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SELENOSULFONATION OF ALLENES

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Abstract—Se-Phenyl *p*-tolueneselenosulfonate (**1a**) undergoes highly regioselective, photoinitiated, free-radical addition to allenes ($R_1CH{=}C{=}CR_2R_3$) to afford the regioisomer $R_1CH(SePh)C(SO_2Ar){=}CR_2R_3$ (**13**) arising from addition of the *p*-tolylsulfonyl group to the central carbon of the allene and transfer of the phenylseleno group to the less highly substituted of the two terminal carbons. This regioselectivity, which contrasts with that observed in the majority of radical additions to allenes, can be explained by reference to concepts proposed by Heiba as being important in determining the orientation in different radical additions to allenes. Oxidation of the PhSe group in **13** to PhSe(O) gives allylic selenoxides that undergo a reaction sequence of facile, concerted, [2,3]-sigmatropic rearrangement followed by hydrolysis of the resulting selenenate to afford β-tolylsulfonyl-substituted allylic alcohols, $R_1CH{=}C(SO_2Ar)C(OH)R_2R_3$ (**14**) in 70–98% yield. Photoaddition of **1a** to allenes, followed by the conversion of **13** to **14** thus provides a simple, high-yield route to a wide variety of **14**, a class of compounds that would seem to have a number of interesting possible uses in synthesis.

During the past decade the discovery and development of a sizable array of useful synthetic transformations[1,2] have changed organoselenium chemistry from an esoteric subject into part of the mainstream of organic research. Among the organoselenium reactions of value in the elaboration of simple unsaturated functionalities are the additions of selenenyl halides and pseudohalides to olefins.[3] Most such additions involve heterolytic mechanisms and an electrophilic addition of the selenenylating agent to the carbon–carbon double bond.

Although first described in 1947,[4] Se-aryl areneselenosulfontates, $ArSeSO_2Ar'$, received no further significant attention until 1980. At that time two groups[5,6] discovered that Se-phenyl areneselenosulfontates (**1**), easily synthesized by the reaction of benzeneseleninic acid with either an arenesulfonhydrazide[5b] or an arenesulfinic acid,[6b] undergo facile *free-radical* 1,2-addition to alkenes to give β-phenylseleno sulfones (**2**) in excellent yield (eqn (1)).[7] The mechanism for eqn (1) was shown[5,6] to be the radical chain mechanism outlined in eqns (2a)–(2c).

$$\underset{\mathbf{1}}{PhSeSO_2Ar} + CH_2{=}CHR \xrightarrow[\text{or }\Delta]{h\nu} \underset{\mathbf{2}}{ArSO_2CH_2\underset{\displaystyle SePh}{\underset{|}{C}}HR} \tag{1}$$

$$PhSeSO_2Ar \xrightarrow[\text{or } h\nu]{\Delta} PhSe\cdot + ArSO_2\cdot \tag{2a}$$

$$ArSO_2\cdot + CH_2{=}CHR \longrightarrow \underset{\mathbf{3}}{ArSO_2CH_2\dot{C}HR} \tag{2b}$$

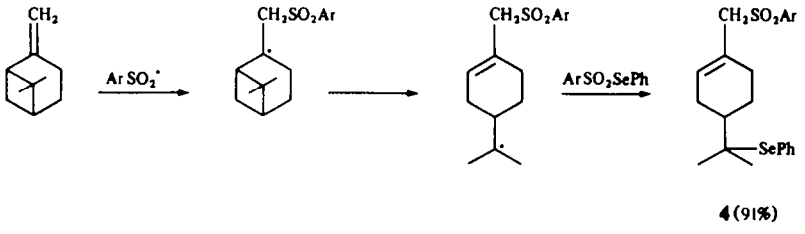
$$\underset{\mathbf{3}}{ArSO_2CH_2\dot{C}HR} + PhSeSO_2Ar \longrightarrow ArSO_2CH_2\underset{\displaystyle SePh}{\underset{|}{C}}HR + ArSO_2\cdot \tag{2c}$$

As would be expected from the behavior of other radical addition reactions, when the radical (**3**) resulting from addition of $ArSO_2\cdot$ to the olefin can undergo a rapid intramolecular reaction prior to reacting with **1**, free-radical addition of **1** can result in the formation of more varied products than the simple 1,2-adducts of eqn (1). With β-pinene, for example, the addition product is **4**;[8] this arises in the manner shown in eqn (3). With 1,5-cyclooctadiene (eqn (4)) transannular ring closure of the initial adduct radical competes effectively enough with its direct reaction with **1** so that free-radical addition of **1** to 1,5-cyclooctadiene results in the formation of roughly equal amounts of the bicyclo[3.3.0]octane derivative (**6**) and the simple 1,2-adduct (**5**).

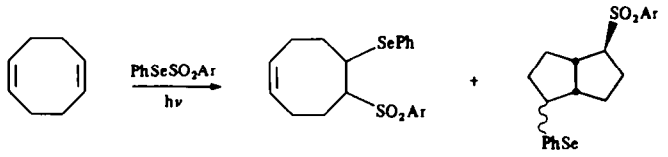
The synthetic value of all of these additions of **1** to alkenes, which Back and Collins[5] have named "selenosulfonations", lies in the fact that the phenylseleno group in the adduct can be oxidatively eliminated, by treatment either with *m*-chloroperbenzoic acid (MCPBA)[5] or hydrogen peroxide,[6] to afford unsaturated sulfones of utility for further synthetic transformations. Thus, oxidation of **2** (eqn (5)) gives selenoxides that undergo elimination[1a,b] of PhSeOH to give α,β-unsaturated sulfones (**7**), a class of compounds of established value in synthesis.

