Regiospecific, Stereospecific Ring Closure of Alkenylperoxyl Radicals generated by Oxygenation of Benzenethiol–Triene Mixtures

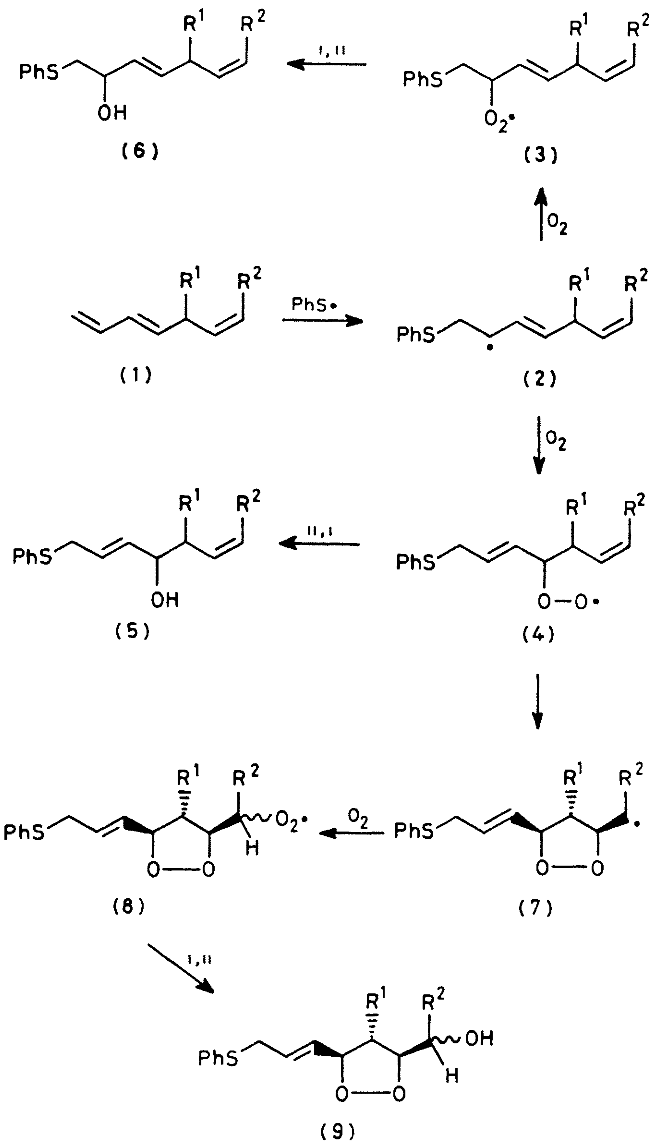
By Athelstan L. J. Beckwith* and Rudolf D. Wagner
(*Organic Chemistry Department, University of Adelaide, Adelaide, South Australia* 5000)

Summary Oxygenation of mixtures of benzenethiol and octa-1,3,6-triene (**1a**) or 5-methylhepta-1,3,6-triene (**1b**) with free-radical initiation affords, after treatment of the initial products with triphenylphosphine, the 1,2-dioxolans (**9a**) and (**9b**), respectively, *via* mechanisms involving stereospecific and regiospecific ring closure of the alkenylperoxyl radicals (**4a**) and (**4b**).

Substituted alkenylperoxyl radicals generated by co-oxidation of benzenethiol and 1,4-dienes have been shown[1] to undergo regiospecific, stereoselective ring closure to afford mainly the *cis* isomers of 3,5-disubstituted 1,2-dioxolans. We now report that ring closure of alkenylperoxyl radicals, similarly generated[1] from 1,3,6-trienes, is both regiospecific and stereospecific.

When (*E*,*Z*)-octa-1,3,6-triene (**1a**) was co-oxidised with benzenethiol as previously described,[1] and triphenylphosphine was then added, the products, separated by preparative t.l.c. and determined by h.p.l.c., were the acyclic alcohols (**6a**) (24%) and (**5a**) (7%) and two epimers (32 and 27%) of the 1,2-dioxolan (**9a**). Similar treatment of (*E*)-5-methylhepta-1,3,6-triene (**1b**) afforded (**5b**), (14%), (**6b**) (28%), and the dioxolan (**9b**) (49%). No isomer of (**9b**) could be detected by t.l.c., h.p.l.c., or n.m.r. spectroscopy.

