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SELENOSULFONATION OF ALLENES AND SUBSEQUENT REARRANGEMENT OF THE ADDUCTS: A FACILE SYNTHETIC ROUTE TO β-ARYLSULFONYL-SUBSTITUTED ALLYLIC ALCOHOLS[1]

Young-Hee Kang and John L. Kice*
Department of Chemistry, Texas Tech University
Lubbock, Texas 79409

Abstract: Se-Phenyl areneselenosulfonates add readily to allenes in a highly regiospecific fashion (eq 3) to give 5. Oxidation of the PhSe group in 5 to PhSe(O) is followed by [2,3]-sigmatropic rearrangement to 6 and hydrolysis of 6 to the β-arylsulfonyl-substituted allylic alcohol 7, thereby providing a simple, high-yield route to these interesting compounds.

Se-Phenyl areneselenosulfonates ($ArSO_2SePh$) readily undergo free-radical addition to alkenes (eq 1)[2] and alkynes (eq 2)[3], affording 1 and 2, respectively. Upon oxidation of the PhSe group to PhSe(O) these adducts eliminate PhSeOH, and vinylic (3) and acetylenic (4) sulfones are formed in high yield, providing an excellent route to these synthetically useful compounds.

$$RCH{=}CH_2 \xrightarrow[h\nu]{ArSO_2SePh} \underset{\mathbf{1}}{RCH(SePh)CH_2SO_2Ar} \xrightarrow{[O]} \xrightarrow{-PhSeOH} \underset{\mathbf{3}}{RCH{=}CHSO_2Ar} \qquad (1)$$

$$RC{\equiv}CH \xrightarrow[\Delta]{ArSO_2SePh} \underset{\mathbf{2}}{RC(SePh){=}CHSO_2Ar} \xrightarrow{[O]} \xrightarrow{-PhSeOH} \underset{\mathbf{4}}{RC{\equiv}CSO_2Ar} \qquad (2)$$

We now wish to report that areneselenosulfonates also readily undergo free-radical addition to allenes. The addition is highly regiospecific, the arylsulfonyl group adding to the central carbon of the allenic system and the phenylseleno group becoming attached to the less highly substituted of the two terminal carbons (eq 3). Table I shows the results with the different allenes studied. In each case the yield of adduct 5 is essentially quantitative.

$$R_1CH{=}C{=}C\begin{matrix}R_2\\R_3\end{matrix} + ArSO_2SePh \xrightarrow{h\nu} \underset{\mathbf{5}}{R_1CH(SePh)\text{-}C(ArSO_2)=C\begin{matrix}R_2\\R_3\end{matrix}} \qquad (3)$$

When the PhSe group in 5 is oxidized to PhSe(O) with hydrogen peroxide there ensues, not an elimination of PhSeOH, but rather a [2,3]-sigmatropic rearrangement[4] to selenenate 6, followed by hydrolysis of 6 and the formation of the β-arylsulfonyl-substituted allylic alcohol

Table I

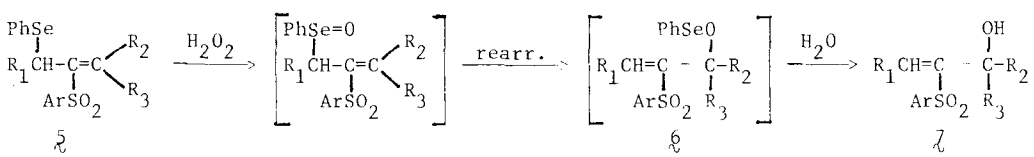
Selenosulfonation of Allenes and Rearrangement of the Adducts Upon Oxidation

Allene	Selenosulfonation product (eq 3, Ar = p-tolyl), 5[a,b]	Product upon oxidation of 5 (eq 4, Ar = p-tolyl), 7 (yield), mp[c,d]
$CH_2=C=C(CH_3)_2$	$PhSeCH_2\underset{\underset{ArSO_2}{\mid}}{C}=C(CH_3)_2$, oil	$CH_2=\underset{\underset{ArSO_2}{\mid}}{C}-\overset{\overset{OH}{\mid}}{C}(CH_3)_2$ (75%), 57-58°C
$CH_3CH=C=C(CH_3)_2$	$CH_3\overset{\overset{PhSe}{\mid}}{C}HC=C(CH_3)_2$, oil	$CH_3CH=\underset{\underset{ArSO_2}{\mid}}{C}-\overset{\overset{OH}{\mid}}{C}(CH_3)_2$ (98%), 76-77°C[f]
$CH_2=C=\underset{\underset{CH_3}{\mid}}{C}CH_2CH_3$	$PhSeCH_2\underset{\underset{ArSO_2}{\mid}}{C}=\overset{\overset{CH_3}{\mid}}{C}CH_2CH_3$, oil[e]	$CH_2=\underset{\underset{ArSO_2}{\mid}}{C}-\overset{\overset{OH}{\mid}}{C}CH_2CH_3$ (92%), 47.5-48°C
$CH_2=C=CH(CH_2)_5CH_3$	$PhSeCH_2\underset{\underset{ArSO_2}{\mid}}{C}=CH(CH_2)_5CH_3$, oil[f]	$CH_2=\underset{\underset{ArSO_2}{\mid}}{C}-\underset{\underset{OH}{\mid}}{CH}(CH_2)_5CH_3$ (92%), oil
$CH_2=C=CHPh$	$PhSeCH_2\underset{\underset{ArSO_2}{\mid}}{C}=CHPh$, 96-97°C	$CH_2=\underset{\underset{ArSO_2}{\mid}}{C}-\underset{\underset{OH}{\mid}}{CHPh}$ (70%), 77-78°C

(a) Selenosulfonations carried out by photolyzing a CCl_4 solution of $ArSO_2SePh$ (1.0 M) and the allene (1.5 M) in pyrex for 2.5-3.0 hr. (Rayonet reactor, RPR-2537 lamp). (b) Each 5 had an NMR spectrum consistent only with the assigned structure; satisfactory C,H analyses and IR spectra also obtained. (c) Adduct 5 treated with excess H_2O_2 in THF at -20°C for 2 hr; then Et_3N added and solution allowed to warm to room temperature. (d) Each 7 had an NMR spectrum consistent only with the assigned structure; satisfactory C,H analyses obtained for all 7. (e) NMP indicates product is mixture of E- and Z-isomers. (f) NMR indicates product is E-isomer.

7 (eq 4). Yields of 7 range from 70-98% (Table I). The rearrangement to 6 takes place even when R_1 has a hydrogen located such that elimination of PhSeOH is possible (entry 2 of Table I).

3-Arylsulfonyl-substituted allylic alcohols (7) would seem to have the potential for much



5 6 7 (4)

interesting chemistry. Their facile synthesis via eqs 3 and 4 now makes them easily available.

References and Notes

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