

CYCLOADDITION REACTIONS

COMMUNICATION 1. REACTION OF SULFENES WITH

α,β -UNSATURATED SULFIDES

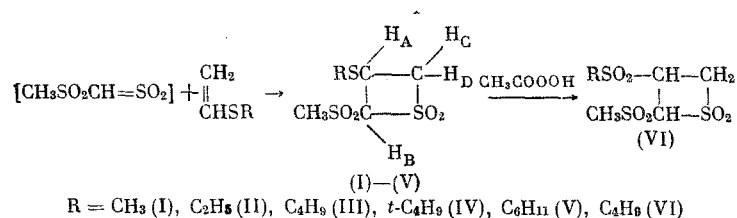
E. N. Prilezhaeva, N. P. Petukhova,
V. I. Kurilkin, A. U. Stepanyants,
and V. P. Lezina

UDC 542.91:547.379

In recent years the reactions of sulfenes $[RCH=SO_2]$, which are most frequently generated by the alkaline cleavage of sulfochlorides [1, 2], are attracting the attention of investigators. Sulfenes are capable of entering into the cycloaddition reaction with the formation of thietane dioxide derivatives [3, 4]. The reactions for the cycloaddition of sulfenes to α,β -unsaturated sulfides with electron-donor substituents (alkyl- or arylthio groups) have not been studied up to now.

We studied the cycloaddition of sulfenes to α,β -unsaturated sulfides. It proved that neither the alkyl vinyl nor the cycloalkyl vinyl sulfides, which have a $C=C$ bond that is substantially less nucleophilic than, for example, the enamines, which easily react with sulfenes [5, 6], react with either sulfene or phenylsulfene. The reactions are accompanied by pronounced tarring; only the starting vinyl sulfide can be isolated from the reaction mixture.

However, the use of the more reactive methylsulfonylsulfene, which is activated by the strongly electron-acceptor sulfonyl group, makes it possible to synthesize the dioxithietanes (I)-(V).



The reactions go easily at -40° , in a nitrogen stream, in absolute acetonitrile solution. The methylsulfonylsulfene was generated from methylsulfochloride and triethylamine, which were, respectively, taken on the basis of 2 and 3 moles/mole of the vinyl sulfide [7]. The yield of the dioxithietanes increased somewhat with increase in the electron-donor nature of the substituent attached to the double bond of the vinyl sulfide. Thus, when going from methyl vinyl to *tert*-butyl vinyl sulfide the yield of the cycloadduct changed from 30 to 80% (Table 1). The reaction does not go with phenyl vinyl sulfide or vinyl thiolacetate, and also with ethylthioacetylene, the nucleophilicity of whose multiple bonds is low when compared with the alkyl vinyl and cycloalkyl vinyl sulfides. It is interesting to mention that not in a single case did we detect acyclic adducts, isomeric with the dioxithietanes (I)-(V), similar to those that were found by other authors for the vinyl ethers [8].

The purity of the synthesized dioxithietanes (I)-(V) was checked by the TLC method. The structure of the compounds was confirmed by the IR and NMR spectra, and for (III) also by its oxidation to the disulfone (VI). The character of the NMR spectra and the multiplet nature of the signals exclude for adducts (I)-(V) the isomeric linear structure of type $(RSCH=CHSO_2CH_2SO_2CH_3)$, for which the olefinic protons would give a spectrum of the AX system, located downfield.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 8, pp. 1827-1831, August, 1974. Original article submitted January 10, 1974.

