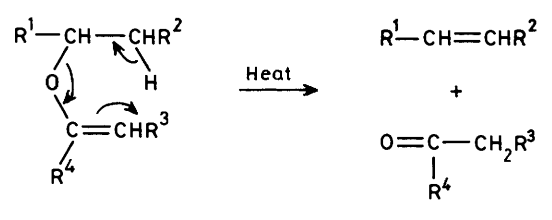
The Mechanism of Thermal Eliminations. Part 26.[1] Substituent Effects at Each Carbon of Vinyl Ethers: Non-planarity of the Transition State

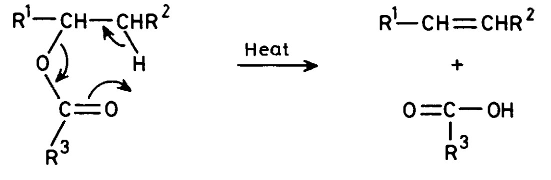
Roger Taylor
School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ, Sussex

A range of 1-arylethyl vinyl ethers and 1-arylvinyl isopropyl ethers, 2-phenylethyl vinyl ether, isopropenyl isopropyl ether, and isopropyl *cis*- and *trans*-phenylvinyl ether have been synthesized and their rates of thermal elimination measured between 585.9—666.4 K. The E_i mechanism for vinyl ether pyrolysis has less $E1$ character than that for pyrolysis of the corresponding esters, so nucleophilic attack by the double bond upon the β-hydrogen is more important for the former. Electron supply to the double bond therefore increases the pyrolysis rate, so that isopropenyl isopropyl ether is more reactive than isopropyl vinyl ether (5.85-fold at 600 K), whereas acetates and formates are almost equally reactive. Likewise isopropyl 1-phenylvinyl ether is 2.2 times more reactive than isopropenyl isopropyl ether, slightly greater than the reactivity difference between the corresponding esters (benzoates and acetates). The rate-enhancing effect of a 2-phenyl substituent in ethyl vinyl ether (5.81-fold per β-hydrogen) is a little less than the corresponding effect in ethyl acetate. In the 2-phenylvinyl ethers both *cis* and *trans* phenyl groups produce slight rate acceleration, due to the combined effects of loss of conjugation on going to products, and increase in electron supply to the double bond. The *trans* compound is more reactive than the *cis*, confirming that the six-membered transition state for β-elimination is not planar. Aryl ring substituents in 1-arylvinyl isopropyl ethers produce only very small rate effects; the effects could not be determined for electron-supplying substituents because these induced very rapid oxidation to isopropyl benzoates, and atmospheric hydrolysis also occurs. Isopropyl 2-phenylvinyl ethers were likewise oxidized to benzaldehyde and isopropyl formate. 1-Arylethyl vinyl ethers eliminate abnormally rapidly with concurrent rearrangements to aldehydes and other products.

In this series of papers we have stressed the division of thermal eliminations into two categories: those in which C_α–O bond breaking is primarily rate determining, and those in which nucleophilic attack of the double bond upon the β-hydrogen is the most important step within the overall electrocyclic process. Esters fall within the former category whereas β-hydroxy-alkenes, -ketones, and -esters for example fall within the latter, which are notable for the fact that electron supply to the double bond produces significant increases in rate. In a study of the effects of α-alkyl substituents, we showed that vinyl ethers pyrolyse *via* a less polar transition state (**1**) than that for pyrolysis of the corresponding acetates (or other esters) (**2**).[2] As a consequence the relative reactivities of alkyl vinyl ethers to alkyl acetates depends upon the nature of the alkyl group, being (at 600 K) 4.40 (Et), 1.53 (Pr^i), and 0.24 (Bu^t). A less polar, more E_i-like transition state implies greater importance of nucleophilic attack in the vinyl ethers even though the C=CH$_2$ group is less nucleophilic than the C=O group in esters.

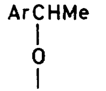


(**1**)



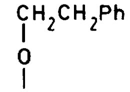
(**2**)

In order to throw more light on the nature of the transition state in vinyl ether pyrolysis, compounds (**3**)—(**7**) have been prepared and their rates of elimination examined. While this has to some extent achieved the original objective, an unexpectedly facile oxidation of compounds (**6**) and (**7**) and an unexpected side-reaction of compounds (**3**) prevented all of the hoped-for rate data being obtained.



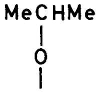
$\mathrm{ArCHMe{-}O{-}HC{=}CH_2}$

(**3**)



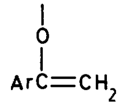
$\mathrm{CH_2CH_2Ph{-}O{-}HC{=}CH_2}$

(**4**)



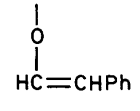
$\mathrm{MeCHMe{-}O{-}MeC{=}CH_2}$

(**5**)



$\mathrm{MeCHMe{-}O{-}ArC{=}CH_2}$

(**6**)



$\mathrm{MeCHMe{-}O{-}HC{=}CHPh}$

(**7**, *cis* and *trans*)

Results and Discussion

Isopropenyl Isopropyl Ether (**5**).—The first-order rate data are given in Table 1 along with the Arrhenius parameters. These latter are both larger than those (168.1 kJ mol^{-1}, 11.98 s^{-1}) reported previously by Flowers and Honeyman.[3] Their Arrhenius plot (determined over the temperature range 554.1—610.3 K) showed some curvature, due we believe to some

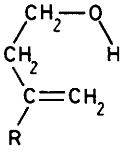
Table 1. Rate data for pyrolysis of isopropyl vinyl ethers, $\mathrm{Pr^iOCR^2{=}CHR^1}$