Several examples of the utilization in synthetic sequences of selenosulfonation followed by oxidative elimination of the PhSe group have recently appeared.[9]

Free-radical addition of **1** to acetylenes is also a facile



4 (91%) (3)



5 (39%) 6 (34%) (4)

$$ArSO_2CH_2\underset{\underset{SePh}{|}}{CHR} \xrightarrow[\text{or } H_2O_2]{MCPBA} \left[ArSO_2CH_2\underset{\underset{O=SePh}{|}}{CHR}\right] \xrightarrow{-PhSeOH} ArSO_2CH{=}CHR \qquad (5)$$

2 7

process, occurring regiospecifically and stereoselectively to afford the *E*-isomer of a *β*-(phenylseleno) vinyl sulfone (**8**) in high yield (eqn (6)).[10,11] The reaction proceeds by a radical chain mechanism analogous to that in eqn (2).

$$PhSeSO_2Ar + HC{\equiv}CR \xrightarrow{\Delta} \underset{H}{\overset{ArSO_2}{}}C{=}C\underset{SePh}{\overset{R}{}} \qquad (6)$$

8

The high stereoselectivity of the addition indicates that chain transfer of PhSe from **1** to the adduct vinyl radical, $ArSO_2\dot{C}H{=}CR$, must be faster than the rate of inversion of that radical. Since inversion of vinyl radicals is normally quite rapid, this is evidence of the high reactivity of **1** as a chain-transfer agent.

Oxidative elimination of the PhSe group from **8** occurs smoothly to afford a high-yield route to acetylenic sulfones (**9**), eqn (7); such sulfones, like **7**, are compounds of considerable synthetic interest and utility.

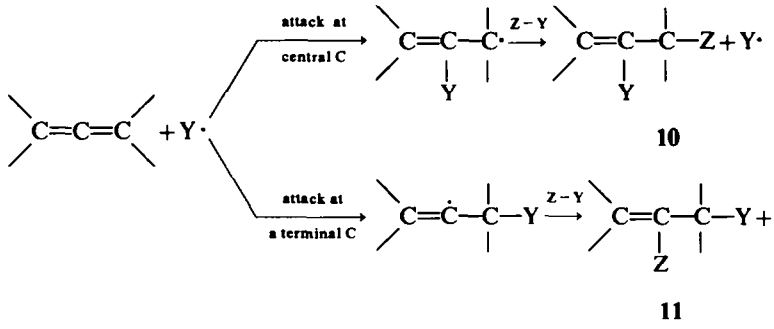
$$\underset{H}{\overset{ArSO_2}{}}C{=}C\underset{SePh}{\overset{R}{}} \xrightarrow{MCPBA} \underset{H}{\overset{ArSO_2}{}}C{=}C\underset{O=SePh}{\overset{R}{}} \xrightarrow[\text{or base}]{\Delta} ArSO_2C{\equiv}CR \qquad (7)$$

9

Like alkenes and alkynes, free-radical additions to allenes are also known.[12–17] This fact, and the ease of free radical addition of **1** to both alkenes and alkynes, suggested that 1,2-addition of **1** to allenes might also be possible. The probable regioselectivity of such an addition was uncertain, however, as will be evident from the considerations outlined in the following paragraph.

Addition of a free radical to an allene can occur either at the central or a terminal carbon of the allene system.[12] Some additions, such as that of Me_3SnH,[14] or of HBr in the gas phase,[13b] yield adducts (**10**, eqn (8)) resulting from initial radical attack on the central carbon, while a larger number, such as that of CF_3I,[15] RSH,[16,17a] $CH_3C(O)SH$,[16a] or HBr in the liquid phase,[17b] give adducts (**11**, eqn (9)) arising from initial radical addition to a terminal carbon. The observation that in the additions of HBr or PhSH there is a marked decrease in the ratio of **11** : **10** with decreasing [YZ] led Heiba and Haag[17] to suggest that central attack predominates only in those cases where addition of the radical to the terminal carbon is reversible and the concentration of the chain-transfer agent, YZ, is relatively low. Steric hindrance to attack at the terminal carbons can also increase the likelihood of attack on the central carbon.[14] However, it is also clear[12b] that there is not complete acceptance of the explanation in Ref. 17, nor sufficient agreement on the factors, and their relative importance, governing the site of radical attack on allenes that accurate *a priori* prediction of the regioselectivity or specificity can be made for any particular system.

The first objective of the present study[18] was to determine whether or not free radical addition of **1** to allenes would occur, and, if so, its regioselectivity. The adducts were anticipated to be of potential synthetic interest regardless of the regioselectivity of the addition. Thus, if the addition were to follow the course in eqn (9) the adduct **11** (Y = $ArSO_2$, Z = PhSe) upon oxidation should give a selenoxide that would under-



(8)

(9)

go elimination to afford an allenic sulfone (). On the other hand, if the addition were to take the course shown in eqn (8), the adduct **10** (Y = $ArSO_2$, Z = PhSe) would give an allylic selenoxide when oxidized. This might be expected to undergo a [2,3]-sigmatropic rearrangement to a selenenate. Hydrolysis of the latter would then afford a β-arylsulfonyl-substituted allylic alcohol, an interesting class of compound not readily synthesized by other means.

