

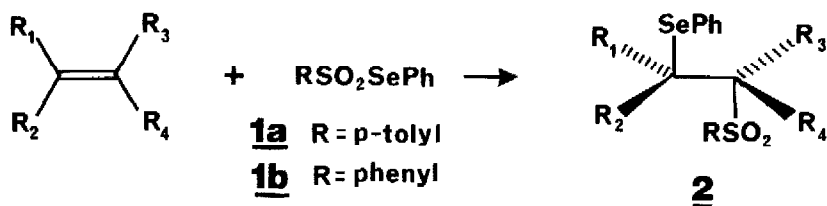
"SELENOSULFONATION" THE ADDITION
OF SELENOLSULFONATES TO OLEFINS

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Abstract The reaction of phenyl areneselenolsulfonates with unhindered olefins affords β -phenylselenosulfone adducts, usually with high regio- and stereoselectivity

There is much current interest in the additions of selenenyl halides and pseudohalides to alkenes¹. Apart from being mechanistically intriguing, such reactions are of considerable synthetic value as the incorporation of selenium-containing residues into unsaturated systems permits their further functionalization by a variety of methods². To our knowledge, selenolsulfonates 1 have never been studied in this context.

We have found that selenolsulfonates 1a and 1b³ react with a variety of unhindered olefins to afford novel β -phenylselenosulfones 2, often in a highly regio- and stereoselective fashion. This process permits the simultaneous introduction of a phenylseleno group and a sulfonyl moiety into the substrate, it is depicted below.



This "selenosulfonation" reaction is conveniently performed by treatment of the olefin with an equimolar amount of 1a or 1b in dichloromethane solution at room temperature in the presence of a catalytic amount of boron trifluoride etherate. The addition may also be effected in the

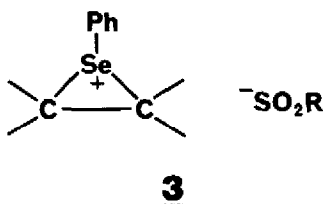
absence of catalyst by refluxing the reactants in chloroform or benzene, or by heating them neat in a sealed glass tube. The products were isolated by preparative tlc on silica-gel and are listed in the Table along with conditions and physical data.

The boron trifluoride - catalyzed reaction of styrene with 1a provided the Markovnikoff adduct 2a exclusively while similar treatment of methyl 10 - undecenoate with either 1a or 1b gave 2c and 2d as *ca.* 2:1 mixtures (nmr) of the two regioisomers which could not be separated. Markovnikoff addition provided the major product in both cases. Furthermore, the addition of 1a to cyclohexene (catalyzed by boron trifluoride) and to indene (uncatalyzed) afforded solely the *trans* adducts 2e⁴ and 2f⁵ respectively.

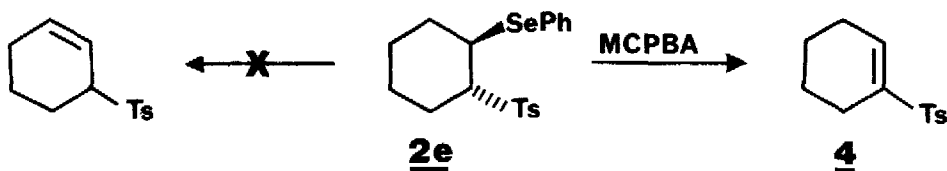
The uncatalyzed selenosulfonation of styrene and of allyl phenyl ether with 1a and 1b respectively provided the anti-Markovnikoff adducts 2b and 2g in good yield. The corresponding Markovnikoff products were not observed (tlc, nmr). Treatment of 2b with a trace of boron trifluoride etherate in dichloromethane at room temperature failed to produce its regioisomer 2a.

The addition of 1a to *trans*-5-decene was best effected in the absence of catalyst and solvent and provided a 9:1 mixture (gc) of two stereoisomers. The major product was assumed to form *via anti* addition and was separated from its counterpart by crystallization. More hindered olefins failed to form adducts with 1a or 1b.

