

Isomerisation of Allyl Phenyl Ethers and Allylphenols with Transition Metal Catalysts

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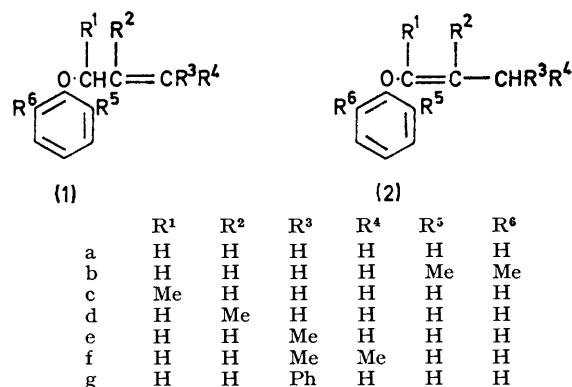
Isomerisation of allyl phenyl ethers with $\text{PdCl}_2(\text{PhCN})_2$ in boiling benzene gives quantitatively phenyl prop-1-enyl ethers with the *cis*-isomer predominating. Varying the substituents in all three positions of the allyl group shows that the reaction is sensitive to steric effects and the results are discussed in terms of an intermediate π -allyl-(hydrido)palladium complex and also a sigmatropic [1,3] hydrogen shift within a π -olefinpalladium complex. The effect of other transition metals on the isomerisation is summarised. The isomerisation of allylphenols to *trans*-(prop-1-enyl)phenols is discussed in terms of these mechanisms and conformations of the side chains.

WE report transformations of allyl phenyl ethers and allylphenols in the presence of transition metal catalysts. The work was prompted by the suggestion that the Claisen rearrangement may be involved in the biogenesis of natural products, *e.g.* in the formation of prephenic acid from chorismic acid¹ and in the biogenesis of allylphenols.² Such rearrangements, carried out at ambient temperatures, would require the presence of a catalyst, which could either be a Lewis acid or a transition metal complex.

The possibility was also considered that the [3,3] migration of the Claisen rearrangement can be changed by involvement of a transition metal since Frye *et al.*³ have reported the rearrangement of 4-vinylcyclohexene to cyclo-octa-1,5-diene in the presence of dichlorobis(benzonitrile)palladium(II). This reaction may occur by a [1,3] sigmatropic migration of carbon assisted by the transition metal.⁴ Dichlorobis(benzonitrile)palladium(II) was thus chosen as the first catalyst for our studies of the effect of transition metals on allyl phenyl ethers and allylphenols.

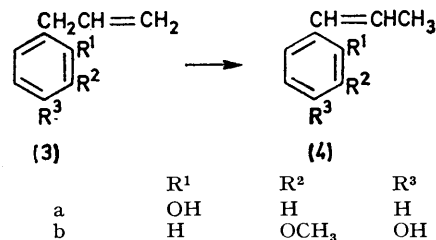
Allyl phenyl ether (1a) in the presence of the palladium catalyst in boiling benzene isomerised quantitatively to the prop-1-enyl ether (2a) (~30% *trans* and ~70% *cis*). Similar results were obtained with allyl 2,6-dimethylphenyl ether (1b) thus showing that methyl substituents in the *ortho*-positions do not impede the reaction. However, severe limitations are imposed on the reaction by substituents in the side chain. Thus with 2-methylallyl (1d), 3,3-dimethylallyl (1f), and cinnamyl (1g) phenyl ethers no reaction occurs, even in refluxing xylene. No isomerisation was observed for 2-methylallyl phenyl ether on prolonged reflux in benzene even using dichlorotris(triphenylphosphine)ruthenium(II) as catalyst despite the claim⁵ that other ruthenium complexes caused isomerisation of this and other allyl phenyl ethers. Partial isomerisation was observed in refluxing benzene for 1-methylallyl and 3-methylallyl phenyl ethers (1c and e). In an attempt to make the isomerisations quantitative the reaction was carried out with higher concentrations of catalyst and also in boiling xylene:

with more catalyst the [1,3] hydrogen isomerisation was suppressed. At 130° in refluxing xylene the Claisen rearrangement occurs to give *o*-allylphenols, and with



o-(but-2-enyl)phenol some further isomerisation gave the but-1-enyl isomer.

Quantitative isomerisation was observed when 2-allylphenol (3a) and eugenol (3b) were converted into their



corresponding (prop-1-enyl)phenols with dichlorobis(benzonitrile)palladium(II) in refluxing benzene. In contrast to the isomerisation products from allyl phenyl ethers, allylphenols gave predominately the *trans*-prop-1-enyl phenol. Previously⁶ eugenol has been converted into isoeugenol by treatment with potassium hydroxide at 200° as part of a commercial preparation of vanillin. This simple non-alkaline isomerisation with dichlorobis(benzonitrile)palladium(II) can also provide an entry into lignan syntheses.⁷ One further isomerisation which was attempted was that of phenyl prop-2-ynyl

¹ T. A. Geissman and D. H. Crout, 'Organic Chemistry of Secondary Plant Metabolism,' Freeman, Cooper and Co., San Francisco, 1969, p. 140.

