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ON THE [2,3]-SIGMATROPIC REARRANGEMENTS OF SULFENATE ESTERS DERIVED FROM ALKENYNOLS: SYNTHESIS OF VINYLALLENE AND VINYLACETYLENE SULFOXIDES.

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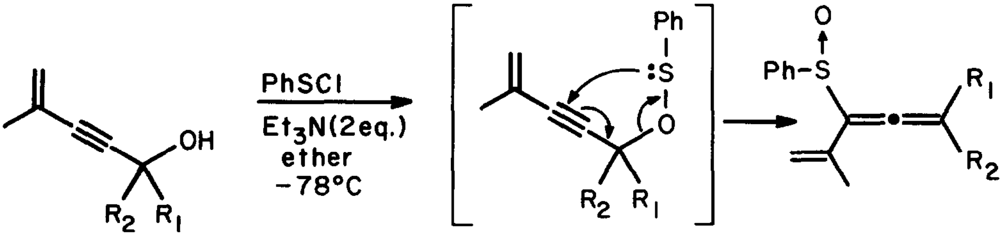
Summary: The reactions of various alkenynols with phenylsulfenyl chloride result in the formation of either vinylallene sulfoxides or vinylacetylene sulfoxides, depending on the substitution pattern of the starting material.

Vinylallenes[1] are useful intermediates in organic synthesis, for example in the preparation of cyclopentenones[2] as well as polyenes such as vitamins A (retinoids)[3] and D.[4] The vinylallene moiety is also present in certain natural products, such as the sex attractant of the male Dried Bean Beetle.[5] The development of simple new routes to usefully functionalized vinylallenes should therefore be extremely valuable. Accordingly, we have explored the feasibility of utilizing Horner's[6] allenylphenylsulfoxide synthesis for the preparation of vinylallene sulfoxides. Reactions of alkynols with phenylsulfenyl chloride were shown to yield allene sulfoxides, but the analogous reactions using various alkenynols appear not to have been previously studied.

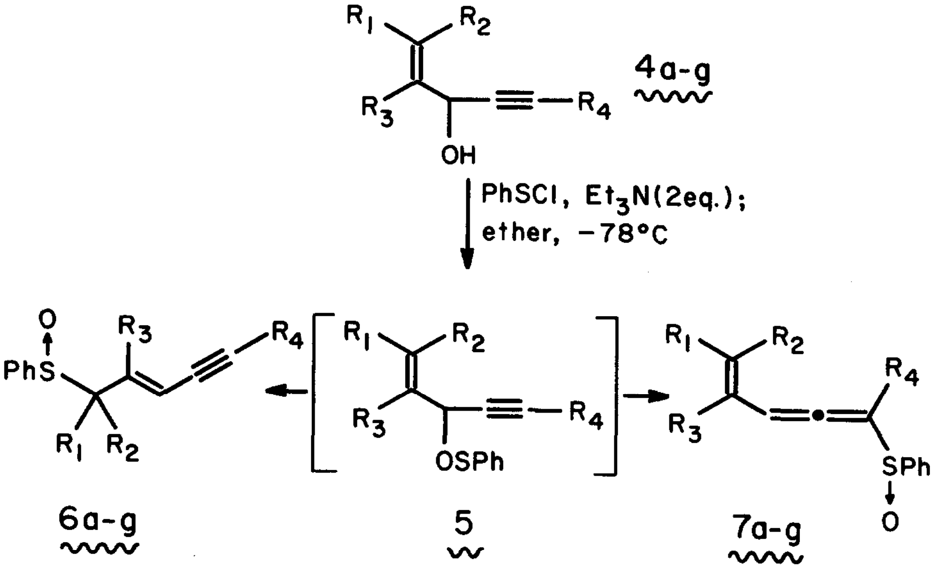
In the simpler (1) of the two alkenynol types (1 and 4) examined, the vinylallene sulfoxides 3a-c[7] were obtained in nearly quantitative yields (as yellow oils of purity >90%, according to ^{1}H-NMR) upon treatment of the alkenynols 1a-c[8] with one equivalent of phenylsulfenyl chloride[9,10] in the presence of excess base (Et_3N) at -78 °C. The initially formed sulfenate esters 2 are considered to undergo a [2,3]-sigmatropic propargylic rearrangement during the course of the reaction to produce 3. In the second type of alkenynol examined, namely 4,[11] complications due to competing [2,3]-allylic rearrangement[13,14] of the sulfenate esters 5, which results in the



