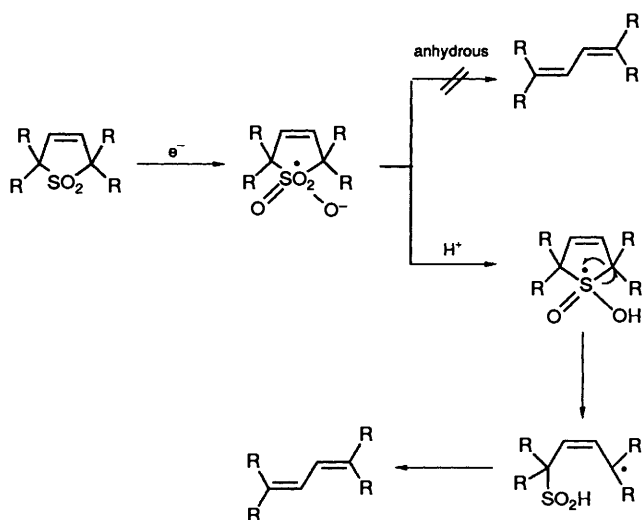


proton source on several other 2,2,5,5-tetrasubstituted 3-sulfolenes,† the results are summarized in Table 1.

The discrepancy in the mode of reaction (entry 1 versus entry 2 or 4) suggests that different mechanisms may be involved in the reactions performed with or without a proton source. Although the detailed mechanism has not been established for the UDP-induced SO₂ extrusion reaction from di- and tri-substituted 3-sulfolenes under anhydrous conditions,⁴ the stereospecificity of the formation of the corresponding dienes implies a concerted, cheletropic reaction accelerated by the transfer of an electron from potassium to the sulfone functionality. However, for the concerted ring-opening process of a 2,2,5,5-tetrasubstituted 3-sulfolene to take place, there is a high energy barrier derived from the repulsive interactions among the substituents. Therefore, the reaction does not proceed at moderate temperatures. It is speculated that by adding a proton source to the reaction mixture, the protonation of the sulfone radical anion may initiate a stepwise cleavage of the two carbon–sulfur bonds. The energy barrier in each step is lower so

† 2,5-Dihydrothiophene 1,1-dioxide.

‡ All of the 2,2,5,5-tetrasubstituted 3-sulfolenes were prepared by the one-pot multialkylation reactions of 3-sulfolenes described in ref. 7.



that the reaction can take place readily at room temperature (Scheme 1). Attempts to remove SO_2 from compound **11** by UDP–water or UDP–Bu'OH were unsuccessful. The steric crowding of the six alkyl groups on this molecule are probably responsible for this failure.

The speed of the addition of the proton source has a determining influence on the success of the reaction. The standard procedure is to add dropwise a dilute solution (0.45 mol dm^{-3}) of water on Bu'OH in THF to the reaction mixture and the desired reaction is fast enough so that the reactive potassium is not interfered with. However, if the proton source is added too rapidly or at too high a concentration, the potassium is destroyed by the proton source instantaneously and the reaction is terminated. The use of a large excess of UDP should be avoided. In an experiment where a 1:6:6 molar ratio of sulfone–UDP–Bu'OH was used, only insoluble polymer was obtained. Presumably the excessive base generated from the reaction of potassium and Bu'OH could induce the polymerization of the end product.

Typical Reaction Procedure.—To a suspension of ultrasonically dispersed potassium (UDP, 4.5 mmol) in toluene (10 cm^3)⁹ in an ultrasonic cleaning bath under N_2 was added a solution of **1** (1.5 mmol) in toluene (10 cm^3). The sonication was continued for 30 min during which time a bright-blue colloid developed. A solution of Bu'OH in THF (0.45 mol dm^{-3} ; 4.4 mmol) was added dropwise over a period of 30 min whereupon the potassium was completely consumed. The mixture was filtered through a short silica gel column to remove the solid precipitate and the filtrate was concentrated under reduced pressure. The essentially clean product was purified by HPLC (LiChrosorb column, hexane) to give compound **6** in 92% yield.

Acknowledgements

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