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Reactions of Conjugated Diallenes with Sulfur Dioxide. Formation of 2,5-Bis(alkylidene)-2,5-dihydrothiophene-1,1-dioxide Derivatives

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Reactions of sulfur dioxide with conjugated diallenes (*1*) take place at room temperature with formation of [4 + 2] cycloaddition products *viz.* 2,5-bis(alkylidene)-2,5-dihydrothiophene-1,1-dioxides (*2*) in good yields. The stereochemistry of the reaction shows that it is disrotatory with the two most bulky groups moving away from each other.

In compounds containing two allenic linkages separated by one single bond the two central double bonds are conjugated (Fig. 1). Such compounds represent a unique diene system and thus are prone to [4+2] cycloadditions; at the same time they also maintain the structural characteristics of an allene which means that they should be capable of undergoing [2+2] cycloadditions. This potentially ambident character of conjugated diallenes has been tested with some olefinic reagents,[1] but only [4+2] type cycloadditions have been observed. In the present work the addition of sulfur dioxide to various conjugated diallenes (*1*) is reported to yield exclusively the [4+2] cycloaddition products of the general structure *2*.

Several methods for the preparation of conjugated diallenes are available, but few have any general application. Recently a two-step procedure leading to diallenes has been developed, which involves reaction of conjugated dienes with dibromocarbene and treatment of the resulting bis-adducts with methyllithium.[2,3] *1a*, *1b*, *meso-1c*, and *meso-1d* were prepared by this method, while the remaining diallenes were prepared by other methods reported in the literature (see Experimental). The diallenes were dissolved in as little as possible of an alkane or benzene or a mixture of the two at room temperature, and a gentle stream of gaseous sulfur dioxide was passed into the stirred solution. The reactions were followed by thin layer chroma-

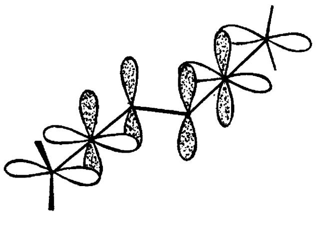
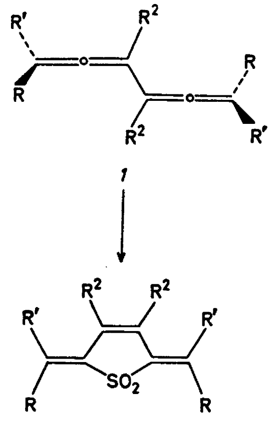


Fig. 1.



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a. R = Me; R′ = Me; R^2 = H
b. R = Me; R′ = Et; R^2 = H
c. R = Me; R′ = Ph; R^2 = H
d. R = Me; R′ = *t*-Bu; R^2 = H
e. R = Ph; R′ = Ph; R^2 = H
f. R = Ph; R′ = Ph; R^2 = Br
g. R = Ph; R′ = *t*-Bu; R^2 = Br

Table 1. Spectral properties of 2,5-bis(alkylidene)-2,5-dihydrothiophene-1,1-dioxides (*2*).

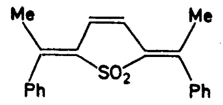
Compound	Yield %	NMR δ ($CDCl_3$)	IR (cm^{-1},KBr)	UV λ max (nm, ethanol)	ε
2a	85	1.95 (s) 6H	1710 w	203	7 400
		2.27 (s) 6H	1630 str		
		6.47 (s) 2H	1270 str	290	23 400
			1115 str		
2b	80	[a]	1625 str	200	15 500
			1275 str		
			1120 str	293	22 100
2c	78	2.64 (s) 6H	1750 w	200	29 800
		6.40 (s) 2H	1605 str		
		7.40 (m)10H	1280 str	317	29 300
			1120 str		
2d	74	1.29 (s) 18H	1600 str	199	15 900
		2.38 (s) 6H	1270 str		
		7.05 (s) 2H	1115 str	298	25 600
2e	73	6.65 (s) 2H	1580 (m)	215	57 500
		7.4 (m)20H	1560 (m)		
			1300 (str)	245	25 600
			1125 (str)	353	32 000
2f	73		1575 (str)	200	48 500
			1555 (str)	247	23 000
			1320 (str)	284	21 300
			1140 (str)	308	19 000
				362	25 000

[a] Mixture of isomers; two overlapping triplets at 1.1, 6 H; two quartets at 2.3 and 2.7, 4 H; two singlets at 1.94 and 2.25, 6 H; singlet at 6.47, 2 H.

tography (TLC), and reaction times from 30 min to 7 h were needed for completion. The only product obtained in each case was the sulfolene derivative *2*.