© 1975 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

TABLE 1

No.	Compound name	Yield, %	Mp, °C	Empirical formula	Found/calculated, %				IR spectrum, ν_{SO_2} , cm ⁻¹
					C	H	N	S	
(I)	3-Methylthio-4-methylsulfonyl-1,1-dioxethane	32	137,5—138 *	C ₅ H ₁₀ O ₄ S ₃	26,12 26,08	4,33 4,35		41,70 41,75	1150 1320
(II)	3-Ethylthio-4-methylsulfonyl-1,1-dioxethane	61	109—110 *	C ₆ H ₁₂ O ₄ S ₃	29,80 29,49	4,95 4,90		38,90 39,38	1146 1315
(III)	3-Butylthio-4-methylsulfonyl-1,1-dioxethane	75	73,5—74,5 *	C ₈ H ₁₆ O ₄ S ₃	35,46 35,27	5,93 5,92		35,43 35,31	1130 1335
(IV)	3-tert-Butylthio-4-methylsulfonyl-1,1-dioxethane	80	158—158,5 *	C ₈ H ₁₆ O ₄ S ₃	35,59 35,27	5,88 5,92		34,90 35,30	1153 1340
(V)	3-Cyclohexylthio-4-methylsulfonyl-1,1-dioxethane	48	116—117 *	C ₁₀ H ₁₈ O ₄ S ₃	40,37 40,25	5,82 6,02	—	32,04 32,23	1160 1320
(XI)	2-Methylthio-3-diethylamino-4-phenyl-1,1-dioxethane	20	78—79 *	C ₁₄ H ₂₁ NO ₂ S ₂	56,30 56,15	6,95 7,07	4,79 4,67	21,23 21,42	1155 1320
(XII)	2-Ethylthio-3-diethylamino-4-phenyl-1,1-dioxethane	70	82—83 *	C ₁₅ H ₂₂ NO ₂ S ₂	57,12 57,48	7,53 7,39	4,63 4,47	20,54 20,46	1150 1325
(XIII)	2-Ethylthio-3-diethylamino-1,1-dioxethane	45	41—41,5 †	C ₉ H ₁₉ NO ₂ S ₂	45,50 45,53	7,89 8,07	6,03 5,90	26,91 27,02	1150 1320
(XIV)	2-Ethylthio-3-diethylamino-4-propyl-1,1-dioxethane	1	‡	—	—	—	—	—	—
(XV)	2-Ethylthio-3-piperidino-4-phenyl-1,1-dioxethane	40	92—93 **	C ₁₆ H ₂₃ NO ₂ S ₂	58,89 59,03	7,05 7,12	4,25 4,31	19,62 19,71	1155 1320
(XVI)	2-Ethylthio-3-morpholino-4-phenyl-1,1-dioxethane	45	129—130 *	C ₁₅ H ₂₁ NO ₃ S ₂	54,95 55,02	6,32 6,45	4,15 4,25	18,85 19,13	1120 1320

* From methanol.

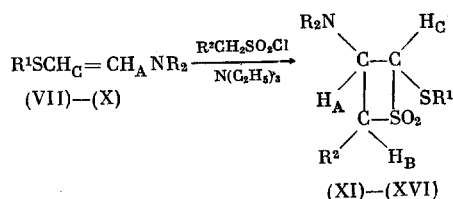
† From petroleum ether.

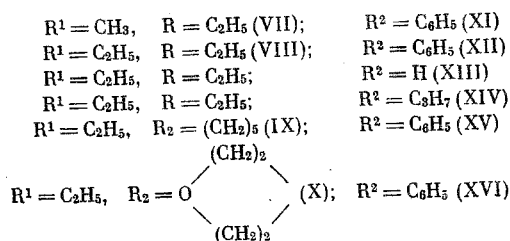
‡ Identified as the picrate.

** Acetone: ether, 1:1.

Starting with the assumption that the insertion of two alkylthio groups will increase the nucleophilicity of the double bond in an unsaturated sulfide, we studied the cycloaddition reactions of sulfenes for cis-1,2-diethylthioethene and ketene 1,1-diethylmercaptal. However, these compounds failed to enter into the cyclization reaction not only with either sulfene or phenylsulfene, but also with the substantially more active methylsulfonylsulfene. Apparently, the insertion of two alkylthio groups into the molecule even decreases somewhat the nucleophilicity of the multiple bond of the sulfide, since the possibility of another distribution of the electrons appears here, in which the d-orbitals of sulfur take part, with a decrease in the π -electron density of the C—C bond. Similar data were obtained recently when the tetrathioethylenes were calculated by the MO method [9].

The insertion of a strong electron donor like the alkylamino group into the unsaturated sulfide molecule greatly facilitates the cycloaddition reaction. The 1,2-trans-alkylaminothioethenes (VII)–(X) also react easily with inactivated sulfenes to give the dioxethanes (XI)–(XVI). Compounds (VII)–(X) were synthesized by heating the appropriate alkyl ethynyl sulfides with excess amine. Based on the NMR data, adducts (VII)–(X) have the trans-configuration. This is most probably explained by the isomerization of the initially formed cis-isomers, the formation of which could be expected in harmony with the rule of trans-nucleophilic addition, when they are heated for a long time in the presence of the amine.





The sulfenes were generated from the corresponding sulfochlorides and triethylamine, taken in an equimolar ratio. The yield of the cycloadducts is determined by the character of the polarization of the multiple bonds of the unsaturated sulfide and sulfene. Thus, with sulfides (VII)-(X) having approximately the same nucleophilicity, alkyl substituents in the sulfochloride molecule, for example, in the case of butylsulfochloride, lower the electrophilicity of the sulfene, which leads to a reduction in the yield of the dioxethietanes to 1-2%. In this case we were able to isolate the cycloadduct (XIV) only as the picrate. Phenyl substitution in the sulfene facilitates reaction. The yield of the cycloadducts increases up to 70% (see Table 1). The polarity of the employed solvents (ether, benzene, acetonitrile), and also variation in the reaction temperature from 0 to -30° , are essentially without effect on the yield of the dioxethietanes.