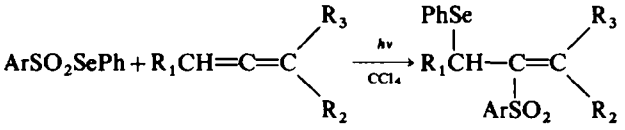
RESULTS AND DISCUSSION

Photoaddition of **1a** *to allenes*

Photoaddition of Se-phenyl *p*-tolueneselenosulfonate (**1a**, Ar = *p*-$CH_3C_6H_4$) to five different substituted allenes: $Me_2C{=}C{=}CH_2$ (**12a**), $Me_2C{=}C{=}CHMe$ (**12b**), n-$C_5H_{11}CH{=}C{=}CH_2$ (**12c**), $PhCH{=}C{=}CH_2$ (**12d**), and $Et(Me)C{=}C{=}CH_2$ (**12e**), has been investigated. In each instance irradiation of a degassed carbon tetrachloride solution of **1a** (1.0 M) and the allene (1.5 M) leads to the formation in >95% yield of a 1 : 1 adduct of **1a** and the allene. The ^{1}H-NMR spectra of the crude adducts show that one regioisomer constitutes over 90% of the product in each case, and that addition has taken place across the *less highly substituted* of the two double bonds in the allene. While these spectra are consistent in every instance with a structure for the adduct where it is the $ArSO_2$ group that is bonded to the central carbon of the original allenic system, completely unequivocal proof that this is the regioisomer formed is not possible from the ^{1}H-NMR spectra. Such proof is available, however, from oxidation of the PhSe group of the adduct and identification of the decomposition products of the resulting selenoxide. These oxidation experiments, which are described in detail in a subsequent section, establish that photoaddition of **1a** gives the regioisomer (**13**) arising from addition of the arylsulfonyl group of the selenosulfonate to the central carbon of each allene and transfer of the phenylseleno group to the less highly substituted of the two terminal carbons (eqn (10)).

Note that the regiospecificity of the free-radical addition of **1a** to allenes is exactly the opposite of that found[3g] for the electrophilic addition of benzeneselenenyl chloride (PhSeCl) to the same substrates. In that reaction the phenylseleno moiety becomes attached to the *central* carbon of the allene.

The olefinic proton resonance in α,β-unsaturated sulfones $ArSO_2C{=}CH{-}$ is normally found 0.5–1.0 ppm further downfield in the geometric isomer where the arylsulfonyl group and the hydrogen are *cis* than in the isomer where they are *trans*.[19] Thus, with $ArSO_2CH_a{=}CH_bBu\text{-}n$ H_b in the *E*-isomer is at δ 7.0, while in the *Z*-isomer it is at δ 6.4; for $ArSO_2CH_a{=}CH_bPh$ the signal for H_b is at δ 7.99 in the *E*-isomer and at δ 7.4 in the *Z*-isomer. In the adduct formed from **1a** and **12c** the only olefinic proton resonance is a triplet centered at δ 6.90. This indicates that photoaddition of **1a** to 1,2-nonadiene apparently gives almost exclusively (*E*)-**13c**, the amount of the *Z*-isomer formed being too little to give rise to a detectable signal for its olefinic proton. Similarly, the photoaddition of **1a** to **12d** also gives primarily (*E*)-**13d**,



(10)

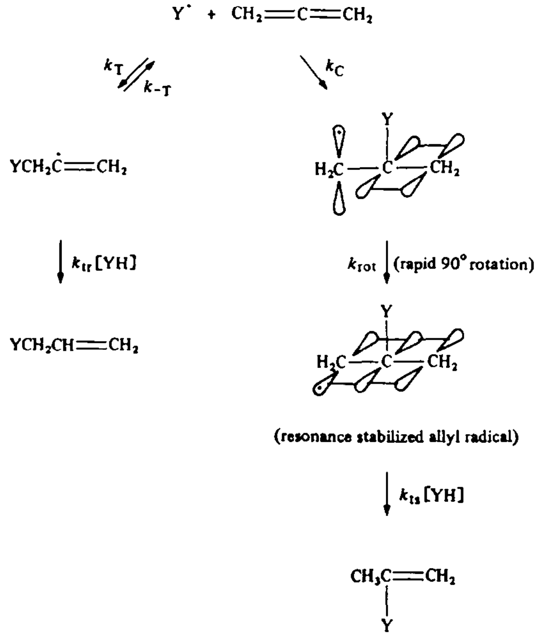
1a, Ar = *p*-tolyl

12

	R_1	R_2	R_3
a	H	CH_3	CH_3
b	CH_3	CH_3	CH_3
c	H	H	n-C_5H_{11}
d	H	H	Ph
e	H	CH_3	CH_3CH_2

13

	R_1	R_2	R_3
a	H	CH_3	CH_3
b	CH_3	CH_3	CH_3
c	H	H	n-C_5H_{11}
d	H	H	Ph
e	H	CH_3	CH_3CH_2



Scheme 1. Proposed[17] mechanism for radical additions of thiophenol (Y = PhS) and hydrogen bromide (Y = Br) to allene.

as evidenced by the fact that the olefinic proton in the adduct is a singlet at δ 7.85.[20]

In contrast to the situation with the adducts formed from **12c** and **12d**, that from **12e** is a mixture of (*E*)- and (*Z*)-**13e**, in approximately equal proportions. This is deduced from the ^{1}H-NMR which shows two singlets of approximately equal intensity at δ 4.07 and 4.01 for the CH_2Se groups of the two different isomers.[21]

The strong preference for the $ArSO_2\cdot$ radical from **1a** to become bonded to the central, rather than to a terminal carbon of the different allenes is in contrast to the regioselectivity more commonly observed[12] in free radical additions to allenes. It can, however, be rationalized by reference to the ideas developed by Heiba and Haag[17] to explain the origin of the regioselectivity, and its variation with reaction conditions, in the radical additions of HBr and thiophenol to allene in solution.