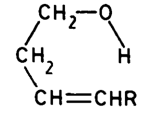
R^1	R^2	T/K	$10^3k/s^{-1}$	log (A/s^{-1})	E/kJ mol^{-1}	Corr. coeff.	$10^3k/s^{-1}$ (600 K)	k_{rel}
H	H			12.48[a]	182.5		0.388	1.0
H	Me	585.9	0.949	12.47	176.9	0.999 79	2.27	5.85
		600.5	2.38					
		615.6	5.71					
		636.5	18.1					
		652.4	38.0					
H	Ph	600.5	5.13	12.23	166.7	0.999 69	5.09	13.1
		615.5	12.4					
		636.4	34.5					
		652.4	74.5					
H	4-ClC_6H_4	600.5	5.98	11.77	160.7	0.999 54	5.93	15.3
		615.5	13.9					
		636.4	36.1					
		652.4	79.9					
H	$3\text{-NO}_2C_6H_4$	600.5	5.25	12.41	168.7	0.999 68	5.23	13.5
		615.5	12.8					
		636.4	35.7					
		652.4	79.0					
cis Ph	H	600.7	0.458	13.00	187.8	0.999 88	0.437	1.13
		615.5	1.16					
		634.8	3.39					
		650.6	8.34					
trans Ph	H	600.7	0.578	12.94	186.1	0.999 87	0.550	1.40
		615.5	1.41					
		635.2	4.22					
		650.6	10.2					

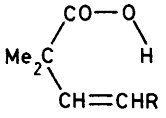
[a] This value differs slightly from the value previously given [2] as a result of thermocouple recalibration; arguments in this and the previous paper [2] are not affected.

surface-catalysed elimination at the lowest temperatures that they employed. (Surface catalysis is always potentially more intrusive at lower temperatures because the activation energy is lower.) Significantly, their elimination rates at the highest temperatures fall precisely on our correlation line. Our Arrhenius data are very close to those previously obtained for isopropyl vinyl ether,[2] and from the rate coefficients calculated at 600 K [Table 1 (R^1 = H, R^2 = Me)] the methyl group at the γ-carbon (**1**) increases the reaction rate 5.85-fold.

The substantial activating effect of the γ-methyl appears, as noted by Flowers and Honeyman, to indicate electron deficiency at the γ-carbon. This contrasts with ester elimination where this carbon is known to have an electron excess.[4] Alkyl substituents at the corresponding site also increase the elimination rate of esters, though the effects are generally smaller and have been attributed to steric acceleration.[4] For example, at 600 K ethyl acetate (**2**; R^1, R^2 = H, R^3 = Me) is 1.5-fold more reactive than ethyl formate (**2**; R^1, R^2, R^3 = H),[5,6] and isopropyl pivalate (**2**; R^1 = Me, R^2 = H, R^3 = Bu^t) is 1.37-fold more reactive than butyl pivalate (**2**; R^1, R^2 = Me, R^3 = Bu^t).[4] Since the steric environment of ester and vinyl ether eliminations is similar the greater effect in vinyl ethers must be largely electronic in origin. It is noteworthy that in the pyrolysis of β-hydroxyalkenes (**8**), a methyl group at the corresponding position produces a comparable) (8.4-fold) increase in reactivity.[2] This suggests that the mechanism for vinyl ether pyrolysis is intermediate between those for esters and β-hydroxyalkenes, and this conclusion is supported by the previously observed effects of substituents at the α-carbon.

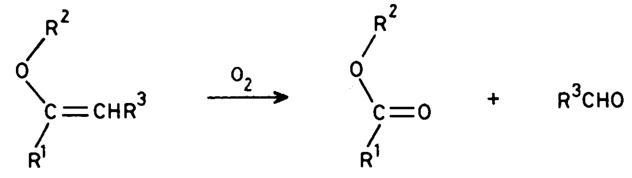

(**8**; R = H, Me, Ph)


(**9 a**; R = Ph
b; R = H)


(**10 a**; R = Ph
b; R = H)

Isopropyl 1-*Phenylvinyl Ether* (**6**; Ar = Ph).—The rate data for this compound (Table 1) show that it eliminates 13.1-fold faster than isopropyl vinyl ether. This rate difference is again much larger than that (2.1—4.0-fold, depending upon the data used for the formate) between the corresponding esters, isopropyl benzoate (**2**; R^1 = Me, R^2 = H, R^3 = Ph),[6] and isopropyl formate (**2**; R^1 = Me, R^2 = H, R^3 = Me).[7,8] For ester elimination the accelerating effect of phenyl is consistent with inductive electron-withdrawal aiding polarization of the C_α–O bond,[4] confirmed by the positive ρ-factors for elimination from substituted benzoates, *e.g.* 0.335 for isopropyl benzoates, (**2**; R^1 = Me, R^2 = H, R^3 = Ar).[9] Given that the transition state for vinyl ether elimination is less *E*1-like than for ester elimination, the phenyl group should increase the rate of elimination less than in the ester case. The larger increase observed suggests that the phenyl group is conjugatively supplying electrons to the double bond, and this is a bigger effect than that of increasing the rate through aiding C_α–O bond breakage. Again it is noteworthy that in β-hydroxyalkenes elimination of phenyl group at the corresponding position also produces a substantial (9.4-fold) increase in reaction rate.

1-*Arylvinyl Isopropyl Ethers* (**6**).—Attempts to obtain a complete set of rate data for these compounds containing 4-MeO, 4-Me, 4-Cl, and 3-NO_2 substitutents were thwarted by the discovery that they undergo oxidation to esters (Scheme) which is so rapid at ambient conditions that neither the 4-MeO nor 4-Me compounds could be obtained pure; the reaction is evidently strongly aided by electron supply to the double bond. Details of this reaction are given in a separate publication.[10] On



Scheme. Atmospheric oxidation of vinyl ethers to esters

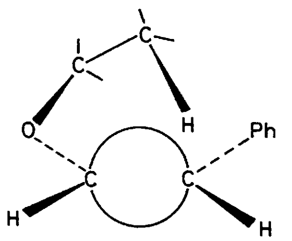


Figure. Non-planar structure of the transition state for vinyl ether pyrolysis

standing, both the 4-Me and 4-OMe compounds also produced isopropyl alcohol due to atmospheric hydrolysis. Vinyl ethers are readily hydrolysed by acids, due to formation of a cation at the carbon bearing the alkoxy group which stabilizes it. In compounds (**6**) the increased electron supply from the aryl group containing the 4-Me and 4-OMe groups is evidently such that acid catalysis of hydrolysis is not needed. Both the 3-NO_2 and 4-Cl compounds produced very small rate increases (Table 1), the 4-Cl compound being the most reactive. The small overall substituent effect and anomalous reactivity order may reflect the dual role for the γ-aryl group postulated above.

