Tetrahedron Letters,Vol.29,No.12,pp 1445-1448,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Press plc

SELENOSULFONATION OF 1,3-DIENES: ONE-POT SYNTHESIS OF 2-(PHENYLSULFONYL)-1,3-DIENES

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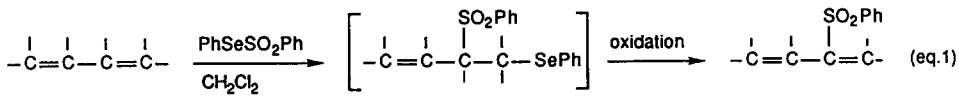
Summary: A one-pot procedure for the transformation of a 1,3-diene into the corresponding 2-(phenylsulfonyl)-1,3-diene was developed. The reaction involves a 1,2-selenosulfonation-oxidation sequence.

2-(Phenylsulfonyl)-1,3-dienes have recently been shown to be versatile synthons in organic transformations.[2-5] They can be used as multicoupling reagents and as Diels-Alder dienes with a dual electron demand.[3] In addition, regioselective epoxidation of either double bond leads to synthetically useful epoxy sulfones.[4] The previous procedure for the synthesis of 2-(phenylsulfonyl)-1,3-dienes from 1,3-dienes was based on a 1,2-sulfonylmercuration-elimination sequence. A drawback with this procedure is that it involves the use of mercury. Because of the increasing importance of these sulfonyldienes, alternative methods[6] for their preparation seemed highly desirable. In this communication we report a one-pot procedure for the preparation of 2-(phenylsulfonyl)-1,3-dienes that is based on a selenosulfonation-oxidation[7] sequence (eq. 1).

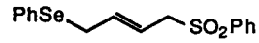
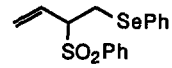
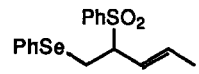
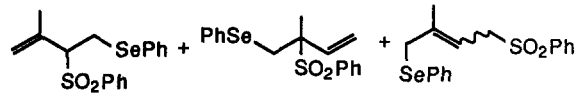
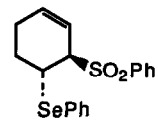
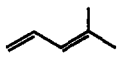
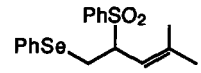
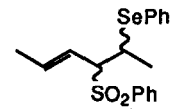
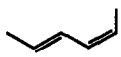
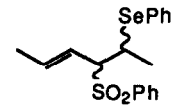
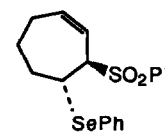


(eq.1)

It has been reported that selenosulfonation of olefins by $PhSeSO_2Ph$ occurs in the presence of BF_3.[7,8] Furthermore, it was shown that the oxidation of these adducts leads to an elimination of selenium to give vinylic sulfones. This selenosulfonation-elimination would be a possible route to 2-(phenylsulfonyl)-1,3-dienes from 1,3-dienes. However, examples of the use of the selenosulfonation on conjugated dienes are scarce and the only example reported is for 1,3-cyclohexadiene.[8] We therefore decided to study the selenosulfonation of conjugated dienes to determine the regioselectivity, efficiency, and scope of the reaction.

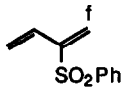
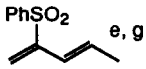
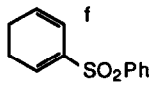
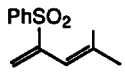
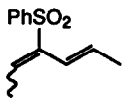
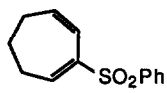
Selenosulfonation of conjugated dienes were performed in methylene chloride using $PhSeSO_2Ph$[9] in the presence of BF_3. Results from some representative examples are given in Table 1. Except for isoprene, the selenosulfonation of the conjugated dienes could be made highly 1,2-selective. Interestingly, butadiene afforded a quantitative yield of the 1,4-adduct at room temperature, but selectively gave the 1,2-adduct at 0 °C. The selenosulfonation of cyclic 1,3-dienes was stereospecific and occurred trans.[10] However, the addition to 2,4-hexadienes was non-stereospecific and afforded mixtures of erythro and

Table 1. Selenosulfonation of 1,3-dienes[a]

Entry	Diene	Reaction cond.	% Yield[b]	Product(s)[c]
1		20°C, 14 h	~100[d]	
2		0°C, 22 h	57	
3		20°C, 41 h	69	
4		0°C, 56 h	60	
				(27%)[e,f] (27%)[e,f] (45%)[e] [E/Z: 2.5]
5		0°C, 21 h	100	
6		20°C, 66 h	60	
7		20°C, 21 h	48	 [1/4][g]
8		-20°C, 21 h	80	[1/1][g]
9		20°C, 24 h	96[h]	[1/1][g]
10		20°C, 21 h	66	 [1/2][g]
11		0°C, 22 h	72	[1/1.5][g]
12		20°C, 66 h	61	

a. Unless otherwise noted the selenosulfonation was performed in methylene chloride using the diene and $PhSeSO_2Ph$ in a 1:1 ratio. b. Isolated yields after flash chromatography unless otherwise noted. c.The products were homogeneous by TLC and HPLC and were characterized by IR, ^1H NMR and ^{13}C NMR. d.The crude product was pure enough and needed no further purification. Attempted column chromatography led to decomposition of the product. e. From ^1H NMR (300 MHz). f. From ^{13}C NMR (75 MHz). g. Erythro/threo ratio as determined from ^1H NMR. h. A five-fold excess of diene was used.