The yields recorded in Table 1 refer to recrystallized analytically pure material. The structures were determined on the basis of spectroscopic evidence. Furthermore, a compound assigned structure *2a*, obtained by the base-catalyzed condensation of acetone with 2,5-dihydrothiophene-1,1-dioxide,[4] was indentical with our product. The structures of the sulfolene derivatives *2c* and *2d* were particularly interesting since both starting diallenes *1c* and *1d* had the *meso* configuration. A [4+2] cycloaddition of sulfur dioxide could theoretically yield three isomeric compounds, *viz.* *2c*, *3* and *5*, or *2d*, *4* and *6*, respectively.

The products were homogenous as shown by TLC. The NMR spectra (Table 1) consisted in both cases of three singlets, excluding unsymmetrical structures *5* and *6*. The chemical shift of a methyl group attached to a double



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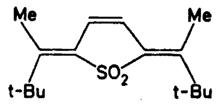

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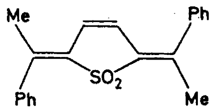

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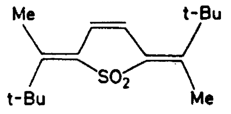

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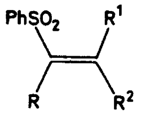
Table 2. NMR spectra of vinylsulfones.



R	R^1	R^2	$\delta(R^1)$	$\delta(R^2)$
Solvent: CCl_4; Ref. 5.				
H	CH_3	H	2.14	
H	H	CH_3		1.90
CH_3	CH_3	H	2.13	
CH_3	H	CH_3		1.72
Solvent: $CDCl_3$; Ref. 6.				
H	CH_3	$NHCH_2Ph$	2.16	
H	$NHCH_2Ph$	CH_3		1.86
H	CH_3	SPh	2.44	
H	SPh	CH_3		1.75

bond depends strongly on its *E* or *Z* relationship to a vicinal group and in vinyl sulfones methyl-groups in *E* position are shifted upfield (Table 2). In compound *2a* the methyl groups appear at δ 1.95 and 2.27, and are therefore assigned to *E*- and *Z*-methyl groups, respectively. The methyl groups of the products from the diallenes *1c* and *1d* absorb at 2.64 and 2.38 compatible with structures *2c* and *2d* which have a *Z* configuration of the methyl groups. Additional evidence for structure *2d* is also provided by the strong deshielding effect of the *t*-butyl group on the vinyl protons; compared with compound *2a*; a down-field shift of 0.58 ppm was observed.

It would be interesting to compare the UV spectrum of compound *2c* with that of 1,6-diphenyl-*1Z,3Z,5Z*-hexatriene, but the compound is unknown; however, Lunde and Zechmeister [7] who measured the UV spectra of the *1Z,3E,5Z*- and *1Z,3Z,5E*-isomers conclude that the all-*Z* isomer should absorb well below 334 nm. The absorption maximum at 317 nm as well as the lack of fine structure in the UV spectrum of *2c* is fully in accordance with this prediction.

Even without kinetic measurements it is clear that the reactivity of the diallene diminishes from *1a* to *1f*; the diallene *1g* was extremely unreactive as it was recovered unchanged after one hour in neat sulfur dioxide at 100 °C.

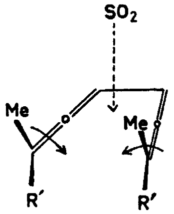


Fig. 2.

According to Woodward and Hoffmann [8] the concerted addition of sulfur dioxide to conjugated dienes is thermally allowed as a linear cheletropic reaction; the required disrotatory process has been observed.[9] The formation of sulfolene derivatives *2* from the diallenes *1* and sulfur dioxide show that the reaction is formally a [4+2] cycloaddition, and the stereochemical results strongly indicate that it is concerted. In such a process sulfur dioxide will most probably approach a cisoid diallene from the least hindered side, followed by a disrotatory move in which the two most bulky groups rotate away from each other as depicted in Fig. 2.

One can certainly imagine both radical and ionic mechanisms since unusual allylic stabilization of the intermediates is predictable; however, it would be very much a coincidence, if such reaction paths should exhibit the clean stereochemistry observed in the above cycloaddition reaction.