Isopropyl cis- *and* trans-*Phenylvinyl Ether* (**7**).—Both these compounds are only slightly more reactive than the unsubstituted parent, isopropyl vinyl ether. This follows because the increased nucleophilicity of the double bond due to the phenyl group is compensated by the loss of conjugation between the double bond and phenyl on going to products. In pyrolysis of β-hydroxyalkenes, the compound with the terminal phenyl group (**9a**) was 4.4-fold less reactive than parent molecule (**9b**).[11] Likewise pyrolysis of the phenyl-substituted alkenoic acid (**10a**) was 7.5-fold slower than pyrolysis of the parent (**10b**),[12] and for both these classes of compounds the loss of conjugation is evidently more serious. This is understandable because in the vinyl ethers there will be conjugation between oxygen and the double bond, so conjugation in the ground state between the latter and the phenyl group will be less.

We believe this is the first kinetic study of thermal elimination in which the effect of stereochemistry about the double bond has been examined and it is noteworthy that there is a difference in the reactivity of the *cis* and *trans* compounds. Some *cis*→*trans* isomerization under the reaction conditions cannot be ruled out, so the true *trans*/*cis* rate ratio may be higher than that observed. Although the transition state for vinyl ether elimination, and similar six-centre electrocyclic reactions, is implicitly planar as normally drawn, it cannot be so because the π-electrons of the double bond are orthogonal to the plane of the orbitals containing the other electrons; moreover, substituents on the α- and β-carbons are eclipsed. Partial twisting of the bonds in the ring must therefore occur[13] (see Figure), hence a rate difference between the geometric isomers could be expected as we have now found. Steric hindrance by the *cis* phenyl group can account for the lower reactivity of the *cis* isomer. The n.m.r. data show the *cis* phenyl ring to be non-coplanar with the double bond, in contrast to the *trans* phenyl group. The latter should therefore lose more conjugation on going to the transition state, so the rate difference due to the steric effect could be greater than actually observed. A non-planar (chair) conformation for the transition state has been proposed for the Claisen rearrangement in view of retention of stereochemistry,[14] and this has been supported by calculations.[15]

Table 2. Rate data for pyrolysis of ethyl vinyl ethers, $R^1CH_2CHR^2$-$OCH{=}CH_2$

R^1	R^2	T/K	10^3k/ s^{-1}	log (A/s^{-1})	E/kJ mol^{-1}	Corr. coeff.	10^3ks^{-1} (600 K)	k_{rel}
H	H			11.78[a]	185.92		0.0391	1.0
Ph	H	615.6	0.363	11.47	192.05	0.999 77	0.151	3.86
		635.2	1.105					
		652.5	2.58					
		666.4	5.00					
H	Ar	Satisfactory data could not be obtained with these compounds due to rearrangement—see text.						

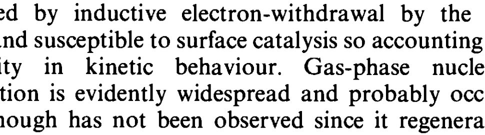
[a] Ref. 2.

2-*Phenylethyl Vinyl Ether* (**4**).—Rate data for this compound (Table 2) show that the phenyl group increases the elimination rate 5.8-fold per β-hydrogen. Substituent effects at the β-position in elimination are difficult to interpret satisfactorily since they are a combination of changing the acidity of the β-hydrogen by inductive effects, stabilization of the forming double bond by conjugative effects, steric acceleration, and even long-range inductive effects upon the remote α-position. The effect (per β-hydrogen) of a 2-phenyl substituent has been measured previously in pyrolysis of ethyl acetate (6.9-fold)[16] and of 1-phenylethyl acetate (3.95-fold).[17] The rate acceleration for esters is consistent with $-I$ electron-withdrawal by the phenyl group increasing the β-hydrogen acidity (2-aryl groups give Hammett correlations with positive ρ-factors).[16,18] The difference in the values for the esters is consistent with the transition state for 1-phenylethyl acetate pyrolysis being more $E1$-like than that for ethyl acetate pyrolysis (so β-C–H bond breaking is less kinetically significant).[18] It is also consistent with there being less conjugation with the forming double bond in the 2-substituted 1-phenylethyl acetate since this is already conjugated with the 1-phenyl group. The 2-phenyl substituent effect in vinyl ether pyrolysis is qualitatively consistent with those in acetate pyrolysis, and this is true also of the effects of β-alkyl-[2] and β-chloro-[19] substituents so the mechanisms of the two reactions are evidently fairly similar.

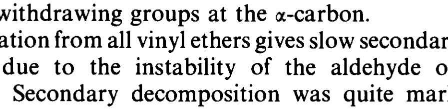
1-*Arylethyl Vinyl Ethers* (**3**).—The behaviour of these compounds was unusual. Preliminary studies with 1-phenylethyl vinyl ether gave good first-order kinetics (though there was a slow secondary reaction) and an excellent Arrhenius plot. However, while the activation energy was reasonable 176.5 kJ mol^{-1}, the log A value, 13.14, seemed rather high. The effect of substituents was also as expected, good first-order kinetics were obtained (after allowing for the secondary decomposition) and the rate data gave a reasonable correlation against σ^+-values, with ρ −0.4 at 600 K, indicating that the α-carbon is electron-deficient, as expected from the effects there of alkyl substituents.[2] However, the stoicheiometry of the reactions was in each case too low (*ca.* 1.5). Subsequently we were unable to reproduce either the quality of the kinetics or the rate data, rate coefficients being *ca.* 50% lower and the effect of substituents appeared indeterminate; the stoicheiometry of the reaction was still too small.