Heiba[17a] found that *above* [PhSH] = 2.5 M the ratio of products from terminal vs central attack was constant and favored the regioisomer resulting from terminal attack by a factor of about three to one. *Below* [PhSH] $\cong$ 1.5 M the ratio of the terminal to the central carbon adduct decreased linearly with decreasing [PhSH], with the regioisomer arising from attack at the central carbon becoming the principal product at [PhSH] $\leqslant$ 0.5 M. Generally analogous results were found[17b] for the addition of HBr to allene in pentane solution. Heiba and Haag[17] explained these results by the mechanism shown in Scheme 1.

Addition of both thiyl radicals and bromine atoms to carbon–carbon double bonds is known to be reversible, and the vinyl radical formed by attack at the terminal carbon in Scheme 1 undergoes loss of Y· (step k_{-T}) at a rate that is sufficiently rapid to be faster than its rate of chain transfer with Y-H (step k_{tr}) when [YH] $\leqslant$ 1.5 M. Addition of Y· to the central carbon is *not* reversible, however, because the initially formed radical immediately undergoes a rotation of 90° about the C—C axis (step k_{rot}) to give a resonance-stabilized allyl radical, a process that is highly exothermic. The stability of the allyl radical compared to the initial adduct radical means that loss of Y· from $\cdot CH_2C(Y){=}CH_2$ is energetically too unfavorable to be important, and so every $\cdot CH_2C(Y){=}CH_2$ radical formed goes on to product (step k_{ts}). At high concentrations of Y-H where $k_{tr}[YH] > k_{-T}$ the ratio of products from terminal vs central attack is equal to k_T/k_C; at low [YH] where $k_{tr}[YH] < k_{-T}$ it is equal to $k_T k_{tr}[YH]/k_C k_{-T}$, and at low enough concentrations of YH the regioisomer resulting from initial attack at the central carbon becomes virtually the exclusive product.

Addition of arylsulfonyl radicals to carbon–carbon double bonds is also easily reversible.[22] The fact that heating selenosulfonation adduct **2** (R = Ph) in toluene with R_3SnH (an excellent chain transfer agent) leads,[5b] not to $ArSO_2CH_2CH_2Ph$, but rather to styrene, shows that loss of $ArSO_2\cdot$ from $ArSO_2CH_2\dot{C}HPh$ must be quite rapid indeed, and it suggests that the rate constant (k'_{-T}) for the process:

$$ArSO_2CH_2\dot{C}{=}C\!< \xrightarrow{k'_{-T}} ArSO_2\cdot + CH_2{=}C{=}C\!<$$

might well be significantly faster than k_{-T} for loss of $C_6H_5S\cdot$ in Scheme 1.

Based on the difference in the ratio of nortricyclyl to norbornenyl adducts in the free radical additions of **1a**[6b] and ArSH[23] to norbornadiene, **1a** is somewhat less reactive than an aryl thiol as a chain-transfer agent. Thus it also appears reasonable to believe that the rate constant (k'_{tr}) for the transfer reaction:

$$\mathbf{1a} + ArSO_2CH_2\dot{C}{=}C\!< \xrightarrow{k'_{tr}} ArSO_2\cdot + ArSO_2CH_2C(SePh){=}C\!<$$

will be smaller than k_{tr} for C_6H_5SH in Scheme 1.

From these considerations it seems entirely possible that (k'_{tr}/k'_{-T}) will be sufficiently smaller than (k_{tr}/k_{-T}) so that in the addition of **1a** to allenes the regioisomer resulting from initial radical attack on the central carbon will be the almost exclusive product even when the concentration of **1a** is as high as 1 M, in accord with our experimental observations.

This explanation for the initially somewhat unexpected regioselectivity of the **1a**-allene additions predicts that at considerably higher **1a** concentrations formation of the regioisomer resulting from initial attack of $ArSO_2\cdot$ on the less-substituted terminal carbon should become competitive with the formation of **13**. Limitations on the solubility of **1a**, however, prevent exploration of this domain.[24]

Although photoaddition of **1a** to all of the

substituted allenes in eqn (10) proceeds in high yield, irradiation at room temp of a degassed sealed tube containing **1a** (1.0 M) and allene (1.5 M) in carbon tetrachloride results in the formation of only the products associated[6b] with the photodecomposition of **1a** in CCl_4 in the absence of olefins. Given the success of the photoaddition of **1a** to substituted allenes, the failure to obtain an adduct from allene itself under these conditions is undoubtedly due to the fact that, as a result of its low boiling point (−35°), all of the 1,2-alkadiene is in the vapor phase at room temp, with virtually none being present in the carbon tetrachloride solution where the selenosulfonate is undergoing photodecomposition.