² A. J. Quillinan and F. Scheinmann, *Chem. Comm.*, 1971, 966; T. R. Chamberlain and M. F. Grundon, *J. Chem. Soc. (C)*, 1971, 910.

³ H. Frye, E. Kuljian, and J. Viebrock, *Inorg. Nuclear Chem. Letters*, 1966, 2, 119.

⁴ F. D. Mango, *Adv. Catalysis*, 1969, 20, 291.

⁵ Rhone-Poulenc S.A., Ger. P. 1936727/1969.

⁶ *E.g.* J. D. Roberts and M. C. Caserio, 'Modern Organic Chemistry,' W. A. Benjamin Inc., New York, 1967, p. 952.

⁷ J. M. Harkin in 'Oxidative Coupling in Phenols,' eds. W. I. Taylor and A. R. Battersby, M. Dekker, New York, 1967, p. 243; F. M. Dean, 'Naturally Occurring Oxygen Ring Compounds,' Butterworths, London, 1963, p. 49; I. A. Pearl, 'The Chemistry of Lignin,' Marcel Dekker, New York, 1967, p. 136.

TABLE 1
Isomerisation of allyl 2,6-dimethylphenyl ether with various catalysts

	Product (%)	<i>cis</i> (%)	<i>trans</i> (%)
CoCl ₂ (PPh ₃) ₃	0		
Mn ₂ (CO) ₁₀	0		
NiBr ₂ (PEt) ₃	0		
NiBr ₂ (PPh) ₃	0		
RhCl ₃	0		
(RhClcyclo-octa-1,5-diene) ₂	12.7	70.5	29.5
RhCl(PPh ₃) ₃	48.5	91.5	8.5
RhH(CO)(PPh ₃) ₃	49.2	62.6	37.4
RuCl ₂ (PPh ₃) ₃	100	75.0	25.0

ether (5) which was unchanged after 35 h in refluxing benzene.

that only dichlorotris(triphenylphosphine)ruthenium(II) gives quantitative isomerisation and that in the other cases either no reaction or incomplete reaction occurred after 35 h. In all cases where isomerisation did occur the *cis*-isomer predominated. Previous work⁸ showed that allyl phenyl ether can also be quantitatively isomerised by pentacarbonyliron(0) on irradiation but only 60% isomerisation occurs on prolonged heating with the catalyst. Ruthenium complexes⁵ are also claimed to give high yields of isomerised product at 130°.

The ready isomerisation of allyl phenyl ethers to their isomeric alk-1-enyl ethers may have synthetic value since alk-1-enyl ethers are readily hydrolysed to alde-

TABLE 2
I.r.^a and n.m.r.^b absorptions of phenyl prop-1-enyl ethers

Compound	ν_{\max} -C=C- (cm ⁻¹)	Aromatic H (τ)	Allyl substituents ^c (τ)			Coupling constants (Hz)			
			C-1	C-2	C-3	<i>cis</i> -isomer $J_{H,H}$	<i>cis</i> -isomer J_{H,CH_3}	<i>trans</i> -isomer $J_{H,H}$	<i>trans</i> -isomer J_{H,CH_3}
(2a)	1678	3.15(m)	3.85 (m, H)	4.89 (m, H, <i>trans</i>) 5.41 (m, H <i>cis</i>) 5.51 (m, H)	8.38 (q, CH ₃ <i>cis</i>) 8.62 (q, CH ₃ <i>trans</i>) 8.20 (q, CH ₃ <i>cis</i>) 8.63 (q, CH ₃ <i>trans</i>)	5.8	7	12	7
(2b)	1675	3.07(s)	3.72 (q, H <i>trans</i>) 4.12 (q, H <i>cis</i>) 8.45 (m, CH ₃)	5.20 (m, H) 4.73 (m, H <i>trans</i>) 5.49 (m, H <i>cis</i>)	8.45 (m, CH ₃) 7.87 (m, CH ₂ <i>trans</i>) 8.26 (m, CH ₂ <i>trans</i>) 9.13 (t, CH ₃)	5.7	6.5	12	6.5
(2c) ^d	1700	3.00(m)				6.3	7 ^e	12	7 ^e
(2e)	1670	3.19(m)	3.92 (m, H)				7 ^f		7 ^f

^a Liquid film. ^b C₆D₆ Solvent. ^c Assignments were checked by double irradiation experiments. ^d Spectra too complex for complete analysis. ^e J_{H,CH_2} . ^f J_{CH_2,CH_3} .