We attribute these anomalies to rearrangement of the vinyl ethers to aldehydes (**11**) (confirmed by g.l.c.–m.s. analysis of reaction products). This is thus analogous to the rearrangement of, for example, *O*-alkyl thioacetates to *S*-alkyl thioacetates (**12**) and likewise of *O,O'*-dialkyl thiocarbonates to *O*-alkyl *S*-alkyl thiocarbonates where low stoicheiometry due to formation of a more stable derivative was also observed.[20] A similar rearrangement has been reported previously for 1-methoxystyrene (which is unable to undergo the normal elimination), and this gave ethyl phenyl ketone,[21] In that work other products were obtained and appeared to have arisen from reaction of the ketone and vinyl ether, with an overall stoicheiometry of 1.0. We also obtained additional products of *m/z* 196, 210, and 210 which are probably 1,2-diphenylpropane, and 1,3- and 2,3-diphenylbutanes, though their mechanism of formation is obscure and probably involves decomposition of the aldehyde; the recently reported[22] addition of aromatics to the styrene (the normal elimination product) may also be involved. Under our conditions the rearrangement is most probably an S_Ni reaction, facilitated by inductive electron-withdrawal by the phenyl group, and susceptible to surface catalysis so accounting for the variability in kinetic behaviour. Gas-phase nucleophilic substitution is evidently widespread and probably occurs for esters though has not been observed since it regenerates the same compound. Partial pyrolysis of ^{18}O-labelled ethyl acetate indicated no scrambling of the label[23] but it is possible that scrambling could be observed with esters containing suitable electron-withdrawing groups at the α-carbon.

Elimination from all vinyl ethers gives slow secondary decomposition due to the instability of the aldehyde or ketone products. Secondary decomposition was quite marked with some of the 1-arylethyl vinyl ethers confirming that the aldehyde rearrangement products (**11**) are particularly unstable. Although acetaldehyde, the normal elimination product is unstable, this was not the primary cause of the secondary decomposition because the extent of the latter was much less for 2-phenylethyl vinyl ether which gives the same products by the normal elimination mechanism; moreover the rate of elimination of acetaldehyde (0.2—3.2 × 10^{-6} s^{-1})[24] is considerably slower than the secondary reaction that we observed. (Kinetics with the isopropyl 2-phenylvinyl ethers were particularly free of secondary decomposition, indicating that the aldehydes $PhCH_2CHO$ are fairly stable.)



(**11**)



(**12**)

Experimental

All compounds were fractionally distilled using a low hold-up Vigraux column of eight theoretical plates.

1-Arylethyl Vinyl Ethers and 2-Phenylethyl Vinyl Ether.— These were each prepared by the mercury(II) acetate-catalysed reaction between the corresponding alcohol and ethyl vinyl ether (distilled to remove stabilizer). In a typical preparation, alcohol (25 g), mercury(II) acetate (1 g), and ethyl vinyl ether (140 g) were heated under reflux during 8—48 h (longer times were needed for compounds possessing electron-withdrawing substituents). During work-up, the low-boiling fractions were removed rapidly using a rotary evaporator, to prevent the reverse equilibrium, which reforms starting materials, becoming significant. If the crude product thus obtained showed that insufficient vinyl ether had been produced, further ethyl vinyl ether was added, and heating continued. As noted by Watanabe and Conlon,[25] a side-reaction between the vinyl ether product and unchanged alcohol leads to acetals. We found this especially troublesome, especially if n-butyl vinyl ether was used instead of ethyl vinyl ether (both are commercially available), due probably to the greater electron-supplying effect of the butyl group, and the higher temperature of reflux. Preliminary experiments also showed that much acetal formation occurred during fractional distillation, presumably as the pot temperature increased. Acetal formation could be suppressed by adding sodium carbonate to the reaction mixture, prior to fractional distillation. In this way each of the eight vinyl ethers described below were obtained. G.l.c.-m.s. analysis of 1-phenylethyl vinyl ether showed the presence of a very small amount (<0.5%) of ethyl 1-phenylethyl ether, evidently produced in the exchange reaction with ethyl vinyl ether; it is probable that similar very small quantities of the corresponding ethers are generally present in vinyl ethers produced in this way.

1-*Phenylethyl Vinyl Ether.*—Reaction of 1-phenylethanol as described above gave 1-*phenylethyl vinyl ether* (45%), b.p. 55 °C at 3.5 mmHg; n_D^{20} 1.5062 (Found: C, 80.6; H, 8.1. $C_{10}H_{12}O$ requires C, 81.0; H, 8.2%); δ($CDCl_3$) 7.32 (5 H, s, ArH), 6.33 (1 H, dd, CH=), 4.87 (1 H, q, CH), 4.25 (1 H, dd, *cis*-CH_2), 3.96 (1 H, dd, *trans*-CH_2), and 1.48 (3 H, d, Me).

1-(3-*Tolyl)ethyl Vinyl Ether.*—1-(3-*Tolyl)ethanol.* This compound, b.p. 61—64 °C at 0.35 mmHg, n_D^{20} 1.5223 was obtained in *ca.* quantitative yield by sodium borohydride reduction of 3-methylacetophenone. Reaction of the alcohol as above gave 1-(3-*tolyl)ethyl vinyl ether* (42%), b.p. 40 °C at 0.45 mmHg; n_D^{20} 1.5056 (Found: C, 81.0; H, 8.5. $C_{11}H_{14}O$ requires: C, 81.4; H, 8.7%); δ($CDCl_3$) 7.30—7.05 (4 H, m, ArH), 6.33 (1 H, dd, CH), 4.83 (1 H, q, CH), 4.23 (1 H, dd, *cis*-CH_2), 3.95 (1 H, dd, *trans*-CH_2), 2.30 (3 H, s, ArMe), and 1.48 (3 H, d, Me).