Oxidation of **1a**-*allene adducts* (**13**)

Treatment of **13a** with excess 30% hydrogen peroxide at −20°, followed by addition of triethylamine and warming of the solution to room temp, results in the loss of the PhSe group and the formation (in 75% yield) of a compound whose ^{1}H-NMR spectrum

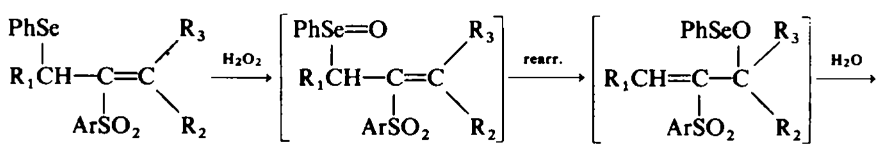
$(CH_2{=}C\langle$, pair of doublets, δ 6.25 and 6.01, J = 1.5 Hz; —OH, δ 3.20; p-$CH_3C_6H_4SO_2$, AA′BB′ pattern δ 8.0–7.12 and singlet at δ 2.42; $(CH_3)_2\overset{|}{C}$—OH, 6H singlet at δ 1.46) and IR spectrum (—OH, 3440 cm^{-1}; SO_2, 1284 and 1115 cm^{-1}) show clearly that it is 2-methyl-3-(p-tolylsulfonyl)-3-buten-2-ol (**14a**). Oxidation of the other **1a** allene adducts (**13b–e**) proceeds in an analogous fashion, giving in each case the β-arylsulfonyl-substituted allylic alcohol that results from the reaction sequence (eqn (11)) of oxidation of the PhSe group in **13** to a selenoxide, followed first by a [2,3]-sigmatropic rearrangement of the allylic selenoxide, and then by hydrolysis of the resulting selenenate. Note that rearrangement of the allylic selenoxide takes place even in a case (**13b**, $R_1 = CH_3$) where elimination of PhSeOH is also possible. That rearrangement should occur in preference to elimination is not surprising, given the facility with which [2,3]-sigmatropic rearrangement of allylic selenoxides is known to take place.[25]

As noted earlier, the fact that oxidation of **13** with hydrogen peroxide leads to **14**, rather than to the isomeric allenic sulfones, $R_1(ArSO_2)C{=}C{=}CR_2R_3$, provides conclusive proof that free radical addition of **1a** to allenes occurs with the regiospecificity shown in eqn (10).

In the ^{1}H-NMR of **14b** the only signal in the olefinic proton region is a single quartet (J = 7 Hz) centered at δ 6.45. This indicates that oxidation of **13b** and subsequent rearrangement results in the formation of only one of the two possible geometric isomers of **14b**. From the chemical shift of the olefinic proton it is not possible to be absolutely certain whether this is the E- or Z-isomer, although based on the chemical shifts of δ 6.4 and 7.0 for H_b in (Z)- and (E)-$ArSO_2CH_a{=}CH_bBu$-n,[19] respectively, it would appear that it is the Z-isomer. Formation of (Z)-**14b** from **13b** would be consistent with the stereospecificity reported by Sharpless and Lauer[25c] for the rearrangement of the selenoxide derived from 2-methyl-3-(phenylseleno)-1-octene.

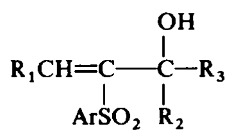
The regiospecificity of the photoaddition of **1** to allenes, and resulting nearly quantitative yields of **13**, combined with the smooth conversion of **13** to **14**, mean that a facile, two-step synthesis (eqn (12)) of a wide variety of β-arylsulfonyl-substituted allylic alcohols from the corresponding allenes is now available. Although another route, starting from aryl α-chloro-β-trimethylsilylethyl sulfones, to some of these compounds has recently been reported,[26] the selenosulfonation pathway in eqn (12) would seem to be considerably simpler and of wider utility.

Compounds with the structure **14** offer interesting chemical possibilities. They are, (1) α,β-unsaturated sulfones, a class of compounds whose synthetic utility has been alluded to earlier in the paper and (2) allylic



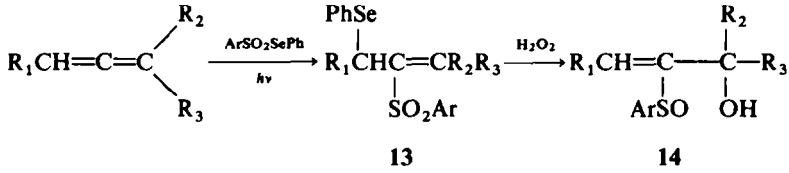
13

	R_1	R_2	R_3
a	H	CH_3	CH_3
b	CH_3	CH_3	CH_3
c	H	H	n-C_5H_{11}
d	H	H	Ph
e	H	CH_3	CH_3CH_2



14 (11)

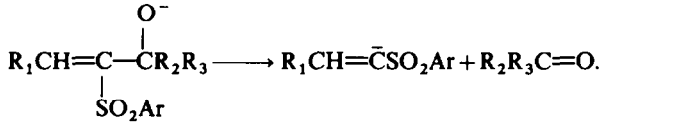
	R_1	R_2	R_3	
a	H	CH_3	CH_3	(75%)
b	CH_3	CH_3	CH_3	(98%)
c	H	H	n-C_5H_{11}	(92%)
d	H	H	Ph	(70%)
e	H	CH_3	CH_3CH_2	(92%)



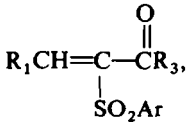
(12)

13 14

alcohols, albeit ones where the presence of the strong electron-withdrawing group ($ArSO_2$) on the β-carbon of the allyl system might cause their reactivity to be significantly different than that normally associated with allylic alcohols. The presence of the arylsulfonyl group might also make the alkoxide ion from the alcohol prone to undergo the cleavage reaction:



In those **14** where R_2 = H oxidation of the secondary alcohol to a ketone will give a compound, where the presence of two strong electron-withdrawing groups on the α-carbon should render the carbon–carbon double bond extremely reactive toward even quite



weak nucleophiles. We hope that the ease with which **14** can now be prepared via eqn (12) will encourage exploration of the possibilities outlined above.