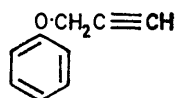
TABLE 3
Isomerisation of allyl phenyl ethers to phenyl prop-1-enyl ethers in benzene using dichlorobis(benzonitrile)palladium(II) as catalyst

	Allyl ether (g)	Catalyst (g)	Solvent (ml)	Reaction time (h)	Product	Yield (%)	<i>cis</i> (%)	<i>trans</i> (%)
(1a)	10	0.4	100	8	(2a)	100	68.9	31.1
(1b)	10	0.4	100	5	(2b)	100	69.5	30.5
(1c)	5	0.25	50	14	(2c)	39.1 ^a		
(1c)	10	0.5	100	28	(2c)	51.8 ^a		
(1c)	2	0.5	20	48	(2c)	21.4 ^a		
(1c)	2	1	20	48	(2c)	21.1 ^a		
(1c)	10	0.5	100 ^b	45	(2c)	5.1 ^{a,c}		
(1d)	5	0.125	50	8	*			
(1d)	2	0.1 ^d	20	48	*			
(1d)	2.5	0.125	25 ^b	16	*			
(1e)	10	0.5	100	15	(2e)	64.7	66.2	33.8
(1e)	2	0.45	20	48	(2e)	37.9	61.2	38.8
(1e)	2	1	20	48	(2e)	38.1	58.7	41.3
(1e)	5	0.25	50 ^b	45	(2e)	25.4 ^e	63.6	36.4
(1f)	5	0.25	50	8	*			
(1f)	5	0.25	50 ^b	6	*			
(1g)	2.5	0.125	25	8	*			
(1g)	2.5	0.125	25 ^b	6	*			
(1g)	5	0.25	50	35	*			

^a *cis*- and *trans*- Isomers not resolved by g.l.c. or n.m.r. analysis. ^b Solvent was xylene. ^d Other products were 1-methylallyl phenyl ether (1c) (25.9%), *o*-(but-2-enyl)phenol (55.3%), and *o*-(but-1-enyl)phenol (10.8%). ^e Catalyst was RuCl₂(PPh₃)₃. ^f Other products were but-2-enyl phenyl ether (1e) (62.6%) and *o*-(1-methylallyl)phenol (10.0%).

* No reaction.

To compare the effect of other catalysts the reaction of allyl 2,6-dimethylphenyl ether (1b) was investigated



(5)

with various complexes of cobalt, manganese, nickel, rhodium, and ruthenium (Table 1). The results show

hydres or ketones. Thus the prop-1-enyl (2b) 1-methylprop-1-enyl (2c), and but-1-enyl (2e) aryl ethers, quantitatively gave the corresponding carbonyl derivatives in the presence of mineral acid. This can thus represent a method of conversion of allyl halides into saturated aldehydes or ketones without the use of a redox reagent.

In the rearrangement of the allyl phenyl ether to the prop-1-enyl ether, the *cis*-isomer predominated, whereas

⁸ P. W. Jolly, F. G. A. Stone, and K. Mackenzie, *J. Chem. Soc.*, 1965, 6416.

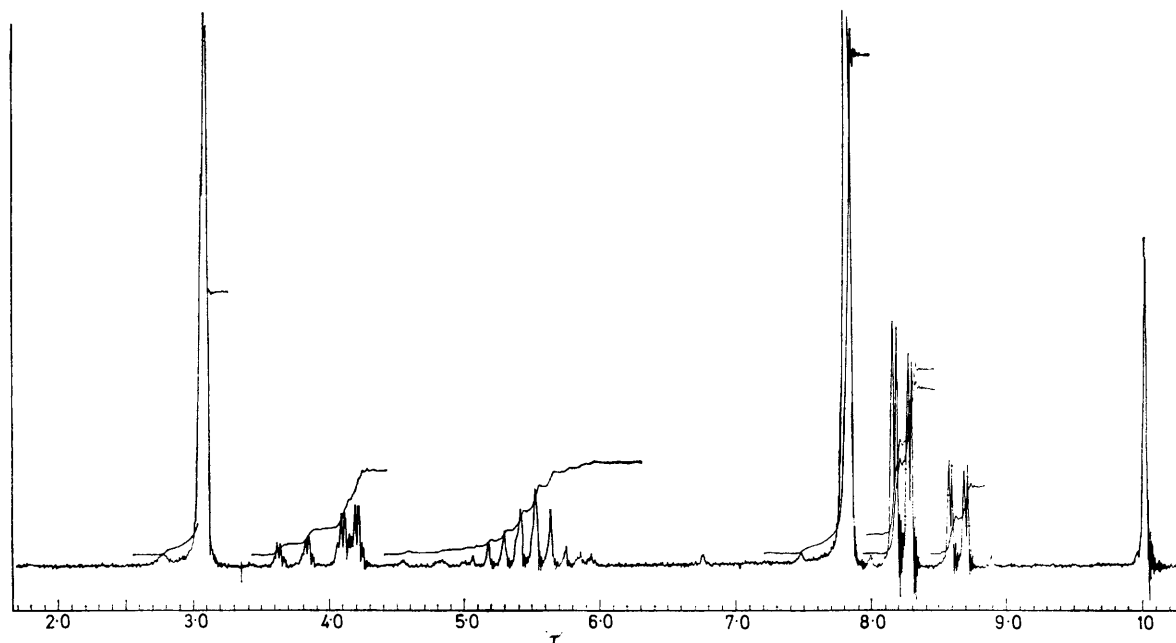
isomerisation of the allylphenols gave predominately the *trans*-(prop-1-enyl) phenols. Control experiments showed that further heating of the phenyl prop-1-enyl ether (2b) in benzene with more catalyst did not alter the *cis* : *trans* ratio. The structures of the products in the reaction mixtures were established by n.m.r. spectroscopy with first order analysis and spin decoupling experiments. The chemical shifts, coupling constants, and olefin stretching frequencies are summarised in Table 2. The percentage of each isomer present was established by gas chromatography and n.m.r. spectroscopy. When both techniques were used the agreement was within $\pm 2\%$ (Table 3 and 4).