EXPERIMENTAL

NMR spectra were recorded on a Varian A60 Spectrometer. A Perkin-Elmer model 457 spectrophotometer was used for obtaining IR spectra, and UV spectra were recorded on a Cary 14 spectrophotometer. Elemental analyses were carried out by Ilse Beetz Microanalytical Laboratory, 8640 Kronach, Germany. All melting points are uncorrected.

2,5-Bis(2-propylidene)-2,5-dihydrothiophene-1,1-dioxide (*2a*). Sulfur dioxide was passed during 2 h into a stirred solution of 3.4 g (26 mmol) of 2,7-dimethyl-2,3,4,5-octatetraene (*1a*) in 50 ml dry pentane. Filtration gave 4.5 g (86 %) of *2a*, m.p. 261 – 263 °C (decomp) from acetone (lit.[4] m.p. 261 – 263 °C).

2,5-Bis(2-butylidene)-2,5-dihydrothiophene-1,1-dioxide (*2b*). Sulfur dioxide was passed during 2 h into a stirred solution of 1.0 g (6.1 mmol) of 3,7-dimethyl-3,4,6,7-decatetraene (*1b*) [3] in 20 ml of dry pentane. Filtration yielded 1.1 g (80 %) of *2b*, m.p. 142 – 143 °C (decomp) from acetone-water, (Found: C 63.71; H 7.78. Calc. for $C_{12}H_{18}SO_2$: C 63.68; H 8.02).

anti,anti-2,5-Bis(1-phenylethylidene)-2,5-dihydrothiophene-1,1-dioxide (*2c*). Sulfur dioxide was passed during 1 h into a stirred solution of 0.15 g (0.58 mmol) of *meso*-3,7-diphenyl-2,3,5,6-octatetraene *(1c)* [3] in 10 ml of heptane-benzene 1:1. TLC showed that the diallene had been consumed after 30 min. Evaporation of the solvents and recrystallization of the residue from acetone-water gave 0.14 g (78 %) of *2c*, m.p. 155 °C. (Found: C 74.62; H 5.61. Calc. for $C_{20}H_{18}SO_2$: C 74.52; H 5.63).

anti,anti-2,5-Bis-(2,2-dimethyl-3-butylidene)-2,5-dihydrothiophene-1,1-dioxide (*2d*). Sulfur dioxide was passed during 2 h into a stirred solution of 0.25 g (1.1mmol) of *meso*-2,2,3,8,9,9-hexamethyl-3,4,6,7-decatetraene (*1d*) [3] in 10 ml of dry hexane. The product was filtered and recrystallized from hexane to give 0.23 g (74 %) of *2d*, m.p. 173 °C. (Found: C 68.94; H 9.27. Calc. for $C_{14}H_{26}SO_2$: C 68.05; H 9.28).

2,5-Bis(diphenylmethylidine)-2,5-dihydrothiophene-1,1-dioxide (*2e*). Sulfur dioxide was passed during 3 h into a stirred solution of 0.30 g (0.78 mmol) of 1,1,6,6-tetraphenyl-1,2,4,5-hexatetraene (*1e*) [10] in 30 ml benzene. The solvent was evaporated and the residue recrystallized from petroleum ether (60–80 °C–benzene to give 0.25 g (73 %) of *2e*, m.p. 229 °C (decomp). (Found: C 80.86; H 5.24. Calc. for $C_{30}H_{22}SO_2$: C 80.69; H 4.97). In cyclohexane *2e* crystallized with two molecules of solvent, m.p. 224 °C (decomp). (Found: C 82.15; H 7.32. Calc. for $C_{42}H_{46}SO_2$; C 82.04; H 7.54).

2,5-Bis(diphenylmethylidene)-3,4-dibromo-2,5-dihydrothiophene-1,1-dioxide (*2f*). Sulfur dioxide was passed during 7 h into a stirred solution of 0.27 g (0.50 mmol) of 3,4-dibromo-1,1,6,6-tetraphenyl-1,2,4,5-hexatetraene (*1f*) [11] in 10 ml of benzene and 5 ml of hexane. The product was precipitated by addition of hexane. Filtration and recrystallization from diethyl ketone gave 0.22 g (73 %) of *2f*, m.p. 260 °C (decomp.). (Found: C 59.67; H 3.48. Calc for $C_{30}H_{20}SO_2Br_2$: C 59.61; H 3.34).

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