1a-c 2a-c 3a-c

a. $R_1 = R_2 = H$ b. $R_1 = H$; $R_2 = CH_3$ c. $R_1 = R_2 = CH_3$

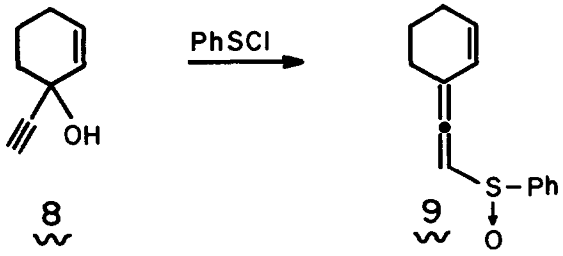
vinylacetylene sulfoxides **6**, are possible. In the event, depending upon the substitution pattern of **4**, either the vinylacetylenes **6** or the allenes **7**[7] (or a mixture) were obtained upon treatment



of **4** with PhSCl at -78 °C.[9] The results are compiled in the Table.[15] The formation of **6** or **7** was readily established by IR (allene at about 1950 cm^{-1} or acetylene at about 2050 cm^{-1}) and ^{1}H-NMR spectroscopy (terminal acetylenic hydrogen at about δ3.00). In several cases ^{13}C-NMR spectral data provided additional confirmation of structure. In the only cyclic olefin studied, the alcohol **8**[11] yielded only the vinylallene sulfoxide **9**.

Table

Entry	R_1	R_2	R_3	R_4	Starting Material	Product(s)
1	H	H	H	H	**4a**	**6a**
2	CH_3	H	H	CH_3	**4b**	**6b**
3	H	H	CH_3	H	**4c**	**6c**
4	CH_3	H	H	H	**4d**	**6d**/**7d** ≈ 4/1
5	CH_3	CH_3	H	H	**4e**	**7e**
6	CH_3	CH_3	H	CH_3	**4f**	**7f**
7	C_6H_5	H	H	H	**4g**	--[18]



In order to establish the reversibility of the rearrangement of the sulfoxides and sulfenate esters, and to obtain information on the thermodynamic stability of the vinylacetylene versus the vinylallene sulfoxides, thermal studies were performed. It was found that refluxing a solution of 6a in either ether (48 h) or benzene (2 h) resulted in the isomerization of 6a into its cis-isomer 6a' and allene 7a[19] (ratio 6a:6a':7a ≈ 1.0:1.2:1.5). On further heating (benzene, 5 h) the ratio changed to (6a + 6a'):7a ≈ 1:20, while about 40% of the material decomposed. An analogous cis-trans isomerization was observed for compound 6b (ether, 5 h), but vinylallene 7b could not be detected. The characteristic ^{1}H-NMR signals of the vinylacetylenes disappeared after 16 h in refluxing benzene.[20] Finally, the 4:1 mixture of 6d (as a cis/trans mixture) and 7d afforded on refluxing in ether (5 h) a new vinylacetylene,[21] while the ratio vinylacetylenes: vinylallenes changed to about 0.4:1.0. After 16 h (ether, reflux), in addition to decomposition, only vinylallene 7d was present; no acetylenes could be detected. These results demonstrate the reversibility of the rearrangement of the sulfenate esters 5. Furthermore, they show that the vinylacetylene sulfoxides are the kinetically controlled products, while the vinylallene sulfoxides are thermodynamically more stable.

The utility of the vinylallene and the vinylacetylene sulfoxides in synthesis is being further investigated.