multiplet centred at τ 5.5 which also contains the signal due to an olefinic proton of the *cis*-isomer. The *cis*-isomer shows well-defined signals due to the methyl group [τ 8.20 (J 6.5 and 1.5 Hz)] and one olefinic proton (τ 4.2) having *cis*-olefin coupling (J 5.7 Hz) further split (J ca. 1.5 Hz) by the methyl group.

The assignments given to both the *cis*- and *trans*-prop-1-enyl ethers (2b) were supported by double irradiation experiments and the data is summarised for the *trans*-isomer. Thus double irradiation at the signals due to the methyl group of the *trans*-isomer simplified the signals at τ 3.72 and at 5.5 to show the olefinic protons with *trans*-coupling. Double irradiation at τ

TABLE 4
Conversion of (1e) into (2e) using dichlorobis(benzonitrile)palladium(II) as catalyst

Catalyst (%)	Solvent	Reaction time (h)	(1e) (%)	<i>cis</i> (%)	<i>trans</i> (%)	(2e) (%)	<i>cis</i> (%)	<i>trans</i> (%)
5	Benzene	15	100	14.0	86.0	64.7	42.7	22.0
22.5	Benzene	48	62.1	18.8	43.3	37.9	23.2	14.7
50	Benzene	48	61.9	20.2	41.7	38.1	22.4	15.7
5	Xylene	45	62.6	18.2	44.4	25.4	16.2	9.2



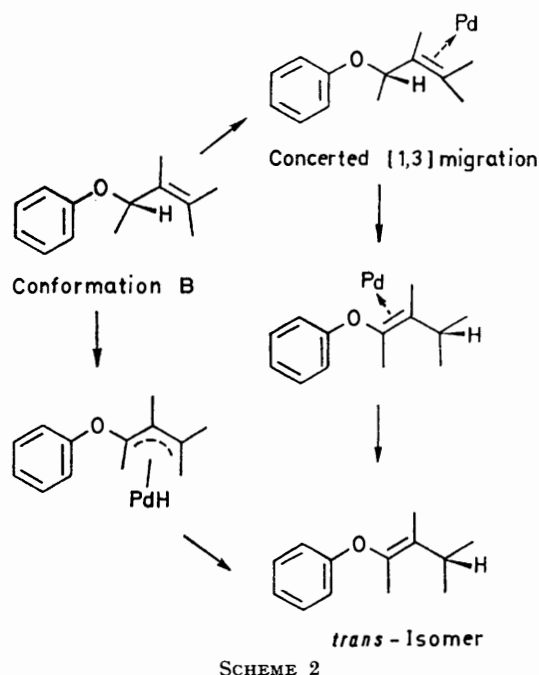
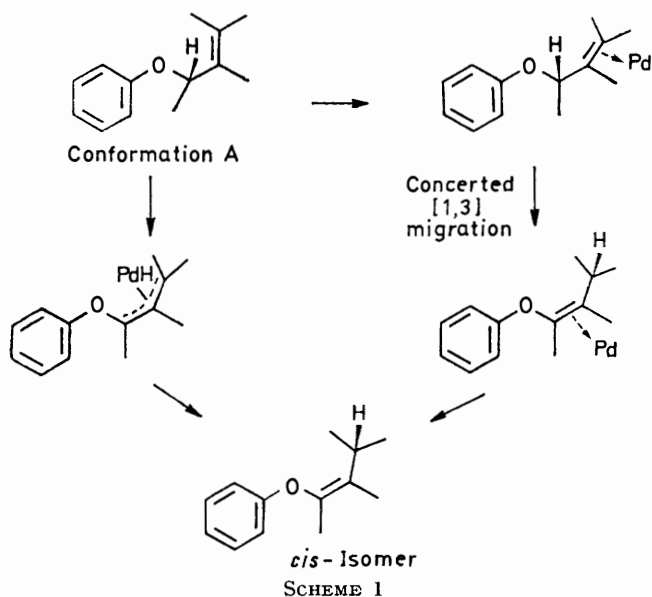
The n.m.r. spectrum of 2,6-dimethylphenyl prop-1-enyl ether measured at 60 MHz in $[^2\text{H}_6]$ benzene at a sweep width of 500 Hz

