The Mechanism of Thermal Eliminations. Part 25.[1] Arrhenius Data for Pyrolysis of Isochroman-3-one, Benzyl Methyl Ether, 2-Hydroxyethylbenzene, Phenyl Acetate, and 3,4-Dihydro-2*H*-pyran

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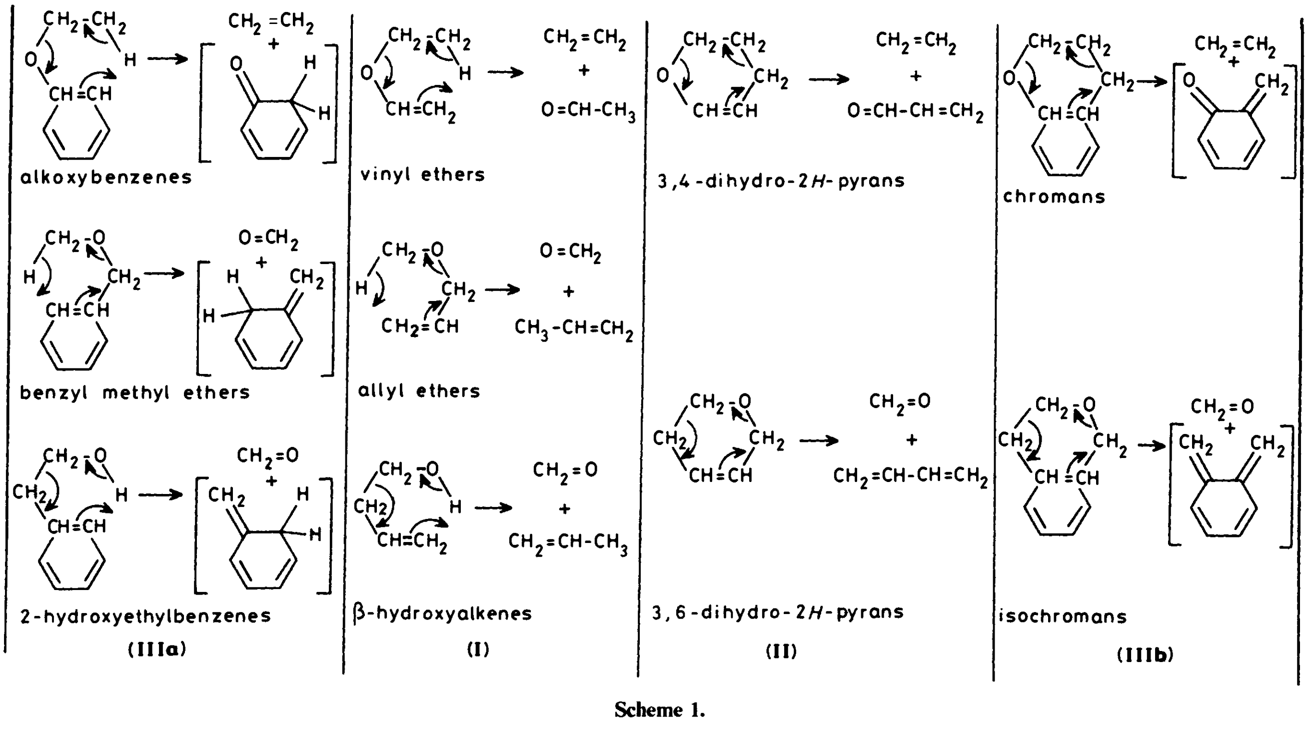
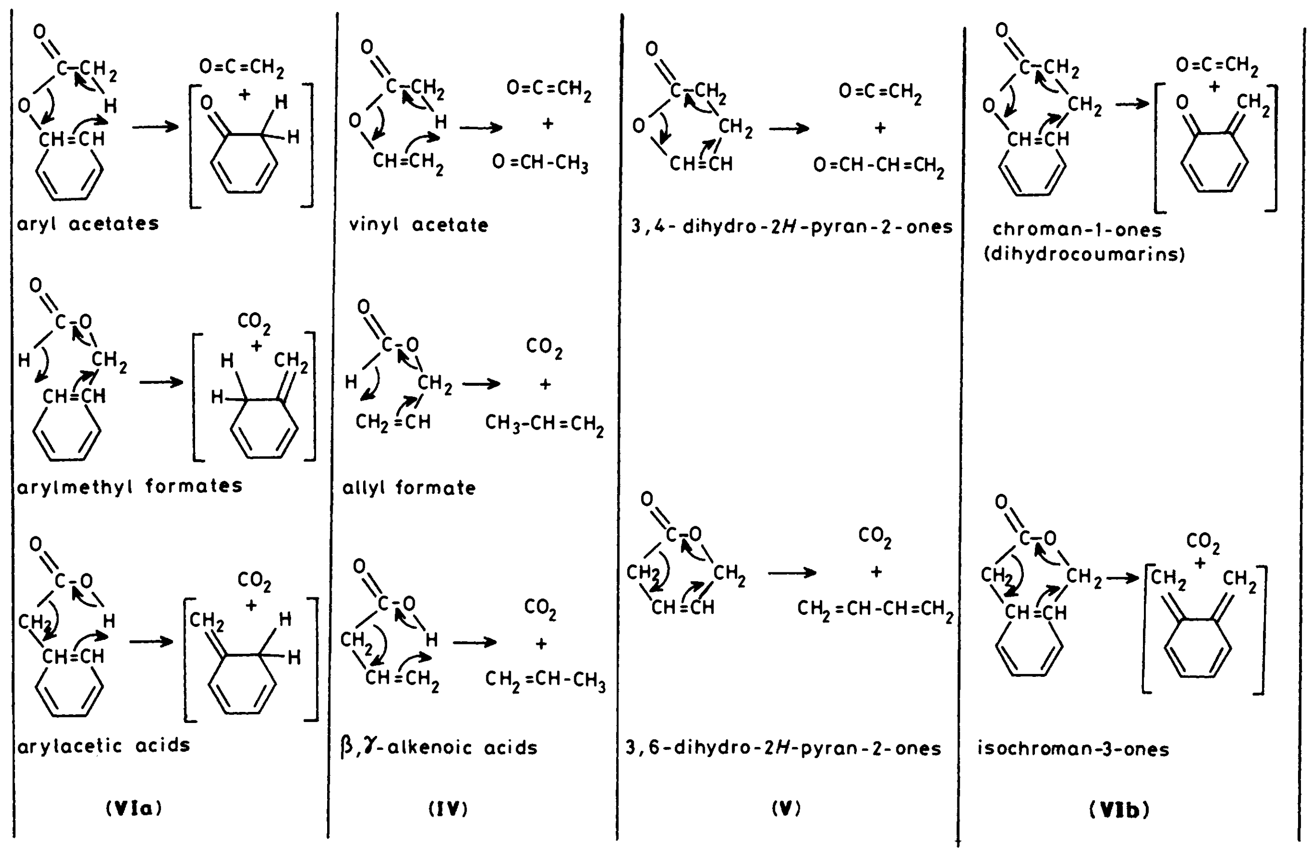
The thermal decomposition of isochroman-3-one to benzocyclobutene and carbon dioxide, of benzyl methyl ether and 2-hydroxyethylbenzene to toluene and formaldehyde, and of phenyl acetate to phenol and ketene are each first-order unimolecular reactions. The Arrhenius parameters [E/kJ mol^{-1}, log (A/s^{-1})] are 221.1, 14.305; 231.7, 12.92; 200.5, 11.21; and 221.8, 11.78, respectively. The frequency factors indicate that each reaction involves a cyclic semi-concerted mechanism; for phenyl acetate this is a four-centre process analogous to that involved in the formation of ketene from pyrolysis of either acetic acid, acetyl bromide, or acetamide. The higher log (A/s^{-1}) value for isochroman-3-one is typical of elimination from cyclic compounds, because their ground states are already constrained into the geometry required in the transition state. Chroman-1-one (dihydrocoumarin) is very much more stable than isochroman-3-one (and on decomposition gives mainly coumarin and benzo[*b*]furan, evidently due to the favourable gain in aromaticity). Decomposition of 3,4-dihydro-2*H*-pyran into ethene and propenal takes place according to the rate equation log k = 13.556 − 209.01/19.142 K, the rate coefficients being lower than the literature values which may therefore have been affected by surface catalysis. A 2-methyl group in the pyran produces a *ca.* 4.5-fold rate acceleration, very similar to that produced in the analogous vinyl ethers. The relationship between the elimination rates for a range of cyclic compounds and their open-chain counterparts is examined and it is found that their reactivities are closely similar. Hydrogen is shown to be transferred as an incipient anion in allyl ether pyrolysis, whereas in most eliminations it is transferred as an incipient cation.