The purity of compounds (XI)-(XVI) was checked by the TLC method. The structure of adducts (XI)-(XVI) was confirmed by the IR and NMR spectra. Besides the characteristic signals of the substituents, three groups of multiplet signals are observed in the NMR spectra of these compounds, which are caused by the protons of the ring, the assignment of which was made taking into account the data on the double resonance. The value of the spin-spin coupling constant for compounds (XI)-(XVI) ($J_{AC} = 9$ Hz) indicates that the trans-configuration of the sulfide does not change in the cycloaddition process. A similar value of the spin-spin coupling constant for the trans-protons in dioxethietane molecules was found by other authors [10].

EXPERIMENTAL METHOD

The IR spectra were taken on a UR-10 spectrometer either as KBr pellets or as a thin layer, while the NMR spectra were taken on a Varian HA-100 spectrometer using HMDS as the internal standard. The GLC was run on an LCM-7A instrument equipped with a flame-ionization detector, using a $2 \text{ m} \times 4 \text{ mm}$ column packed with 1.5% Silicone SE-30 deposited on Chromatone AN (0.2-0.25 mm), at $150-175^\circ$. The melting points were determined on a Kofler block. The employed solvents had been dried and distilled in advance.

Cycloaddition Reactions of Vinyl Sulfides

3-Butylthio-4-methylsulfonyl-1,1-dioxethietane (III). To a stirred solution of 7.6 g of triethylamine and 2.8 g of vinyl butyl sulfide in 100 ml of absolute acetonitrile was added, in a nitrogen stream, at -40° , in drops, a solution of 5.72 g of methylsulfochloride in 30 ml of absolute acetonitrile in 2 h. The reaction mixture was kept at -40° for 1 h, and then at 20° for 0.5 h. The precipitate was filtered, the filtrate was evaporated, and the obtained oil was diluted with a little acetone. A total of 6.45 g (93%) of triethylamine hydrochloride was obtained. The acetone was evaporated, and the obtained oil was treated with methanol. Recrystallization from methanol gave 5.2 g (75%) of adduct (III).

NMR spectrum (in CDCl_3), δ , ppm: 3.11 (3H, CH_3SO_2); 5.31 q (H_B); 3.97 oc (H_A); 4.09 oc (H_C); 4.68 q (H_D), $^3J_{AB} = 5.8$; $^4J_{BC} = 2.2$; $^3J_{AD} = 11.6$; $^3J_{AC} = 5.8$; $^2J_{CD} = 15.7$ Hz. Disulfone (VI), with mp $142-143^\circ$ (methanol), was obtained by the oxidation of (III) with 70% $\text{CH}_3\text{CO}_3\text{H}$ in absolute ether at 0° . Found: C 31.74; H 5.46; S 31.64%. $\text{C}_8\text{H}_{16}\text{O}_6\text{S}_3$. Calculated: C 31.57; H 5.27; S 31.61%. Infrared spectrum (ν , cm^{-1}): 1146, 1340, 1360 (SO_2 group).

Cycloadducts (I), (II), and (IV) were synthesized in a similar manner. The constants and the elemental and spectral analysis data are given in Table 1. The values of the chemical shifts and spin-spin coupling constant in the NMR spectra are analogous to those indicated above for adduct (III).

Cycloaddition Reactions of Sulfenes to trans-1,2-Aminothioethenes

The trans-aminothioethenes (VII)-(X) were obtained by the addition of amines to either methyl- or ethylthioacetylene, which were synthesized as described in [11]. The constants of compounds (VIII) and

(IX) coincided with the literature data [12, 13]. Benzylsulfochloride, mp 91.5–92° (from CHCl₃), while the butylsulfochloride was distilled.

Data of NMR spectra for compounds (VII)–(X): signals of olefinic protons with δ 4.41–4.67 (=CHNR₂), 6.10–6.34 (=CHSR¹), $J_{\text{trans}} = 13$ Hz.

trans-1-Methylthio-2-diethylaminoethene (VII). A mixture of 4.7 g of methylthioacetylene and 14.8 g of diethylamine in an ampul, blown with nitrogen, was heated at 76–80° for 8 h. We obtained 4.1 g (50%) of (VII), bp 64–65° (4 mm); n_D^{20} 1.5190. Found: C 57.82; H 10.53; N 9.20; S 22.45%. C₇H₁₅NS. Calculated: C 57.91; H 10.33; N 9.25; S 22.08%. Infrared spectrum (ν , cm⁻¹) 1600 (C=C).

trans-1-Ethylthio-2-morpholinoethene (X). A mixture of 3 g of ethylthioacetylene and 6 g of morpholine was heated at 90–100° for 6 h to give 3.5 g (50%) of (X), bp 65–67° (0.02 mm); n_D^{20} 1.5450. Found: C 55.19; H 8.61; N 8.17; S 18.56%. C₈H₁₃NOS. Calculated: C 55.34; H 8.71; N 8.06; S 18.46%. Infrared spectrum (ν , cm⁻¹) 1600 (C=C).