The method of n.m.r. analysis is illustrated by consideration of the Figure which shows the spectrum of the mixture of *cis*- and *trans*-2,6-dimethylphenyl prop-1-enyl ether (2b) obtained from the isomerisation of allyl 2,6-dimethylphenyl ether (1b). The *trans*-isomer shows the signal of the methyl group centred at τ 8.63 as a quartet (J 6.5 and ca. 1 Hz) due to coupling with both olefinic protons. The absorption of the olefinic proton adjacent to the ether oxygen is a quartet centred at τ 3.72 showing *trans*-olefin coupling (J 12 Hz) and long-range coupling with the methyl group (J ca. 1 Hz). The signal from the remaining *trans*-olefinic proton forms part of the

3.72 transformed the methyl signals of the *trans*-isomer from a quartet to a doublet (J 6.5 Hz) and simplified the multiplet at τ 5.5 to show clearly the component due to the adjacent olefinic proton of the *trans*-isomer. Similar results were obtained from irradiation of the signals attributed to the side chain of the *cis*-isomer. The percentage of *cis*- and *trans*-isomers in the reaction product follow from integration of the methyl signals and also of the olefinic protons in the region of τ 4. Quantitative hydrolysis of the enol ether and preparation of propionaldehyde 2,4-dinitrophenylhydrazone provides chemical confirmation for the interpretation of the

spectral data. The other analytical data given in Tables 1—4 were obtained in a similar manner.

In the isomerisation of olefins using dichlorobis(benzonitrile)palladium(II) it is generally accepted⁹ that migration of hydrogen occurs with the involvement of a



π -allyl complex.⁹⁻¹¹ Examination of molecular models suggests two possible mechanisms for a suprafacial transfer of hydrogen. In one case⁹ the π -allyl(hydrido)-

⁹ (a) J. F. Harrod and A. J. Chalk, *J. Amer. Chem. Soc.*, 1966, **88**, 3491; A. J. Hubert and H. Reimlinger, *Synthesis*, 1970, 405; C. P. Casey and C. R. Cyr, *J. Amer. Chem. Soc.*, 1973, **95**, 2248; (b) B. Hudson, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1972, 1204.

¹⁰ F. G. Gault, J. J. Rooney, and O. Kemball, *J. Catalysis*, 1962, **1**, 255.

palladium complex is the intermediate for the [1,3] transfer of hydrogen. In the other case⁴ co-ordination of the transition metal with the olefin can allow a concerted [1,3] hydrogen shift within an allyl group whereby the hydrogen migrates suprafacially but on the opposite side to the co-ordinated palladium. Isomerisation by either mechanism gives the same *cis* or *trans* isomer. Two conformations, A and B (Schemes 1 and 2), are responsible for the formation of prop-1-enyl ethers from allyl phenyl ethers. Conformation A (Scheme 1) by both mechanisms leads to the formation of the *cis*-propenyl ether whereas conformation B (Scheme 2) gives the *trans*-isomer. Our results, with formation of the *cis*-propenyl ether as the predominating product, indicate that conformation A is preferred for complex formation: alternatively the greater stability of the resulting *cis*-olefin complex controls the isomerisation process.¹¹ In conformation A there is also the possibility of a lone pair of electrons on oxygen assisting or directing π -complex formation. However, for conformation B the oxygen would appear to be too remote from the double bond to be directly involved in π -complex formation.

