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A GENERAL SYNTHESIS OF ALLENIC SULFONES FROM ACETYLENES USING SELENOSULFONATION

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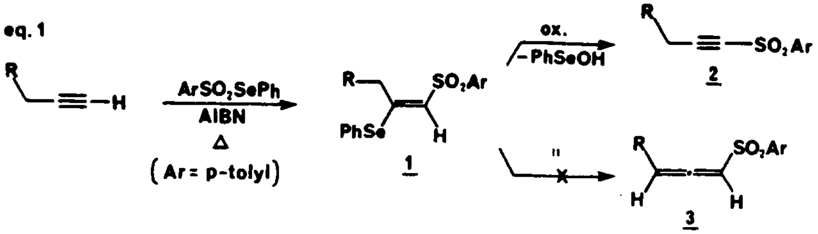
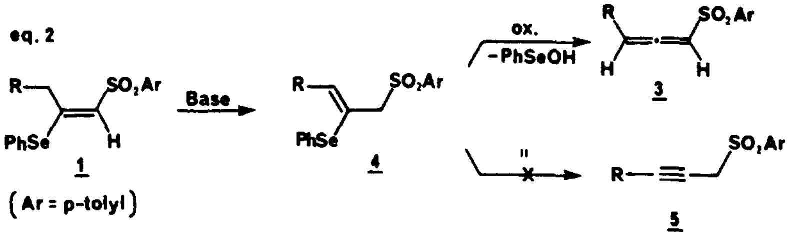
Abstract: Terminal acetylenes were converted to 1- and 3-substituted allenic sulfones via selenosulfonation, deprotonation, alkylation and selenoxide elimination.

The free-radical selenosulfonation of acetylenes[1] provides β-(phenylseleno)vinyl sulfones 1 in a regio- and stereoselective manner. These compounds in turn serve as precursors of a host of useful products[1,2], including acetylenic sulfones 2, by selenoxide elimination (equation 1). It is interesting to note that the competing formation of allenic sulfones 3 is generally not observed when 1 contains a vinylic hydrogen atom[1b] (i.e. 1 is derived from a terminal acetylene). Since allenic sulfones are of growing synthetic importance, especially as dienophiles[3] and dipolarophiles[4] in cycloaddition reactions, we endeavoured to find an alternative protocol to that shown in equation 1, which would permit their selective formation instead of the observed acetylenic sulfones.

eq. 1



We now report that the selenosulfonation products 1 isomerize readily and nearly quantitatively to the corresponding allylic sulfones 4 under base-catalyzed conditions.[5] In contrast to the original adducts 1, compounds 4 undergo oxidation and selenoxide elimination to afford the desired allenic sulfones 3 (equation 2), in generally excellent yield (Table 1).



In several instances the isomerization step was completed simply by refluxing the adduct 1 with triethylamine in chloroform. More resistant cases succumbed to treatment with stronger bases such as potassium t-butoxide or LDA in THF at -78°. The highly regioselective selenoxide elimination to afford allenes 3 may be due either to the Z-geometry[6] in compounds 4, where the trans orientation of the vinylic hydrogen atom and the selenium residue precludes syn-elimination to 5, or alternatively, to the acidifying effect of the sulfone moiety upon the allylic hydrogen atoms, which favours the formation of 3. In one exceptional case, the oxidation of 4b afforded mixtures of the allenic and acetylenic sulfones 3b and 5b, whose ratio depended upon the precise experimental conditions. The highest proportion of 3b (3b:5b = 78:22) was obtained with t-butyl hydroperoxide[7] in chloroform. The use of m-chloroperbenzoic acid or hydrogen peroxide as the oxidant resulted in larger amounts of the acetylene 5b, which was also favoured by prolonged reaction times or the inclusion of an amine during the elimination step[8]. Control experiments revealed that the allene 3b readily isomerizes to the acetylene 5b under these

Table 1. Preparation of 3-Substituted Allenic Sulfones 3[a]

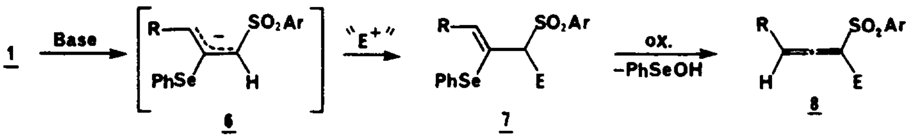
Starting material	Base	Oxidation-elimination method	Product	Isolated yield (%)
1a R = H	LDA-THF, -78° 5 min	MCPBA-$CHCl_3$, reflux 1.5 h	3a	92
1b R = n-C_7H_{15}	KOt-Bu-THF, -78°, 1.5 h	t-BuOOH-$CHCl_3$, R.T., 24 h	3b	73[b]
1c R = Cl	Et_3N-$CHCl_3$, reflux 3 h	MCPBA-$CHCl_3$, reflux 1 h	3c	98
1d R = $CH_2OC(=O)Ph$	Et_3N-$CHCl_3$, reflux 3 h	MCPBA-$CHCl_3$, reflux 1 h	3d	93

a) All products were consistent with their IR, NMR and mass spectra. All new compounds gave satisfactory elemental analyses.
b) The product was obtained as a 78:22 mixture of 3b and 5b in 93% yield.

conditions, suggesting that the allene is the initial kinetic product and that the acetylene is produced from its subsequent isomerization, and not directly from the selenoxide 4b. Similar isomerizations were not observed in the other examples in Table 1.