2-Ethylthio-2-diethylamino-4-phenyl-1,1-dioxythietane (XII). To a stirred mixture of 1 g of aminoethene (VIII) and 0.63 g of triethylamine in 50 ml of ether was slowly added in drops, in a nitrogen stream, at –5 to –7°, a solution of 1.19 g of benzylsulfochloride in 25 ml of ether. The mixture was kept at –5 to –7° for 1 h, and then at 20° for 0.5 h. The precipitate was filtered, and washed in succession with ether and acetone. From the acetone solution we isolated 0.24 g of triethylamine benzylsulfonate, mp 113–114°, which failed to depress the mixed melting point with an authentic specimen. From the ether solution we isolated 1.4 g (70%) of adduct (XII) (see Table 1).

When this reaction was run in benzene solution at 5°, or in acetonitrile solution at –20°, the yield of cycloadduct (XII) was, respectively, 50 and 40%. Besides the signals, characteristic for the protons of the substituents, the NMR spectrum (in CDCl₃) has the following chemical shifts: δ 3.60 q (H_A), 5.09 q (H_B), 5.23 q (H_C), $^3J_{AB} = 8.5$, $^3J_{AC} = 9.1$, $^4J_{BC} = 1.0$ Hz.

Compounds (XI) and (XIII)–(XVI) were synthesized by the above described method, and the constants and analysis results are given in Table 1. The chemical shifts of the ring protons in the NMR spectra and their spin–spin coupling constants are analogous to those indicated for adduct (XII).

Reaction of Butylsulfochloride with trans-1-ethylthio-2-diethylaminoethene (VIII). The reaction was run under the same conditions as in the preparation of (XII). From 1 g of sulfide (VIII), 1 g of butylsulfochloride, and 0.65 g of triethylamine we obtained 0.4 g (44%) of triethylamine hydrochloride and 1.5 g of an oil that tended to tar in the air, to which was added an ether solution of picric acid. We obtained 0.3 g (~1%) of the picrate of adduct (XIV), mp 151.5–152°. Found: C 43.24; H 5.83; N 11.29; S 12.87%. C₁₈H₂₈N₄O₉S₂. Calculated: C 43.37; H 5.66; N 11.24; S 12.86%.

CONCLUSIONS

The reactions of α,β -unsaturated sulfides with sulfenes are quite dependent on the nucleophilicity of the multiple bond of the vinyl sulfide, and on the electrophilicity of the sulfene, and lead to the formation of dioxethietanes, containing various functional groups, in 30–70% yields.

LITERATURE CITED

1. J. F. King and T. Durst, J. Amer. Chem. Soc., **87**, 5684 (1965).
2. J. F. King and T. W. S. Lee, J. Amer. Chem. Soc., **91**, 6524 (1969).
3. G. Opitz, Angew. Chem., **79**, 161 (1967).
4. H. Ulrich, Cycloaddition Reactions of Heterocumulenes, New York–London (1967), p. 287.
5. G. Opitz and H. Adolff, Angew. Chem., **74**, 77 (1962).
6. G. Stark and J. Borowitz, J. Amer. Chem. Soc., **84**, 313 (1962).
7. G. Opitz and D. Bucher, Tetrahedron Lett., 5263 (1966).
8. G. Opitz, K. Riehl, and G. Walz, Tetrahedron Lett., 5269 (1966).
9. D. L. Coffey, J. Q. Chambers, D. R. Williams, P. E. Garrett, and N. D. Canfield, J. Amer. Chem. Soc., **93**, 2258 (1971).
10. L. A. Paquette, J. P. Freedman, and R. W. Houser, J. Org. Chem., **34**, 2901 (1969).
11. J. F. Arens and T. Doornbos, Rec. Trav. Chim., **75**, 481 (1956).
12. H. C. Volger and J. F. Arens, Rec. Trav. Chim., **77**, 1170 (1958).
13. J. F. Arens, H. C. Volger, T. Doornbos, J. Bohmema, J. W. Greidanus, and J. H. Wander, Rec. Trav. Chim., **75**, 1459 (1956).