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7. All new compounds gave satisfactory spectroscopic data (IR, ^{1}H-NMR and high resolution MS and in several cases, ^{13}C-NMR). Exemplifying spectral data of the various types of products are the following: **4-Methyl-3-phenylsulfinyl-penta-1,2,4-triene** (**3a**; recrystallized from ether/ -30 °C; m.p. 75-76.5 °C): IR: 1925 (allene) and 1050 (SO) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 7.70-7.35 (aromatic hydrogens), 5.42 (C-1 hydrogens), 5.34 and 5.06 (C-5 hydrogens) and 1.79 (CH_3); ^{13}C-NMR ($CDCl_3$): δ 205.4 (C-2), 134.1 (C-3), 143.8, 130.8, 128.7 and 124.5 (aromatic carbons), 117.8 (C-4), 114.8 (C-5), 84.9 (C-1) and 22.5 (CH_3); M.S. ($C_{12}H_{12}OS$): exact mass M^+ calculated at m/e 204.0603, found at m/e 204.0610. **5-Phenylsulfinyl-3-penten-1-yne** (**6a**; crude reaction product): IR: 3295 (≡CH str), 2045 (C≡C str) and 1040 (SO) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 7.60 (aromatic hydrogens), 5.96 (dt, $J\approx16$ Hz, $J\approx6$ Hz, C-4 hydrogen), 5.47 (ddt, $J\approx16$ Hz, $J\approx3$ Hz, $J\approx3$ Hz, C-3 hydrogen), 3.51 (dd, $J\approx6$ Hz, $J\approx3$ Hz, C-5 hydrogen) and 2.88 (d, $J\approx3$ Hz, C-1 hydrogen); ^{13}C-NMR ($CDCl_3$): δ 142.2, 128.8, 123.9 and 116.8 (aromatic carbons), 131.3 and 131.0 (C-3,4), 80.7 (C-2), 79.0 (C-1) and 59.6 (C-5); M.S. ($C_{11}H_{10}OS$): exact mass M^+ calculated at m/e 190.0453, found at m/e 190.0437. **6-Methyl-2-phenylsulfinyl-hepta-2,3,5-triene** (**7f**; crude reaction product, 2 diastereomers): IR: 1940 (allene) and 1050 (SO) cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 7.70-7.33 (aromatic hydrogens), 7.46 (m, C-5 hydrogen), 5.76 and 5.57 (d, br, $J\approx10$ Hz, C-4 hydrogen of two diastereomers of **7f**), 1.81 and 1.76 (methyls at C-6) and 1.70 (d, $J\approx3$ Hz, C-1 hydrogens); ^{13}C-NMR ($CDCl_3$): δ 143.3, 130.3, 128.6 and 124.0 (aromatic carbons), 204.3 and 204.0 (C-3), 138.8 and 138.6 (C-2), 117.1 and 117.0 (C-5), 108.8 and 108.7 (C-6), 96.0 (C-4), 25.9 and 18.1 (methyls at C-6), 9.3 and 9.1 (C-1); M.S. ($C_{14}H_{16}OS$): exact mass M^+ calculated at m/e 232.0923, found at m/e 232.0919.

8. Purchased from Farchan Acetylenes.

9. General Procedure: To a cooled (-78 °C) solution of 2.6 mmol of alkenynol and 5.4 mmol of Et_3N (freshly distilled) in 4.5 mL of ether (freshly distilled from $LiAlH_4$) was slowly added (20 min) under stirring a solution of 2.6 mmol PhSCl in 2.5 mL of ether by means of a syringe under a blanket of nitrogen. Stirring was continued during 2 h at -78 °C. The mixture was warmed to room temperature and 5 mL of H_2O was added. The layers were separated and the aqueous layer was extracted twice with 10 mL of ether. The combined organic layers were successively washed with 1 N HCl (3 x 10 mL) and 10% aq. K_2CO_3 (3 x 10 mL), dried over K_2CO_3, filtered and the solvent was evaporated under vacuum.

10. An excess of or the rapid addition of PhSCl should be avoided since diadducts appear to be formed.

11. All compounds, except **4a**,[8] were prepared from the corresponding aldehydes and the appropriate alkynyllithium.[12]

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15. The synthesis of vinylallenes starting from analogous alkenynols using different reagents have been reported, e.g., lithium dialkylcuprates,[5a] diethylchlorophosphite[16] and Grignard reagents.[17]

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18. Neither vinylallene sulfoxide **7g** nor vinylacetylene sulfoxide **6g** were detectable by ^{1}H-NMR or IR.

19. The acetylenic hydrogen of **6a** appears at δ2.88 (d, $J\approx3$ Hz) and of **6a'** at δ3.08 (d, $J\approx2$ Hz) in the ^{1}H-NMR spectra, while the IR spectrum shows an allenic band at 1940 cm^{-1}.

20. This may be due to a subsequent [1,5]-hydrogen shift of the vinylallene sulfoxide **7b**. See References 3 and 4 for examples.

21. The new vinylacetylene appears to be the allylic sulfoxide formed by a [1,3]-shift involving the sulfoxide sulfur in **6d** (see Reference 14).

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