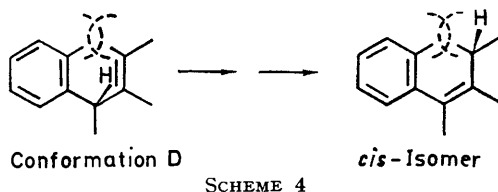
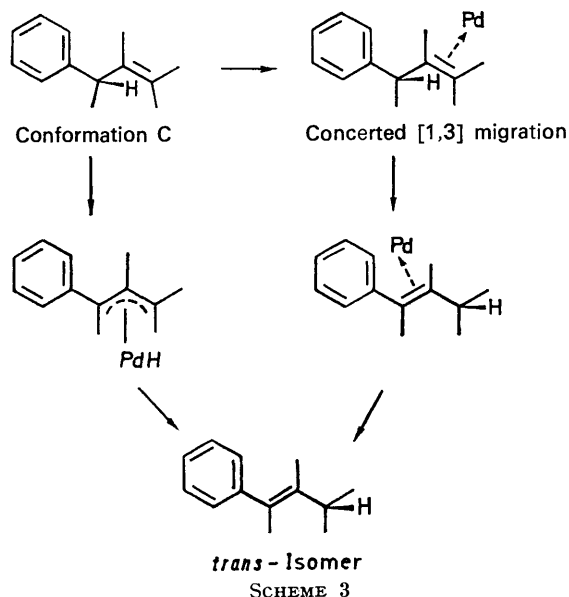
An examination of molecular models based on Schemes 1 and 2 indicates that substituents on the allyl group hinder π -allyl complex formation with dichlorobis(benzonitrile)palladium(II)^{12a} or its dissociation products.^{12b} The failure of 2-methylallyl, 3,3-dimethylallyl, and 3-phenylallyl phenyl ethers to isomerise agrees with this hypothesis. It would appear that with the 1-methylallyl and 3-methylallyl phenyl ethers (1c and e) the steric hindrance is not sufficient to suppress completely the reaction although isomerisation was incomplete even after prolonged boiling in benzene (Table 4). In support of these arguments the 3-methylallyl phenyl ether (1e) which consists of 86% *trans*- and 14% *cis*-forms isomerised to give 64.7% but-1-enyl phenyl ether (2e). The remaining 35.3% was the 3-methylallyl phenyl ether of which 25.1% was *trans*- and 10.2% was the *cis*-isomer. This shows that it is largely the *trans*-3-methylallyl phenyl ether which undergoes isomerisation. Examination of a molecular model confirms that the 3-methyl group in the *cis*-position would hinder π -complex formation. Table 4 also reveals that in the presence of a large amount of catalyst some of the *trans*-3-methylallyl phenyl ether is converted into the *cis*-isomer in agreement with the *trans* to *cis* interconversion of deuteriated ethylene.^{9b} It appears in our case that the *trans* to *cis* isomerisation of 3-methylallyl phenyl ether is a slow process compared with the hydrogen migration and occurs only at high catalyst concentration with prolonged heating.

The isomerisation of *o*-allylphenol (3a) and eugenol (3b) to predominately the *trans*-(prop-1-enyl)phenols (4a

¹¹ N. R. Davies, A. D. Di Michiel, and V. A. Pickles, *Austral. J. Chem.*, 1968, **21**, 385.

¹² (a) J. R. Holden and N. C. Baenziger, *Acta Cryst.*, 1956, **9**, 194; (b) M. B. Sparke, L. Turner, and A. J. Wenham, *J. Catalysis*, 1965, **4**, 332; M. Kubota, B. A. Deuchaud, P. M. McKinney, T. E. Needham, and G. O. Spessard, *ibid.*, 1970, **18**, 119.

and b) is consistent with the steric requirements predicted by the two conformations C and D (Schemes 3 and 4). Conformation C (Scheme 3) avoids steric inter-



action between the side chain and adjacent aromatic hydrogen in both the starting material and product. Conformation C clearly leads to the *trans*-(prop-1-enyl)-phenol whereas conformation D (Scheme 4) gives the *cis*-isomer. Other workers have shown that predominantly *trans* isomerisation of allylbenzenes occurs with dichlorobis(benzonitrile)palladium(II),¹¹ hydridotetracarbonylcobalt(I),^{4,13} and dichlorotris(triphenylphosphine)ruthenium(II).¹⁴

The results on the hydrogen migration of allyl phenyl ethers suggest that complexes of transition metals are probably not involved in biogenetic Claisen rearrangements. In contrast, the recent studies of Schmid *et al.*¹⁵ on charge-induced and charge-controlled sigmatropic rearrangements show that Lewis and proton acids cause carbon migrations at low temperatures.

EXPERIMENTAL

I.r. spectra, for liquid films or Nujol mulls, were recorded with a Perkin-Elmer 257 grating spectrophotometer and

¹³ L. Roos and M. Orchin, *J. Amer. Chem. Soc.*, 1965, **87**, 5502.

¹⁴ J. Blum and Y. Becker, *J.C.S. Perkin II*, 1972, 982.

¹⁵ J. Borgulya, R. Madeja, P. Fahrni, H.-J. Hansen, H. Schmid, and R. Barner, *Helv. chim. Acta.*, 1973, **56**, 14.

¹⁶ M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Amer. Chem. Soc.*, 1938, **60**, 882.

¹⁷ F. Scheinmann, R. Barner, and H. Schmid, *Helv. Chim. Acta.*, 1968, **51**, 1603.

¹⁸ D. S. Tarbell, 'The Claisen Rearrangement in Organic Reactions,' ed. R. Adams, J. Wiley, New York, 1944, vol. II, p. 1.

n.m.r. spectra were measured with Varian A-60 and HA-100 instruments. G.l.c. analyses were determined on a Pye 104 instrument using a 5 ft \times 0.125 in column packed with 5% SE30 on Phase Sep. P.