EXPERIMENTAL

Materials

3-Methyl-1,2-butadiene (Aldrich) and 2-methyl-2,3-pentadiene (Fluka) were used without further purification. 3-Methyl-1,2-pentadiene (ICN Pharmaceuticals, Inc.) was purified by preparative gas chromatography (SE-30 column at 50°). Nona-1,2-diene and 1-phenyl-1,2-propadiene were prepared by published procedures[27,28] and their purity was determined to be >99% by capillary gas chromatography (SE-30 column, 200–250°, 4°/min). Se-Phenyl *p*-toueneselenosulfonate (**1a**), m.p. 76–78°, was prepared and purified as described by Gancarz and Kice.[6b] All solvents were reagent grade and were dried over molecular sieves and redistilled prior to use.

Photoaddition of **1a** *to allenes*

General procedure. Selenosulfonate **1a** (0.312 g, 1 mmol) and the allene (1.5 mmol) were dissolved in 1 ml of degassed carbon tetrachloride and the soln was irradiated in a closed Pyrex vessel under nitrogen until TLC showed that no **1a** remained (≤2.5 hr for all allenes except 1-phenyl-1,2-propadiene, where 3.0 hr was required). The excess allene and the solvent were then removed under reduced pressure. In each case the residue consisted of an essentially quantitative yield of a 1 : 1 adduct of the allene and the selenosulfonate.

3-Methyl-1,2-butadiene. The residue, an oil which TLC analysis indicated was a single compound, was 1-(phenylseleno)-2-(*p*-tolylsulfonyl)-3-methyl-2-butene (**13a**), 0.38 g (100%): IR (neat) 3040, 2900, 1615, 1590, 1570, 1470, 1430, 1305, 1295 (s, SO_2), 1135 (s, SO_2), 1080, 1020, 810, 780, 735, 685 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 8.1–7.0 (m, 9H), 4.05 (s, 2H, $C\underline{H}_2SePh$), 2.40 (s, 3H, $C\underline{H}_3C_6H_4$), 2.02 (s, 3H, $C\underline{H}_3C$=), 1.60 (s, 3H, $C\underline{H}_3C$=); mass spectrum, *m/e* (relative intensity) 380 (M^+, ^{80}Se, 9.1), 378 (M^+, ^{78}Se, 4.4), 224 (12), 223 (M^+ − PhSe, 23.5), 159 (23.4), 158 (16), 157 ($PhSe^+$, 100), 143 (19.5), 139 (79), 93 (27), 92 (17) 91 (77). (Found: C, 57.10; H, 5.44. Calc for $C_{18}H_{20}O_2SSe$: C, 56.98; H, 5.31%.)

2-Methyl-2,3-pentadiene. TLC indicated that the residue consisted of a single compound. It was an oil, 0.39 g (97%), whose structure was assigned as 2-(phenylseleno)-3-(*p*-tolylsulfonyl)-4-methyl-3-pentene (**13b**): IR (neat) 3060, 2970, 2925, 2870, 1615, 1595, 1580, 1475, 1440, 1300 (s, SO_2), 1140 (s, SO_2), 1090, 1025, 815, 745, 693 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 8.1–7.0 (m, 9H), 4.60 (quartet, 1H, J = 7 Hz, $CH_3C\underline{H}(SePh)$), 2.37 (s, 3H, $C\underline{H}_3C_6H_4$), 2.2–1.6 (d and two s, 9H, $C\underline{H}_3CH$ and 2 $C\underline{H}_3C$=); mass spectrum, *m/e* (relative intensity) 394 (M^+, ^{80}Se, 2.8), 392 (M^+, ^{78}Se, 1.4), 237 (M^+ − PhSe, 32), 173 (11), 157 ($PhSe^+$, 100), 139 (67), 131 (10), 93 (21), 92 (112), 91 (50). (Found: C, 58.08; H, 5.71. Calc for $C_{19}H_{22}O_2SSe$: C, 58.01; H, 5.64%.)

Nona-1,2-diene. TLC of the oily residue indicated that it was a single compound. Based on the position of the olefinic proton resonance in the ^{1}H-NMR spectrum it was assigned the structure (*E*)-1-(phenylseleno)-2-(*p*-tolylsulfonyl)-2-nonene (**13c**), 0.42 g (96%): IR (neat) 3059, 2953, 2930, 2856, 1633, 1597, 1577, 1477, 1461, 1437, 1313, 1302 (s, SO_2), 1141 (s, SO_2), 1086, 1022, 814, 740, 715, 692 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 8.1–7.0 (m, 9H), 6.90 (t, 1H, J = 8 Hz, =$C\underline{H}CH_2$), 3.75 (s, 2H, CH_2SePh), 2.37 (s, 3H, $C\underline{H}_3C_6H_4$), 1.93 (dt as a m, 2H, =$CHC\underline{H}_2$—), 1.6–1.0 (m, 8H $(CH_2)_4$), 1.0–0.65 (distorted t, 3H, CH_3).