Clear conclusions regarding the mechanism of selenosulfonation await further study. However, the intermediacy of seleniranium ions 3 would account for the observed stereochemistry⁶. At higher temperatures, product formation could also conceivably arise through a free-radical mechanism.



β -Phenylselenosulfones 2 cleanly undergo selenoxide elimination towards the activated hydrogen to afford vinyl sulfones⁷. For example, oxidation of 2e with excess *m*-chloroperbenzoic acid in chloroform at room temperature gave an immediate exothermic reaction which furnished the known⁸ sulfone 4 in 92% yield.



The mechanism and synthetic utility of selenosulfonation as a method for elaborating olefins *via* the above and other procedures are under continued investigation in this laboratory.

Table
Selenosulfonation of Olefins

| <u>Olefin</u> | <u>Selenol-sulfonate</u> | <u>Product^a</u> | <u>Structure^b</u> | <u>Conditions^c (time, h)</u> | <u>Isolated Yield (%)</u> | <u>m.p.</u> |
|------------------------|--------------------------|----------------------------|------------------------------|---|-------------------------------|-------------|
| Styrene | 1a | 2a | | A (20) | 86 | 159° |
| Styrene | 1a | 2b | | B (24) | 93 | 157-158° |
| Methyl 10-undecenoate | 1a | 2c | | A (24) | 75 | oil |
| Methyl 10-undecenoate | 1b | 2d | | A (24) | 72 | oil |
| Cyclohexene | 1a | 2e | | A (18) | 89 | 58-59° |
| Indene | 1a | 2f | | B (72) | 81 | 90-91° |
| Allyl phenyl ether | 1b | 2g | | C (67) | 72 | 94-95° |
| <i>trans</i> -5-Decene | 1a | 2h | | D (21) | 42 | 79-80° |

(a) All products were identified by their ¹H and ¹³C nmr and by their ir and mass spectra. All solids gave correct combustion analyses, products **2c** and **2d** gave exact mass measurements in close agreement with calculated values. (b) R = (CH₂)₈CO₂CH₃. (c) A: CH₂Cl₂, room temperature, BF₃·Et₂O catalyst. B: CHCl₃, reflux. C: C₆H₆, reflux. D: sealed glass tube, 75°.

Acknowledgement

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References and Notes

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- 2 For reviews, see (a) H J Reich, Acc Chem Res, 12, 22, (1979). (b) D.L.J. Clive, Tetrahedron, 34, 1049, (1978)
- 3 Compounds 1a and 1b were prepared from the corresponding sulfonylhydrazides See T G. Back and S Collins, preceding paper
- 4 The ¹H nmr spectrum of 2e showed signals at δ (CDCl₃) 3.14 (crude q, 1H) and 3.86 (crude q, 1H) Although the nmr spectrum does not permit unambiguous stereochemical assignment, the facile selenoxide elimination to form the vinyl sulfone 4 is most consistent with a *trans* diequatorial structure
- 5 The ¹H nmr spectrum of 2f showed signals at δ (CDCl₃) 3.2 (m, 2H), 3.8 (m, 1H) and 5.07 (d, J = 2Hz, 1H) Compound 2f also readily underwent oxidation and elimination to afford the corresponding vinyl sulfone The *cis* structure would provide an unfavourable transition state for *syn* elimination in the observed direction
- 6 The addition of selenenyl halides and pseudohalides to olefins generally proceeds *via anti* addition For an interesting exception, see D G. Garratt, Can J. Chem, 57, 2180, (1979).
- 7 Vinyl sulfones are themselves useful synthetic intermediates For recent examples, see (a) J J Eisch and J E Galle, J Org Chem., 44, 3277, (1979). (b) *ibid*, p 3279. (c) P D Magnus, Tetrahedron, 33, 2019, (1977) (d) W E Truce, T.C. Klingler and W W Brand in "Organic Chemistry of Sulfur", Ed S Oae, Ch 10, p 582-584, Plenum Press, New York, 1977.
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