Table 2. Tandem selenosulfonation - oxidation of 1,3 - dienes[a]

Entry	Diene	Reaction cond.[b]	% Yield[c]	Product(s)[d]
1		0°C, 22.5 h	75[e]	
2		RT, 19 h	100[e, g]	
3		RT, 17.5 h	100[e]	
4		RT, 17 h	68[h]	
5		RT, 17 h	49[h]	 [E / Z : 4/1][i]
6		RT, 17 h	89[e]	

a. Unless otherwise noted the selenosulfonation-oxidation seqence was performed in methylene chloride using diene: $PhSeSO_2Ph$: m-CPBA in a 1:1:2.5 mol ratio. b. Reaction time refers to the selenosulfonation step. The reaction time for the m-CPBA oxidation step was 15 min in all cases. c. Isolated yields. d.The products were homogeneous by TLC and HPLC and were characterized by IR, ^1H NMR and ^{13}C NMR. e.The crude product was chemically pure as determined by ^1H NMR and ^{13}C NMR and needed no further purification. f. Characterized according to ref. 3. g.The product was isolated and characterized as its dimethylamine adduct (cf. ref. 3). h. Isolated yield after flash chromatography. i. From ^1H NMR. Refers to the 2,3-double bond.

threo isomers.[11] For both (E,E)- and (E,Z)-2,4-hexadiene the threo isomer predominated if the reaction was run at room temperature. Cyclopentadiene, 1,3-cyclooctadiene and 2,5-dimethyl-2,4-hexadiene failed to give a selenosulfonation under the reaction conditions employed.

The desired 2-(phenylsulfonyl)-1,3-dienes are available by the oxidation of the selenosulfones in Table 1. Since the yield for several of the selenosulfones dropped significantly during the work up and purification, we tried to develop a "one-pot" procedure for the synthesis of the sulfonyldienes. The reaction mixture obtained from the usual selenosulfonation was therefore treated with m-chloroperbenzoic acid (m-CPBA) without prior isolation of the selenosulfone. The results given in Table 2 show that this "one-pot" procedure was succesful and afforded the 2-(phenylsulfonyl)-1,3-dienes in good yield.

In all cases the yield of sulfonyldiene was higher than or equal to the corresponding isolated yield of selenosulfone.

The procedure described in Table 2 seems to be a synthetically useful method for the preparation of 2-(phenylsulfonyl)-1,3-dienes. It is more general in its regioselectivity compared to the previous method based on sulfonylmercuration.[2] For example, the previous procedure afforded mixtures of regioisomers for 2,4-hexadiene and 1,3-cycloheptadiene, whereas the present procedure gives highly regioselective reactions for these dienes.

Tandem selenosulfonation-oxidation of 1,3-dienes. General procedure (Table 2). To a solution of the appropriate diene (1 mmol) and $PhSO_2SePh$[9] (1 mmol) in methylene chloride (10 ml) was added a drop of boron trifluoride etherate. The reaction mixture was stirred at room temperature for 17-19 h (see Table 2). A solution of m-chloroperbenzoic acid (2,5 mmol) in methylene chloride was added and the resulting mixture was stirred for 15 min. The organic phase was washed with a 5 % aqueous solution of Na_2CO_3 (3 x 5 ml) and dried ($MgSO_4$). Evaporation of the solvent on a rotary evaporator afforded the 2-(phenylsulfonyl-1,3-diene, which in most cases was pure and needed no further purification.

Acknowledgments. Financial support from the Swedish Natural Science Research Council and the University of Oviedo (for the stay of C.N.) is gratefully acknowledged.

References and Notes

1. Present address: Departamento de Quimica Organometalica, Faculdad de Quimica, Universidad de Oviedo, 33071 Oviedo, Spain.
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4. J.E. Bäckvall and S.K. Juntunen, submitted for publication.
5. T. Cuvigny, C. Hervée du Penhoat, and M. Julia, Tetrahedron, 42, 5329 (1986).
6. (a) Acyclic 1,4-disubstituted 2-phenylsulfonyl-1,3-dienes have been prepared by condensation of an allylic sulfone with an aldehyde and subsequent acetylation elimination.[5] 2-(Arylsulfonyl)-1,3-dienes were generated in situ at high temperature from 3-(arylsulfonyl)-3-sulfolene.[6b] (b) K. Inomata, H. Kinoshita, H. Takemoto, Y. Murata, and H. Kotak, Bull. Chem. Soc. Jpn., 51, 3341 (1978).
7. (a) T.G. Back and S. Collins, Tetrahedron Lett., 21, 2215 (1980). (b) T.G. Back and S. Collins, J. Org. Chem., 40, 3249 (1981).
8. Y.H. Kang and J.L. Kice, J. Org. Chem., 49, 1507 (1984).
9. Prepared according to: T.G. Back and S. Collins, Tetrahedron Lett., 21, 2213 (1980).
10. A trans selenosulfonation of double bonds was observed by Back and Collins.[7]
11. (a) The stereochemical assignment was based on the vicinal proton coupling constants $J_{2,3}$: $(J_{2,3})_{erythro}$ = 6.3 Hz, $(J_{2,3})_{threo}$ = 2.1 Hz. These coupling constants are consistent with a conformation having the $PhSO_2$- and PhSe-groups anti to each other. The assignment made was confirmed by the selenoxide-elimination to diene, which is known to proceed syn.[11b] (b) K.B. Sharpless, M.W. Young, and R.F. Lauer, Tetrahedron Lett., 1979 (1973).

(Received in UK 22 December 1987)