1-Phenyl-1,2-propadiene. The residue was chromatographed on silica gel using benzene as eluant. Trituration with hexane of the oily product left after removal of the benzene gave 0.42 g (99%) of (*E*)-1-(phenylseleno)-2-(*p*-tolylsulfonyl)-3-phenyl-2-propene (**13d**) as a white solid, m.p. 96–97°: IR (KBr) 3053, 2993, 2941, 2922, 1655, 1622, 1597, 1575, 1493, 1475, 1448, 1435, 1302, 1288 (s, SO_2), 1170, 1130 (s, SO_2), 1084, 1020, 931, 815, 733, 692 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 8.0–7.0 (m, 15H), 4.0 (s, 2H), 2.40 (s, 3H); mass spectrum, *m/e* (relative intensity) 428 (M^+, ^{80}Se, 6.6), 426 (M^+, ^{78}Se, 3.2), 271 (M^+ − PhSe, 23), 157 ($PhSe^+$, 11), 155 (30), 139 (18), 115 (100), 91 (84). (Found: C, 61.62; H, 4.71. Calc for $C_{22}H_{20}O_2SSe$: C, 61.82; H, 4.72%.)

3-Methyl-1,2-pentadiene. The residue, 0.40 g, was an oil that TLC suggested was a mixture of two very similar compounds. Based on the ^{1}H-NMR spectrum of the material these are considered to be the *E*- and *Z*-isomers of 1-(phenylseleno)-2-(*p*-tolylsulfonyl)-3-methyl-2-pentene (**13e**): IR (neat) 3050, 2970, 2930, 2878, 1605, 1590, 1575, 1470, 1435, 1305, 1295 (s, SO_2), 1135 (s, SO_2), 1080, 1018, 810, 735 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 8.1–7.0 (m, 9H), 4.07, 4.01 (2s, 2H, CH_2SePh), 2.40 (s, 3H, $CH_3C_6H_4$), 2.2–1.58 (m plus singlets at 1.98 and 1.58, 5H, $CH_3C\underline{H}_2$ and $C\underline{H}_3C$=), 0.90, 0.75 (2t, 3H, $C\underline{H}_3CH_2$). Based on the relative integrated intensities of the two singlets for the $C\underline{H}_2SePh$ protons in the two isomers at δ 4.07 and 4.01, the *E*- and *Z*-isomers appear to be present in approximately equal amount.

Attempted photoaddition of **1a** *to* 1,2-*propadiene*

A solution of **1a** (0.156 g, 0.5 mmol) in 0.5 ml of carbon tetrachloride was placed in a Pyrex tube, connected to a vacuum line, and degassed. A measured amount (0.75 mmol) of 1,2-propadiene was then allowed to condense in on top of the frozen solution, and the tube was sealed off under vacuum. The tube was then irradiated for 5 hr in the usual way. Upon work-up no significant amount of **1a**-allene adduct was obtained. Instead the principal products appeared to be those (diphenyl diselenide, *p*-toluenesulfonic anhydride) associated[6b] with the photodecomposition of **1a** in the absence of alkenes or dienes.

Oxidation of **1a**-*allene adducts* (**13**)

General procedure. The **1a**-allene adduct (1.0 mmol) was dissolved in 4 ml of tetrahydrofuran and cooled to −20°. Cold 30% hydrogen peroxide (1.5 ml) was then added, and the soln was allowed to stand at −20° for 2 hr, at which time TLC showed that no starting material remained. Triethylamine (0.5 ml) was then added and the soln was allowed to warm to room temp and stand overnight. After approx 15 ml of carbon tetrachloride had been added, the organic layer was washed several times with water, dried ($MgSO_4$), and the solvents were removed under reduced pressure. The residue was then worked up as described below for each specific case.

2 - *Methyl* - 3 - (p - *tolylsulfonyl*) - 3 - *buten* - 2 - *ol* (**14a**). The residue from the oxidation of **13a** was recrystallized twice from hexane, giving 0.18 g (75%) of 2 - methyl - 3 - (*p* - tolylsulfonyl) - 3 - buten - 2 - ol (**14a**), m.p. 57–58°: IR (KBr) 3440 (OH), 2978, 2960, 1650, 1590, 1445, 1375, 1293, 1284 (s, SO_2), 1150, 1115 (s, SO_2), 1073, 965, 890, 812, 680 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 8.0–7.1 (m, 4H), 6.25 (d, 1H, J = 1.5 Hz), 6.01 (d, 1H, J = 1.5 Hz), 3.20 (s, 1H, OH), 2.42 (s, 3H, $C\underline{H}_3C_6H_4$), 1.46 (s, 6H, $(CH_3)_2C$). (Found: C, 60.14; H, 6.90. Calc for $C_{12}H_{16}O_3S$: C, 59.98; H, 6.71%.)