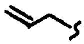
Since the base-catalyzed transformation of 1 to 4 presumably proceeds via the anion 6, it seemed reasonable that this intermediate could be alkylated prior to oxidation-elimination. This would permit the introduction of an additional substituent into the 1-position of the product allenic sulfone 8 (equation 3).

eq. 3



We have found that reactive electrophiles such as methyl iodide, allyl iodide and trimethylsilyl chloride afforded the corresponding alkylated products 7, which either eliminated spontaneously in situ or were oxidized with MCPBA to afford the allenic sulfones 8 in one step from adducts 1. The results are shown in Table 2.

Table 2. Preparation of 1,3-Disubstituted Allenic Sulfones[a] 8

Starting material	Electrophile	Method[b]	Product 8 E	Product 8 Isolated yield (%)
1a R = H	MeI	A	Me	53
1b R = n-C_7H_{15}	MeI	A	Me	80
1b R = n-C_7H_{15}		B		59
1b R = n-C_7H_{15}	Me_3SiCl	B	Me_3Si	82
1c R = Cl	D_2O	C	D	85

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a) All products were consistent with their IR, NMR and mass spectra. All new compounds gave satisfactory elemental analyses.

b) Method A: 1. LDA-THF, -78°; 2. E^+, -78°; 3. MCPBA-$CHCl_3$. Method B: 1. LDA-THF, -78°; 2. E^+; spontaneous elimination of PhSe group occurred. Method C: 1. Et_3N-D_2O-$CHCl_3$, reflux; 2. MCPBA-D_2O-$CHCl_3$, reflux.

In a typical procedure, adduct 1b (0.66 mmol) in THF was added via syringe to a solution of LDA (1.1 mmol) in THF at -78°C. After 10 min, methyl iodide (1.2 mmol) was added to the orange anion solution and after 15 min at -78°C, the reaction was quenched with water, warmed to room temperature, washed with brine, dried ($MgSO_4$) and evaporated in vacuo. The residue was treated with MCPBA (1.2 mmol) in chloroform for 5 min and then washed with 10% K_2CO_3 solution, dried ($MgSO_4$) and refluxed for 2 h. Preparative TLC (silica-gel, 20% ethyl acetate-hexane) afforded the allene 8 (E = Me, R = n-C_7H_{15}) as a pale yellow, distillable oil (Kugelrohr bp 120-125°C at 0.05 mm) in 80% yield. The product was identified by its IR, NMR and mass spectra, and gave a satisfactory elemental analysis (C,H,S).

The last example in Table 2 demonstrates that 1-deuterio sulfonyl allenes are also accessible by base-catalyzed exchange of 1 with D_2O, followed by oxidation-elimination in the usual manner.

In conclusion, variously 1- and 3-substituted allenic sulfones can be efficiently prepared from terminal acetylenes by selenosulfonation followed by the simple transformations shown in equations 2 and 3.

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References

1. a) T.G. Back, S. Collins and R.G. Kerr, J. Org. Chem., 48, 3077 (1983). b) T.G. Back, S. Collins, U. Gokhale and K.W. Law, ibid., 48, 4776 (1983). c) T. Miura and M. Kobayashi, J. Chem. Soc., Chem. Commun., 438 (1982).
2. a) T.G. Back, S. Collins and K.W. Law, Can. J. Chem., 63, 2313 (1985). b) T.G. Back, S. Collins and K.W. Law, Tetrahedron Lett., 25, 1689 (1984). c) T.G. Back, J.R. Proudfoot and C. Djerassi, ibid., 27, 2187 (1986).
3. a) I. Fujii, K. Ryu, K. Hayakawa and K. Kanematsu, J. Chem. Soc., Chem. Commun., 844 (1984). b) K. Hayakawa, H. Nishiyama and K. Kamematsu, J. Org. Chem., 50, 512 (1985). c) G. Barbarella, M. Cinquini and S. Colonna, J. Chem. Soc., Perkin Trans. 1, 1646 (1980). d) A.J. Guildford and R.W. Turner, J. Chem. Soc., Chem. Commun., 466 (1983). e) L. Veniard, J. Benaim and G. Pourcelot, C.R. Acad. Sc. Paris, Ser. C, 266, 1092 (1968).
4. a) A. Padwa, S.P. Carter, U. Chiacchio and D.N. Kline, Tetrahedron Lett., 27, 2683 (1986). b) L. Bruche, M.L. Gelmi and G. Zecchi, J. Org. Chem., 50, 3206 (1985). c) L. Veniard and G. Pourcelot, Bull. Soc. Chim. Fr., 2746 (1973).
5. The base-catalyzed isomerization of other vinyl sulfones to allyl sulfones has been previously reported: a) D.E. O'Connor and W.I. Lyness, J. Am. Chem. Soc., 86, 3840 (1964). b) V. Sváta, M. Procházka and V. Bakos, Coll. Czech. Chem. Commun., 43, 2619 (1978). c) E. Block and M. Aslam, J. Am. Chem. Soc., 105, 6164 (1983). Syn alkyl groups are more acidic than anti alkyl groups in vinyl sulfones: d) J.J. Eisch and J.E. Galle, J. Org. Chem., 44, 3279 (1979). e) E. Block, V. Eswarakrishnan and K. Gebreyes, Tetrahedron Lett., 25, 5469 (1984).
6. The products 4 were formed as nearly pure geometrical isomers which have arbitrarily been depicted with the Z-configuration.
7. T. Hori and K.B. Sharpless, J. Org. Chem., 43, 1689 (1978).
8. H.J. Reich, S. Wollowitz, J.E. Trend, F. Chow and D.F. Wendelborn, J. Org. Chem., 43, 1697 (1978).

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