1-(4-*Tolyl)ethyl vinyl ether.* 1-(4-*Tolyl)ethanol.* This compound, b.p. 62 °C at 0.35 mmHg, was obtained in *ca.* quantitative yield by sodium borohydride reduction of 4-methylacetophenone. Reaction of the alcohol as above gave 1-(4-*tolyl)ethyl vinyl ether* (46%), b.p. 45 °C at 0.50 mmHg; n_D^{20} 1.5042 (Found: C, 81.8, H, 8.6%); δ($CDCl_3$) 7.16 (4 H, s, ArH), 6.31 (1 H, dd, CH), 4.83 (1 H, q, CH), 4.22 (1 H, dd, *cis*-CH_2), 3.93 (1 H, dd, *trans*-CH_2), 2.29 (3 H, s, ArMe), and 1.48 (3 H, d, Me).

1-(4-*Methoxyphenyl)ethyl Vinyl Ether.*—1-(4-*Methoxyphenyl)ethanol.* This compound, b.p. 81 °C at 0.25 mmHg, was obtained in *ca.* quantitative yield by sodium borohydride reduction of 4-methoxyacetophenone. Reaction of this alcohol as above gave 1-(4-*methoxyphenyl)ethyl vinyl ether* (38%), b.p. 66 °C at 0.45 mmHg; n_D^{20} 1.5164 (Found: C, 74.4; H, 8.4. $C_{11}H_{14}O_2$ requires C, 74.3; H, 7.9%); δ($CDCl_3$) 7.30—6.86 (4 H, dd, ArH), 6.33 (1 H, dd, CH), 4.85 (1 H, q, CH), 4.25 (1 H, dd, *cis*-CH_2), 3.96 (1 H, dd, *trans*-CH_2), 3.75 (3 H, s, MeO), and 1.48 (3 H, d, Me).

1-(4-*Fluorophenyl)ethyl Vinyl Ether.*—1-(4-*Fluorophenyl)ethanol.* This compound, b.p. 70 °C at 4 mmHg, was obtained by reaction of acetaldehyde with the Grignard reagent prepared from 4-bromofluorobenzene. Reaction of the alcohol as above gave 1-(4-*fluorophenyl*)*ethyl vinyl ether* (42%), b.p. 54 °C at 6 mmHg; n_D^{20} 1.4862 (Found: C, 72.6; H, 6.9. $C_{10}H_{11}FO$ requires C, 72.4; H, 6.9%); δ($CDCl_3$) 7.38—6.93 (4 H, m, ArH), 6.32 (1 H, dd, CH), 4.87 (1 H, q, CH), 4.25 (1 H, dd, *cis*-CH_2), 3.97 (1 H, dd, *trans*-CH_2), and 1.45 (3 H, d, Me).

1-(4-*Chlorophenyl*)*ethyl Vinyl Ether*.—1-(4-*Chlorophenyl*)-*ethanol*. This compound, b.p. 72 °C at 0.5 mmHg, n_D^{20} 1.5425, was obtained in *ca.* quantitative yield by sodium borohydride reduction of 4-chloroacetophenone. Reaction of the alcohol as above gave 1-(4-*chlorophenyl*)*ethyl vinyl ether* (32%), b.p. 60 °C at 0.65 mmHg; n_D^{20} 1.5217 (Found: C, 65.8; H, 6.1. $C_{10}H_{11}ClO$ requires C, 65.8; H, 6.0%); δ($CDCl_3$) 7.28 (4 H, s, ArH), 6.31 (1 H, dd, CH), 4.86 (1 H, q, CH), 4.22 (1 H, dd, *cis*-CH_2), 3.97 (1 H, dd, *trans*-CH_2), and 1.45 (3 H, d, Me).

1-(3-*Chlorophenyl*)*ethyl Vinyl Ether*.—1-(3-*Chlorophenyl*)-*ethanol*. This compound, b.p. 72 °C at 0.4 mmHg, n_D^{20} 1.5394, was obtained by the reaction of acetaldehyde with the Grignard reagent prepared from 3-bromochlorobenzene. Reaction of this alcohol as above gave 1-(3-*chlorophenyl*)*ethyl vinyl ether* (35%), b.p. 60 °C at 0.65 mmHg; n_D^{20} 1.5220 (Found: C, 65.6; H, 6.0%); δ($CDCl_3$) 7.36—7.18 (4 H, m, ArH), 6.32 (1 H, dd, CH), 4.85 (1 H, q, CH), 4.22 (1 H, dd, *cis*-CH_2), 3.99 (1 H, dd, *trans*-CH_2), and 1.46 (3 H, s, Me).

2-*Phenylethyl vinyl ether*. Reaction of 2-phenylethanol (Aldrich) as above gave 2-*phenylethyl vinyl ether* (60%), b.p. 56 °C at 2 mmHg; n_D^{20} 1.5125 (Found: C, 80.8; H, 8.1%); δ($CDCl_3$) 7.22 (5 H, s, ArH), 6.41 (1 H, dd, CH), 4.07 (1 H, dd, *cis*-CH_2), 3.95 (1 H, dd, *trans*-CH_2) 3.87 (2 H, t, CH_2), and 2.95 (2 H, t, CH_2).

1-*Arylvinyl Isopropyl Ethers and Isopropyl* cis- *and* trans-2-*Phenylvinyl Ethers and Isopropenyl Isopropyl Ether*.—These were each prepared by formation of the dimethoxy acetal from the corresponding aldehyde or ketone according to the method of Bogert and Herrera.[26] These intermediates were then converted into the di-isopropyl acetals by alkyl-group interchange according to the literature method,[27] which involved very slow azeotropic distillation during 10—15 days for each compound. Elimination, catalysed by toluene-4-sulphonic acid (*ca.* 5 mg), then yielded the vinyl ether.[28] We found that the quantity of toluene-4-sulphonic was critical; in a preliminary experiment in which 2,2-di-isopropoxypropane (20 g) was treated with acid (1 g), fractional distillation yielded di-isopropyl ether, acetone, and isopropyl alcohol, but no vinyl ether. These products indicate that the vinyl ether underwent further elimination to propyne; the ether and acetone could also have been produced by four-centre elimination from the acetal derived from the corresponding ketone.