2 - *Methyl* - 3 - (p - *tolylsulfonyl*) - 3 - *penten* - 2 - *ol* (**14b**). The residue from the oxidation of **13b** was recrystallized several times from hexane, yielding 0.25 g (98%) of (*Z*) - 2 - methyl - 3 - (*p* - tolylsulfonyl) - 3 - penten - 2 - ol (**14b**), m.p. 76–77°: IR (KBr) 3505 (OH), 2980, 2920, 1680, 1620, 1578, 1455, 1380, 1280 (s, SO_2), 1200, 1170, 1125 (s, SO_2), 1070, 915, 830, 675 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 8.1–7.15 (AA'BB' pattern, 4H), 6.45 (quartet, 1H, J = 7 Hz, $CH_3C\underline{H}$=), 4.23 (s, 1H, OH), 2.43 (s, 3H, $C\underline{H}_3C_6H_4$), 1.85 (d, 3H, J = 7 Hz, $C\underline{H}_3CH$=), 1.61 (s, 6H, $(CH_3)_2C$). (Found: C, 61.67; H, 7.23. Calc for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13%.)

2 - (p - *Tolylsulfonyl*) - 1 - *nonen* - 3 *ol* (**14c**). The residue from the oxidation of **13c** was purified by preparative TLC (SiO_2, benzene), giving 0.271 g (92%) of 2-(*p*-tolylsulfonyl)-1-nonen-3-ol as a colorless oil that could not be induced to crystallize: IR (neat) 3501 (OH), 2952, 2930, 2858, 1597, 1460, 1400, 1379, 1313, 1302, 1290 (s, SO_2), 1168, 1140 (s, SO_2), 1082, 958, 815, 655 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 8.0–7.2 (AA'BB' pattern, 4H), 6.39 (d, 1H, J = 1 Hz), 6.05 (d, 1H, J = 1 Hz), 4.33 (t, 1H, J = 6 Hz, —C$\underline{H}$(OH)CH_2—), 3.67 (br, s, 1H, OH), 2.42 (s, 3H, $C\underline{H}_3C_6H_4$), 2.0–0.6 (m, 13H, $CH_3(CH_2)_5$—). (Found: C, 64.77; H, 7.95. Calc for $C_{16}H_{24}O_3S$: C, 64.83; H, 8.16%.)

As a further means for identification of **14c** a solid phenylurethane derivative, m.p. 82–83°, was prepared by reacting **14c** with phenyl isocyanate in the usual fashion and was purified by recrystallization from hexane: IR (KBr) 3344 (m, NH stretch), 3060, 3026, 2955, 2928, 1737 (s, C=O), 1601, 1537, 1502, 1444, 1315, 1302 (s, SO_2), 1215 (s, C—O—C(O) stretch), 1143 (s, SO_2), 1082, 964, 814, 754, 693, 655 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.9–7.0 (m, 9H), 6.57 (d, 1H, J = 1 Hz), 6.27 (s, 1H, NH), 6.07 (d, 1H, J = 1 Hz), 5.45 (t, 1H, J = 7 Hz, C$\underline{H}$O), 2.27 (s, 3H, $C\underline{H}_3C_6H_4$), 2.0–0.7 (m, 13H, $CH_3(CH_2)_5$).

1 - *Phenyl* - 2 - (p - *tolylsulfonyl*) - 2 - *propen* - 1 - *ol* (**14d**). The residue from the oxidation of **13d** was purified by preparative TLC (SiO_2, benzene) followed by recrystallization from hexane, giving 0.198 g (70%) of 1-phenyl-2-(*p*-tolylsulfonyl)-2-propen-1-ol (**14d**), m.p. 77–78°; IR (KBr) 3487 (s, OH), 3111, 3032, 2926, 2878, 1631, 1597, 1494, 1454, 1400, 1388, 1290 (s, SO_2), 1259, 1167, 1130 (s, SO_2), 1080, 1043, 974, 814, 777, 742, 704, 684 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.75–7.0 (m, 9H), 6.45 (d, 1H, J = 1 Hz), 5.84 (d, 1H, J = 1 Hz), 5.52 (d, 1H, J = 4 Hz, C$\underline{H}$Ph), 3.19 (d, 1H, J = 4 Hz, OH), 2.40 (s, 3H, $C\underline{H}_3C_6H_4$). (Found: C, 66.53; H, 5.66. Calc for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59%.)

3 - *Methyl* - 2 - (p - *tolylsulfonyl*) - 1 - *penten* - 3 - *ol* (**14e**). The residue from the oxidation of the mixture of the (*E*)- and (*Z*)-isomers of **13e** was purified by recrystallization from hexane, yielding 0.23 g (90%) of 3-methyl-2-(*p*-tolylsulfonyl)-1-penten-3-ol (**14e**), m.p. 47.5–48°: IR (KBr) 3490 (OH), 2970, 2930, 1650, 1593, 1455, 1370, 1290 (s, SO_2), 1200, 1150, 1115 (s, SO_2), 1080, 1043, 955, 920, 880, 820, 730, 680 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 7.9–7.15 (AA'BB' pattern, 4H), 6.35 (d, 1H, J = 1.5 Hz), 5.89 (d, 1H, J = 1.5 Hz), 3.10 (s, 1H, OH), 2.42 (s, 3H, $C\underline{H}_3C_6H_4$), 1.78 (quartet, 2H, J = 7 Hz, $C\underline{H}_2CH_3$), 1.37 (s, 3H, CH_3), 0.75 (t, 3H, $C\underline{H}_3CH_2$). (Found: C, 61.57; H, 7.28. Calc for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13%.)

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