The Formation of Cinnamylphenols by means of an *ortho*–*ortho*-Rearrangement

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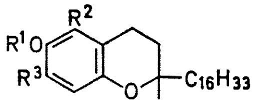
Summary Two minor products of Claisen rearrangement of 3-phenylprop-2-enyl tocyl ether are apparently formed by an *ortho*–*ortho*-rearrangement forbidden by the Woodward–Hoffmann rules.

THE current interest[1] in aromatic sigmatropic rearrangements prompts us to report our recent findings on the Claisen rearrangement of 3-phenylprop-2-enyl tocyl ether (I). The ether was heated (240°, 3 min.) in the absence of solvent to give a mixture of three products which consisted of a major product, tocol (II), as a result of cleavage,[2] and two minor rearrangement products (III, IV), which were obtained as pale yellow oils. The products were obtained in the proportion 20 : 4 : 3.

The u.v. spectrum of (III) [λ_{max} in EtOH 252 (ϵ 16,900) 286 (4900), 295 nm (5900)] was characteristic[3] of a *trans*-cinnamylphenol and its structure as 5-(3′-phenylprop-2′-enyl)tocol was assigned by inspection of its n.m.r. spectrum (see Table), which showed resonances characteristic[4] of the $\mathrm{{\cdot}CH{:}CH{\cdot}CH_2}$ group present in cinnamylphenols and a singlet for the two aromatic protons. Acetylation of (III) yielded a monoacetate (V) [λ_{max} in EtOH 250 (ϵ 22,100), 285 (6100), and 293 nm (4350); ν_{max} 1760 cm $^{-1}$] the n m r. spectrum of which indicated a characteristic AB system for the *ortho*-substituted aromatic protons. The structure of the second rearrangement product as 7-(3′-phenylprop-2′-enyl)tocol (IV) was assigned from its u.v. spectrum [λ_{max} in EtOH 251 (ϵ 18,300), 287 (5950), and 295 nm. (6700)] and n.m.r. spectrum (see Table).



	R¹	R²	R³
(I)	$\mathrm{CH_2{\cdot}CH{:}CHPh}$	H	H
(II)	H	H	H
(III)	H	$\mathrm{CH_2{\cdot}CH{:}CHPh}$	H
(IV)	H	H	$\mathrm{CH_2{\cdot}CH{:}CHPh}$
(V)	Ac	$\mathrm{CH_2{\cdot}CH{:}CHPh}$	H
(VI)	$\mathrm{CH_2{\cdot}CH{:}CHMe}$	H	H
(VII)	H	$\mathrm{CHMe{\cdot}CH{:}CH_2}$	H
(VIII)	H	H	$\mathrm{CHMe{\cdot}CH{:}CH_2}$
(IX)	H	$\mathrm{CH_2{\cdot}CH{:}CHMe}$	H

The formation of the cinnamylphenols (III, IV) is one of the few examples of an apparent *ortho*–*ortho*-Claisen rearrangement,[1,2,5] a type that is forbidden by the Woodward–Hoffmann selection rules.[6] The Claisen rearrangement of the but-2-enyl ethers of tocol and other tocopherols

60 *MHz N.m.r. data for tocol and its derivatives* (*in* $CDCl_3$)

Compound	Aromatic protons			$\cdot CH:CH\cdot CH_2\cdot$ residue	Acetoxy- or hydroxy-group	Phenyl group	Unassigned protons
	5-H	7-H	8-H				
(I)	3·35	3·28	3·28	3·10—3·90(2)m 5·38(2)d(*J* 5)	—	2·66(5)s	7·10—9·30(40)m
(II)	3·41	3·36	3·36	—	5·00(1)s	—	7·00—9·30(40)m
(III)	—	3·38	3·38	3·50—3·80(2)m 6·47(2)m	5·50(1)s	2·75(5)s	7·00—9·30(40)m
(IV)	3·47	—	3·37	3·30—3·95(2)m 6·52(2)d(*J* 5)	5·60(1)s	2·72(5)s	7·00—9·30(40)m
(V)	—	3·15	3·31	3·40—4·00(2)m 6·58(2)d(*J* 5)	7·76(3)s	2·75(5)s	7·00—9·30(40)m
(VI)	3·35	3·29	3·29	3·70—4·55(2)m 5·60(2)d(*J* 5)	—	—	7·10—9·30(43)m
(IX)	—	3·41	3·41	4·00—4·80(2)m 6·70(2)d(*J* 5)	5·50(1)s	—	7·00—9·30(43)m
				$>CH\cdot CH:CH_2$			
(VII)	—	3·38	3·38	3·30—4·90(3)m 6·00—6·40(1)m	4·95(1)s	—	7·10—9·30(43)m
(VIII)	3·47	—	3·39	3·50—5·05(3)m 6·10—6·60(1)m	5·50(1)s	—	7·10—9·30(43)m

Chemical shifts are given on the τ scale and proton integrals in parentheses. Coupling constants, *J*, are in Hz. s = singlet; d = doublet; m = multiplet.

was previously shown[2b] to give normal and abnormal products, and kinetic studies[3] showed that the product of abnormal rearrangement was formed intramolecularly, probably by an *ortho–ortho*-shift. The rearrangement of but-2-enyl tocyl ether (VI) to give two normal products (VII, VIII) and one abnormal product (IX) has been re-examined and the structures of the products confirmed by n.m.r. spectroscopy (Table). The rearrangement of the 3-phenylprop-2-enyl ether of tocol apparently follows a similar course, being unusual in that none of the normal product was isolated.

The anomalous *ortho–ortho*-shift that occurs during the pyrolysis of tocopheryl ethers does not occur to any great extent in phenyl or *para*-alkoxyphenyl ethers[2b] and appears to be characteristic of the 6-chromanyl structure.

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