Transition Metal Catalysts.—Dichlorobis(benzonitrile)-palladium(II) was prepared by the method of Kharasch *et al.*¹⁶ RhH(CO)(PPh₃)₃, RuCl₂(PPh₃)₃, and Mn₂(CO)₁₀ were purchased from Alfa Products and RhCl₃, RhCl(PPh₃)₃, (RhClcyclo-octa-1,5-diene)₂, NiBr₂(PEt)₃, NiBr₂(PPh₃)₃, and CoCl₂(PPh₃)₂ were gifts from I.C.I. Ltd.

Allyl Phenyl Ethers and Phenyl Prop-2-ynyl Ethers.—The following ethers were prepared according to the method of Scheinmann *et al.*¹⁷ Allyl phenyl ether (1a), b.p. 90–91° at 23 mmHg (lit.,¹⁸ 85° at 19 mmHg), ν_{\max} (film) 1650 cm⁻¹, τ (CCl₄) 3.0 (5H, aromatic), 3.95 (m, =CH=), 4.69 (m, =CH₂), and 5.41 (d, -OCH₂-); allyl 2,6-dimethylphenyl ether (1b), b.p. 47° at 0.05 mmHg (lit.,¹⁹ 67–68° at 2 mmHg), ν_{\max} (film) 1650 cm⁻¹, τ (CCl₄) 3.17 (3H, aromatic) 3.97 (m, =CH=), 4.7 (m, =CH₂), 5.74 (d, -OCH₂-), and 7.75 (s, 2 \times *ortho*-CH₃); 1-methylallyl phenyl ether (1c), b.p. 117–119° at 64 mmHg (lit.,²⁰ 42.9–43.0 at 0.8 mmHg), ν_{\max} (film) 1650 cm⁻¹, τ (CCl₄) 2.97 (5H, aromatic), 4.05 (m, =CH=), 4.78 (m, =CH₂), 5.24 (t, -OCH-), and 8.57 (d, -CH₃); 2-methylallyl phenyl ether (1d), b.p. 108–110° at 30 mmHg (lit.,²¹ 54–54.5° at 2.0 mmHg), ν_{\max} (film) 1662 cm⁻¹, τ (CCl₄) 2.95 (5H, aromatic), 5.0 (d, =CH₂), 5.68 (s, -OCH₂-), and 8.21 (s, -CH₃); but-2-enyl phenyl ether (1e), b.p. 98° at 17 mmHg (lit.,²⁰ 87.1–87.5° at 8 mmHg), ν_{\max} (film) 1682 cm⁻¹, τ (CCl₄) 2.95 (5H, aromatic), 4.30 (m, =CH=CH-), 5.57 (d of d, -OCH₂-), and 8.28 (d of d, -CH₃); 3-methylbut-2-enyl phenyl ether (1f), b.p. 83–85° at 1.1 mmHg (lit.,¹⁷ 116–118° at 18 mmHg), ν_{\max} (film) 1675 cm⁻¹, τ (CDCl₃) 2.9 (5H aromatic), 4.7 (t, =CH=), 5.5 (d, -OCH₂-), and 8.22 and 8.27 (2s, 2-CH₃); cinnamyl phenyl ether (1g), m.p. 66–67° (lit.,²² 66–66.5°), ν_{\max} (Nujol) 1663 cm⁻¹, τ (CCl₄) 2.98 (10H, aromatic), 3.71 (m, =CH=CH-), and 5.43 (d, -OCH₂-) predominantly *trans*-isomer (from n.m.r.); phenyl prop-2-ynyl ether (5), b.p. 117–119° at 60 mmHg (lit.,²³ 50–51° at 4 mmHg), ν_{\max} (film) 3300 and 2120 cm⁻¹, τ (CCl₄) 2.9 (5H, aromatic), 5.4 (d, -OCH₂-), and 7.61 (t, =CH). G.l.c. analysis showed (1e) to consist of 86% *trans*- and 14% *cis*-isomers. All the other ethers were shown to be pure.

Allylphenols.—*o*-Allylphenol (3a) was prepared by the literature method,¹⁸ b.p. 137–140° at 67 mmHg (lit.,¹⁸ 99° at 12 mmHg), ν_{\max} (film) 1650 cm⁻¹, τ (CCl₄) 3.08 (4H, aromatic), 4.0 (m, =CH=), 4.54 (s, OH), 4.93 (m, =CH₂), and 6.67 (d, -CH₂-). Commercial Eugenol (3b) was distilled before use, ν_{\max} (film) 1646 cm⁻¹, τ (CCl₄) 3.28 (3H, aromatic), 4.11 (m, =CH=), 4.43 (s, OH), 4.95 (m, =CH₂), 6.24 (s, -OCH₃), and 6.71 (d, -CH₂-).

Isomerisation of Allyl Phenyl Ethers and Phenyl Prop-2-ynyl Ether with Dichlorobis(benzonitrile)palladium(II).—The allyl phenyl ether, dichlorobis(benzonitrile)palladium(II), and solvent were refluxed for several hours (see Table 3). The cooled mixture was filtered, the filtrate was washed twice with Claisen's alkali and then water, dried (MgSO₄),

¹⁹ D. S. Tarbell and J. F. Kincaid, *J. Amer. Chem. Soc.*, 1940, **62**, 728.