For some compounds, particularly those possessing electron-supplying groups in the aryl ring, polymerization of the product vinyl ether occurred. The required vinyl ether could here be obtained more satisfactorily by slow fractional distillation of the di-isopropoxy compound in the absence of the catalysing acid; thermal elimination generated the vinyl ether which was removed as it was formed.

Isopropenyl Isopropyl Ether.—2,2-*Di-isopropoxypropane*. Reaction of 2,2-dimethoxypropane (Aldrich) as above gave, on fractional distillation, 2,2-di-isopropoxypropane (15%), b.p. 85 °C at 150 mmHg; n_D^{20} 1.3989 (lit.,[27] b.p. 41 °C at 5.0 mmHg; n_D^{20} 1.3897, but given as 1.3917 after redistillation; we believe decomposition may have occurred during this); δ($CDCl_3$) 4.03 (1 H, sept, CH), 1.33 (3 H, s, Me), and 1.15 (6 H, d, Me). Elimination as described gave isopropenyl isopropyl ether, b.p. 75 °C at 150 mmHg; n_D^{20} 1.3928; δ($CDCl_3$) 4.23 (1 H, sept, CH), 3.87, 3.80 (2 H, s, *cis*- and *trans*-CH_2), 1.77 (3 H, s, Me), and 1.24 (6 H, d, Me). We confirm the literature report[3] that it is necessary to wash with water prior to distillation, the reason being that the product and isopropyl alcohol form an azeotrope which cannot be fractionally separated.

In a preliminary experiment in which an excess of acid was used to catalyse the elimination, the products were indicated by n.m.r. to be di-isopropyl ether and acetone.

Isopropyl 1-*Phenylvinyl Ether*.—1,1-*Dimethoxy*-1-*phenylethane*. Reaction of acetophenone as above gave 1,1-dimethoxy-1-phenylethane (94%), b.p. 66 °C at 5.8 mmHg; n_D^{20} 1.4902 (lit.,[24] b.p. 90 °C at 20 mmHg); δ($CDCl_3$) 7.55—7.25 (5 H, m, ArH), 3.24 (6 H, s, OMe), and 1.52 (3 H, s, Me).

1,1-*Di-isopropoxy*-1-*phenylethane*. Reaction of the dimethoxy acetal as above gave, on distillation, two main fractions, b.p. 76—82 °C at 6 mmHg; n_D^{20} 1.5090, and 70 °C at 2 mmHg; n_D^{20} 1.4770. Both contained a mixture of 1,1-di-isopropoxy-1-phenylethane and the required isopropyl 1-phenylvinyl ether, none of the latter being present in the lower boiling fraction. (Note that g.l.c. analysis of these products is difficult because both 1,1-dialkoxy compounds undergo on-column elimination.) Treatment of the higher boiling fraction with toluene-4-sulphonic acid produced extensive decomposition and polymerization. Therefore the lower boiling fraction was fractionally distilled using a very high reflux ratio so that thermal elimination occurred to give isopropyl 1-phenylvinyl ether, b.p. 75 °C at 4.5 mmHg; n_D^{20} 1.5133; δ($CDCl_3$) 7.69—7.56 (2 H, m, ArH), 7.41—7.23 (3 H, m, ArH), 4.65 (1 H, d, CH_2), 4.37 (1 H, sept, CH), 4.16 (1 H, d, CH_2), and 1.30 (6 H, d, Me). On storage this compound undergoes slow oxidation to form isopropyl benzoate, indicated by the appearance in the n.m.r. spectrum of peaks at δ 8.13—7.89, due to the *ortho* aromatic protons in the ester, and confirmed by kinetic studies.[10]

1-(4-*Chlorophenyl*)*vinyl Isopropyl Ether*.—1,1-*Dimethoxy*-1-(4-*chlorophenyl*)*ethane*. Reaction of 4-chloroacetophenone as above gave 1,1-dimethoxy-1-(4-chlorophenyl)ethane (95%), b.p. 56—75 °C at 0.3 mmHg; n_D^{20} 1.5062.

1,1-*Di-isopropoxy*-1-(4-*chlorophenyl*)*ethane*. Reaction of the dimethoxy acetal as described above gave, on fractional distillation, four fractions which n.m.r. showed to have the following composition: b.p. 52 °C at 0.3 mmHg (mainly 4-chloroacetophenone), two fractions b.p. 65 °C at 0.2 mmHg, n_D^{20} 1.5283 (87% vinyl ether) and n_D^{20} 1.5255 (80% vinyl ether), b.p. 80 °C at 0.2 mmHg; n_D^{20} 1.4957 [1,1-di-isopropoxy-1-(4-chlorophenyl)-ethane]. The latter three fractions were combined and fractionally distilled using a very high reflux ratio, to give 1-(4-chlorophenyl)vinyl isopropyl ether (45%), b.p. 61 °C at 0.25 mmHg; n_D^{20} 1.5328; δ($CDCl_3$) 7.55 (2 H, d, ArH), 7.27 (2 H, d, ArH), 4.67 (1 H, d, CH_2), 4.41 (1 H, sept, CH), 4.21 (1 H, d, CH_2), and 1.34 (6 H, d, Me). After long storage this compound also shows peaks at δ 8.17—7.82 due to oxidation to isopropyl 4-chlorobenzoate.

Isopropyl 1-(3-*Nitrophenyl*)*vinyl Ether*.—1,1-*Dimethoxy*-1-(3-*nitrophenyl*)*ethane*. Reaction of 3-nitroacetophenone as above gave 1,1-dimethoxy-1-(3-nitrophenyl)ethane (88%), b.p. 130 °C at 0.3 mmHg; m.p. 42 °C.