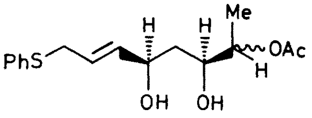
The two isomers of (**9a**) and the dioxolan (**9b**) each gave a mass spectrum and ^{1}H and ^{13}C n.m.r. spectra consistent with the assigned structure. A mixture of the acetates of (**9a**) was reduced with zinc in ammonium chloride to the acetoxy diol (**10**) which was converted into a mixture of 1,3-dioxan (**11**), t.l.c. of which allowed the separation of a pure sample of one epimer and an enriched sample of the other. The assignment of *cis*-stereochemistry to the two ring substituents in each epimer rests primarily on the fact that the ^{13}C n.m.r. spectrum of each contains two resonances for the two acetonide methyl carbons at 30·1 and 19·8 p.p.m. The two *cis*-disubstituted dioxans (**15**) and (**16**) available from earlier work show two separate resonances at *ca.* 30·2 and 20·0 p.p.m. in their ^{13}C n.m.r. spectra whereas their *trans* isomers give a single resonance at *ca.* 25·1 p.p.m. Also, the ^{1}H n.m.r. spectrum of the pure epimer of (**11**) shows, after appropriate double irradiation,



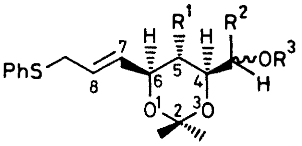
a; R^1 = H, R^2 = Me
b; R^1 = Me, R^2 = H

SCHEME. Reagents: i, PhSH; ii, Ph_3P

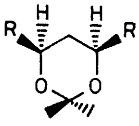
the expected couplings of 10 and 3 Hz between each of the axial protons at C-4 and C-6 and the two protons at C-5. Reduction of the acetate (**11**) gave a mixture of alcohols (**12**) having spectral features consistent with the assigned structure.



(10)



(11) R^1 = H, R^2 = Me, R^3 = Ac
(12) R^1 = H, R^2 = Me, R^3 = H
(13) R^1 = Me, R^2 = H, R^3 = Ac
(14) R^1 = Me, R^2 = H, R^3 = H



(15); R = Me
(16); R = $PhSCH_2$

The dioxolan (**9b**) was similarly converted into the acetoxydioxan (**13**), the ^{13}C n.m.r. spectrum of which shows separate resonances for the two acetonide methyl carbons at 19·7 and 30·2 p.p.m. as expected on the basis of the assigned stereochemistry. ^{1}H N.m.r. measurements on the corresponding alcohol revealed coupling constants [*J* (5-H, 6-H) 10·5; *J* (7-H, 8-H) 15 Hz], respectively, consistent with the diaxial relationship of 5-H and 6-H, and with the *E* configuration of the double bond.

The mechanism of the co-oxidation reactions is outlined in the Scheme. Initial addition of phenylthiyl radicals occurs regiospecifically at the least substituted terminus of the conjugated diene system and is followed by preferential coupling with oxygen at the 4-position.[2] The most significant feature of the reactions is that each of the cyclizations (**4a**) → (**7a**) and (**4b**) → (**7b**) occurs with complete stereospecificity; to the best of our knowledge they constitute the first example of regiospecific, stereospecific ring closures of acyclic radicals.† In each case the structure and stereochemistry of the product are in full accord with guidelines adumbrated in the two accompanying communications.

We thank the Australian Research Grants Committee for its support of this work.

(*Received*, 31*st December* 1979; *Com.* 1340.)

† However, the regio- and stereo-specific ring closure of the radical ions formed by one-electron reduction of alkenones has been recently reported (T. Shono, I. Nishiguchi, H. Ohmigu, and M. Mitani, *J. Am. Chem. Soc.*, 1978, **100**, 545).

[1] A. L. J. Beckwith and R. D. Wagner, *J. Am. Chem. Soc.*, 1979, **101**, 7099.
[2] A. A. Oswald, K. Griesbaum, and B. E. Hudson, *J. Org. Chem.*, 1963, **28**, 2355.