²⁰ H. L. Goering and R. R. Jacobson, *J. Amer. Chem. Soc.*, 1953, **80**, 3277.

²¹ W. N. White and B. E. Morcross, *J. Amer. Chem. Soc.*, 1961, **83**, 3265.

²² L. Claisen and E. Tietze, *Ber.*, 1925, **58**, 275.

²³ I. Iwai and J. Ide, *Chem. Pharm. Bull. (Japan)*, 1963, **11**, 1042.

and the solvent removed. The products were analysed by g.l.c. and n.m.r. spectroscopy (see Tables 2—4).

Effect of Prolonged Heating and Catalyst on 2,6-Dimethylphenyl Prop-1-enyl Ether (2b).—2,6-Dimethylphenyl prop-1-enyl ether (2b) (*cis* 69.5%, *trans* 30.5%) (2 g), dichlorobis(benzonitrile)palladium(II) (0.2 g), and benzene (20 ml) were refluxed for 48 h. The mixture was worked up as described previously and n.m.r. analysis showed the product (2 g) to be 2,6-dimethylphenyl prop-1-enyl ether (2b) (*cis* 70.0%, *trans* 30.0%).

Isomerisation of Allyl 2,6-Dimethylphenyl Ether (1b) with Transition Metal Catalysts.—Allyl 2,6-dimethylphenyl ether (1b) (2 g), transition metal catalyst (0.1 g), and benzene (20 ml) were heated under reflux for 35 h. The mixtures were worked up as described previously. The crude products (2 g) were analysed by g.l.c. and n.m.r. spectroscopy and the results are given in Table 1.

Isomerisation of Allylphenols with Dichlorobis(benzonitrile)palladium(II).—The allylphenol (10 g), dichlorobis(benzonitrile)palladium(II) (0.5 g), and benzene (100 ml) were heated under reflux for 7 h. The cooled mixture was filtered and the filtrate extracted with Claisen's alkali (2 × 25 ml). Acidification of the alkaline washes followed by extraction with benzene gave quantitative yields of the (prop-1-enyl)phenols which were purified by distillation *in vacuo*. *o*-Allylphenol (3a) isomerised to *o*-(prop-1-enyl)phenol (4a) (*cis* 21.0%, *trans* 79.0%), b.p. 64—66° at 0.3 mmHg (lit.,²⁴ 119.4—119.8° at 18 mmHg), ν_{\max} (film) 1665 cm⁻¹, τ (C₆D₆) 3.2 (4H, aromatic), 4.04 (2q, *J* 16 Hz, -CH=CH- *trans*), 4.49 (2q, *J* 11.5 Hz, -CH=CH- *cis*), 5.03 (s, OH), 8.4 (q, *J* 6.5 Hz, CH₃ *trans*), and 8.54 (q, *J* 7 Hz, CH₃ *cis*). Similarly,

²⁴ K. V. Auwers, *Annalen*, 1917, **413**, 298.

²⁵ K. V. Auwers, *Ber.*, 1935, **68**, 1346.

eugenol (3b) isomerised to isoeugenol (4b) (predominantly *trans*-isomer from n.m.r.), b.p. 136—138° at 3.2 mmHg (lit.,²⁵ 141—142° at 13 mmHg), ν_{\max} (film) 1663 cm⁻¹, τ (C₆D₆) 3.11 (3H, aromatic), 4.09 (s, OH), 4.08 (m, *J* 16 Hz, -CH=CH- *trans*), 6.64 (s, -OCH₃), and 8.26 (q, -CH₃, *J*_{HMe} 6.5 Hz and 1.2 Hz).

Hydrolysis of Phenyl Prop-1-enyl Ethers with Brady's Reagent.—2,6-Dimethylphenyl propenyl ether (2b) (1 g) and Brady's reagent²⁶ (80 ml) were warmed gently on a steam-bath for 5 min. The orange precipitate obtained was filtered off and dried to give a quantitative yield of propionaldehyde 2,4-dinitrophenylhydrazone. Recrystallisation from ethanol gave a pure sample, m.p. 154—155°, identical with authentic material. Similarly, 1-methylprop-1-enyl phenyl ether (2c) gave ethyl methyl ketone 2,4-dinitrophenylhydrazone, m.p. 115°, identical with an authentic sample, and but-1-enyl phenyl ether (2e) gave butyraldehyde 2,4-dinitrophenylhydrazone m.p. 125—126°, identical with an authentic sample. I.r. and n.m.r. spectra of the 2,4-dinitrophenylhydrazone derivatives were identical with those of authentic samples.

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²⁶ R. M. Roberts, J. C. Gilbert, L. B. Rodewald, and A. S. Wingrove, 'An Introduction to Modern Experimental Organic Chemistry,' Holt, Rinehart, and Winston Inc., London, 1969, p. 233.