1,1-*Di-isopropoxy*-1-(3-*nitrophenyl*)*ethane*. Reaction of the dimethoxy acetal as above gave, on fractional distillation, a number of fractions ranging from 94 °C at 0.25 mmHg, n_D^{20} 1.5195 (yellow) to 103 °C at 0.25 mmHg, n_D^{20} 1.5015 (lemon). N.m.r. indicated that along this series: (a) the amount of 3-nitroacetophenone present in the fractions diminished, (b) the amount of the di-isopropyl acetal increased, and (c) the required vinyl ether was present in each sample, but a minor component. It appeared therefore that thermal elimination was here unsatisfactory as a means of producing the vinyl ether, the alternative elimination to the ketone and di-isopropyl ether tending to dominate. The fractions were therefore combined and distilled from toluene-4-sulphonic acid to give isopropyl-1-(3-nitrophenyl)vinyl ether, b.p. 96 °C at 0.15 mmHg; n_D^{20} 1.5420; δ($CDCl_3$) 8.43 (1 H, s), 8.14 (1 H, d), 7.93 (1 H, d), 7.46 (1 H, t, all ArH and with additional splitting), 4.80 (1 H, d, CH_2), 4.44 (1 H, sept., CH), 4.33 (1 H, d, CH_2), and 1.33 (6 H, d, Me). The n.m.r. spectrum indicated that *ca.* 5% of 3-nitroacetophenone remained in this fraction, but since this was not expected to interfere with the kinetics, further purification was not attempted. A sample of this vinyl ether which was re-examined after standing during 3 years showed no sign of any oxidation.

Isopropyl 1-(4-*Tolyl)vinyl Ether*.—1,1-*Dimethoxy*-1-(4-*tolyl*)-*ethane*. Reaction of 4-methylacetophenone as above gave 1,1-dimethoxy-1-(4-methylphenyl)ethane (96%), b.p. 78 °C at 5.8 mmHg; n_D^{20} 1.4908.

1,1-*Di-isopropoxy*-1-(4-*tolyl*)*ethane*. Reaction of the dimethoxy acetal as above gave, on fractional distillation, a number of fractions containing the reformed ketone, required vinyl ether, and di-isopropyl acetal in various proportions, but repeated fractional distillation failed to produce pure vinyl ether (for reasons which became evident later—see below). The combined fractions were redistilled from toluene-4-sulphonic acid to give a fraction indicated to be almost pure (>97%) isopropyl 1-(4-tolyl)vinyl ether; δ($CDCl_3$) 7.47 (2 H, d, ArH), 7.06 (2 H, d, ArH), 4.57 (1 H, d, CH_2), 4.34 (1 H, sept, CH), 4.08 (1 H, d, CH_2), 2.25 (3 H, s, Me), and 1.33 (6 H, d, Me). This compound could not be obtained completely pure because it undergoes very rapid atmospheric oxidation even at room temperature, so that oxygen leaking into the heated fractionating column would be sufficient to cause some conversion into isopropyl 4-methylbenzoate, indicated by appearance in the n.m.r. spectrum of peaks at δ($CDCl_3$) 8.02—7.88 (2 H, m, ArH, *ortho* to C=O), 7.38—7.22 (3 H, m, ArH), 5.24 (1 H, sept, CH), 2.38 (3 H, s, ArMe), and 1.35 (6 H, s, Me). The oxidation is however not the only reaction occurring because an additional isopropyl group appears at δ($CDCl_3$) 4.03 (1 H, sept, CH) and 1.20 (6 H, d, Me), corresponding to isopropyl alcohol and confirmed by g.l.c.-m.s. analysis. This must be due to atmospheric hydrolysis, and since the same reaction occurs with the 4-methoxy compound (below) it is evidently aided by electron supply to the double bond.

Isopropyl 1-(4-*Methoxyphenyl)vinyl Ether*.—1,1-*Dimethoxy*-1-(4-*methoxyphenyl*)*ethane*. Reaction of 4-methoxyacetophenone as above gave 1,1-dimethoxy-1-(4-methoxyphenyl)ethane (93%), b.p. 64 °C at 0.15 mmHg; n_D^{20} 1.5020.

1,1-*Di-isopropoxy*-1-(4-*methoxyphenyl*)*ethane*. Reaction of the dimethoxy acetal as above, and slow fractional distillation without the acid catalyst, gave a number of fractions, b.p. 77—95 °C at 0.35 mmHg, containing varying amounts of the dimethoxy acetal, di-isopropyl acetal, 4-methoxyacetophenone, and the required vinyl ether. Redistillation of the fractions containing substantial amounts of the latter gave isopropyl 1-(4-methoxyphenyl)vinyl ether, b.p. 83 °C at 0.4 mmHg; n_D^{20} 1.5300; δ($CDCl_3$) 7.52 (2 H, d, ArH), 6.81 (2 H, d, ArH), 4.54 (1 H, d, CH_2), 4.39 (1 H, q, CH), 4.07 (1 H, d, CH_2), 3.82 (3 H, s, ArMe), and 1.30 (6 H, d, Me); the asymmetry of some of the peaks, and a peak between δ 2.04—1.84, indicated the presence of isopropyl 4-methoxybenzoate arising from oxidation of the ether. Separation from this impurity proved impossible because of the great ease of this oxidation of the ether. On standing the ether produces isopropyl alcohol, as does the 4-methyl ether above.

Isopropyl cis- *and* trans-2-*Phenylvinyl Ether*.—*Phenylacetaldehyde di-isopropyl acetal*. Reaction of phenylacetaldehyde dimethyl acetal (Aldrich) as for the dimethoxy acetals above gave phenylacetaldehyde di-isopropyl acetal, b.p. 92 °C at 3.5 mmHg. To this was added a catalytic amount of toluene-4-sulphonic acid and the mixture was fractionally distilled very slowly into two main fractions, b.p. 76 and 82 °C and 3.5 mmHg. These contained mainly the *trans*- and *cis*-vinyl ether, respectively; there was a third, intermediate fraction. Note that the *trans*-isomer has the *lower* b.p. which is very unusual. The intermediate fraction was further distilled into mainly *cis* and *trans* fractions. The *cis*-rich and *trans*-rich fractions were then separately combined and fractionally distilled to give pure pale lemon isopropyl *cis*- and *trans*-2-phenylvinyl ether, b.p. 44 and 46 °C at 2.5 mmHg; n_D^{20} 1.5386 (both); δ($CDCl_3$) (*cis*) 7.63—7.54 (2 H, m, *ortho*-ArH), 7.35—7.10 (3 H, m, ArH), 7.21 (1 H, d, *J* 7 Hz, CH), 5.17 (1 H, d, *J* 7 Hz, CH), 3.99 (1 H, q, CH), and 1.28 (6 H, d, Me); (*trans*) 6.98 (5 H, s, ArH), 6.65 (1 H, d, *J* 19 Hz, CH), 5.71 (1 H, d, *J* 19 Hz, CH), 3.97 (1 H, q, CH), and 1.22 (6 H, d, Me). The shift of the *ortho*-protons to lower field in the *cis* compound is consistent with the phenyl ring being twisted out of the plane of the double bond.

On standing the *cis* compound rapidly oxidized to benzaldehyde (and hence benzoic acid) and isopropyl formate, these products being identified by g.l.c.-m.s. analysis.

Kinetic Studies.—The general kinetic method has been described previously.[28] For pyrolysis of compounds (**4**), (**5**), and (**7**), excellent and reproducible first-order kinetics were obtained and rates were independent of a five-fold variation in the initial pressure of reagent. The reaction stoicheiometry was 2.0 ± 0.03, and there was no significant secondary decomposition during the time of the primary elimination. The reaction products were only those expected from the normal elimination.

Compounds (**3**) gave satisfactory first-order kinetics after correction for the secondary reaction which took place at *ca.* 5—10% of the rate of the primary elimination. However, the stoicheiometry within the time of the primary elimination was only *ca.* 1.5 and g.l.c.-m.s. analysis of the reaction products showed the formation of an isomer of longer retention time and *m*/*z* 148, with fragments at 133, 119, 105, 91, and 77. After warming of the product to remove acetaldehyde formed by the normal elimination, i.r. showed a peak of 1 730 cm^{-1}, confirming the presence of the aldehyde rearrangement product.

Compounds (**4**) containing the 4-H, 4-Cl, and 3-NO_2 substituents also gave excellent first-order kinetics with no significant secondary decomposition, and only the expected reaction products were obtained. However, the 4-Me and 4-OMe derivatives decomposed unexpectedly rapidly, confirming that oxidation had partially occurred to give the corresponding isopropyl benzoates. For one sample of the methoxy compound oxidation was total and the rate of elimination was identical to the literature elimination rate for the benzoate.[9]

Rate data for those compounds which eliminated by the normal mechanism and gave satisfactory kinetics are given in Tables 1 and 2.

Acknowledgements

We thank Mr. A. Greenaway from the g.l.c.-m.s. analyses.

References

1 Part 25, R. Taylor, *J. Chem. Soc.. Perkin Trans. 2*, 1988, 183.
2 I. McEwen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1179.
3 M. C. Flowers and M. R. Honeyman, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 1923.
4 R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1255.

5 R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1025.
6 A. T. Blades and H. S. Sandhu, *Int. J. Chem. Kinet.*, 1971, **3**, 187.
7 A. T. Blades, *Can. J. Chem.*, 1954, **32**, 366.
8 R. B. Anderson and H. H. Rowles, *J. Phys. Chem.*, 1943, **47**, 454.
9 G. G. Smith, D. A. K. Jones, and D. F. Brown, *J. Org. Chem.*, 1963, **28**, 403.
10 R. Taylor, *J. Chem. Res. (S)*, 1987, 178.
11 G. G. Smith and K. J. Vorhees, *J. Org. Chem.*, 1970, **35**, 2182; 1971, **36**, 1755.
12 D. B. Bigley and R. W. May, *J. Chem. Soc. B*, 1967, 558.
13 R. Taylor, 'The Chemistry of the Functional Groups, Supplementary Volume B. Acid Derivatives,' ed. S. Patai, Wiley, London, 1979, p. 883.
14 E. N. Marvell, J. L. Stephenson, and J. Ong. *J. Am. Chem. Soc.*, 1965, **87**, 1267; H. L. Goering and W. I. Kinoto, *ibid.*, p. 1748.
15 M. Simonetta and G. Favini, *Tetrahedron Lett.*, 1966, 4837.
16 S. de Burgh Norfolk and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1976, 280.
17 G. G. Smith, F. D. Bagley, and R. Taylor, *J. Am. Chem. Soc.*, 1961, **83**, 3647.
18 Ref. 13, p. 898.
19 T. O. Bamkole and E. U. Emovon, *J. Chem. Soc. B*, 1968, 332.
20 Part 24, N. Al-Awadi and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1988, 177.
21 W. M. Lauer and M. A. Spielman, *J. Am. Chem. Soc.*, 1933, **55**, 4923.
22 A. I. Grushin, V. V. Grigor'ev, K. V. Prokof'ev, and N. M. Kozlova, *J. Org. Chem. USSR (Engl. Transl.)*, 1985, **21**, 1991.
23 G. G. Smith, K. J. Vorhees, and F. M. Kelly, *Chem. Commun.*, 1971, 789.
24 T. Bérces, 'Comprehensive Chemical Kinetics,' 1972, vol. 5, p. 234.
25 W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, 1957, **79**, 2828.
26 M. T. Bogert and P. R. Herrera, *J. Am. Chem. Soc.*, 1923, **45**, 238.
27 W. L. Howard and N. B. Lorette, *J. Org. Chem.*, 1960, **25**, 525.
28 Part 19, N. Al-Awadi and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1581.

Received 13*th May* 1987; *Paper* 7/841