For a number of compounds which undergo thermal elimination *e.g.* (I) (Scheme 1), there exist structurally similar cyclic compounds that undergo the related eliminations (II) (Scheme 1). The alkene double bond in each set may be part of an aromatic ring, giving compounds (**IIIa, b**) which correspond to (I) and (II), respectively. No examination of the relationship between the elimination rates of the three classes of compounds has hitherto been made. Many more compounds can exist than those shown in (I)—(III). For example O may be replaced either by S or by NH. A CH_2 group may also be replaced by a CO group to give the compounds (IV)—(VI) shown in Scheme 2. (The compounds in Schemes 1 and 2 are the simplest class



Scheme 1.



Scheme 2.

members and the rates of thermal decomposition of some of them by the mechanism shown are not yet known; in one case it turns out that an alternative four-centre process becomes preferred.) Some qualitative studies of the pyrolysis of the aromatic compounds (**IIIb**) and (**VIb**) have been carried out.[2] These showed that chroman and isochroman give products additional to the intermediates shown, and the latter undergo further electrocyclic rearrangement to give, for example, benzocyclobutene from both isochroman[2] and isochroman-3-one.[3]

In order to evaluate the rate relationship outlined above, and also to confirm that the reported elimination of carbon dioxide from isochroman-3-one takes place *via* a six-centre process, we have measured the pyrolysis rates for this compound. We have also measured pyrolysis rates for benzyl methyl ether, 2-hydroxyethylbenzene, and phenyl acetate, and remeasured the rates of elimination for 3,4-dihydro-2*H*-pyran since the Arrhenius parameters given in the literature for this compound do not correspond with the rate data reported.[4] We have also obtained some limited data for the rate of elimination of its 2-methyl derivative.

Results and Discussion

*Isochroman-*3-*one.*—This compound was well behaved kinetically, and underwent first-order thermal decomposition to >95% reaction. The product of the reaction has previously been shown to be benzocyclobutene[3] arising from electrocyclic ring closure of the intermediate *o*-quinodimethane. Rates at any temperature (Table 1) were reproducible to within ±3% and the data gave a good Arrhenius line with no points deviating significantly from the correlation line. The log (A/s^{-1}) value of 14.305 is typical for cyclic compounds which undergo six-centre electrocyclic elimination (see Table 2) and supports the previous proposal of this mechanism for its decomposition.[3]

*Chroman-*1-*one.*—This compound gave poor kinetics. At 766.8 K it underwent elimination in an approximately first-order reaction, giving $k = 6.7 \times 10^{-5}\ \mathrm{s}^{-1}$, so it is *ca.* 250-fold less reactive than isochroman-3-one. Product runs showed that the major reaction was not the elimination given in Scheme 2, but rather dehydrogenation to give the aromatic coumarin, and hence benzo[*b*]furan by extrusion of carbon monoxide,[5] these being the main products (*ca.* 90%). Evidently the gain in aromaticity provides the driving force for these reaction. Other products were toluene, ethylbenzene, styrene, 2-methylphenol, benzyl methyl ether, and an unidentified compound (possibly indanone) giving *m*/*e* 132. These show that there was a radical component in the eliminations, suggested also by the highly coloured products. By contrast, the other compounds examined in this paper gave products with very little colouration.

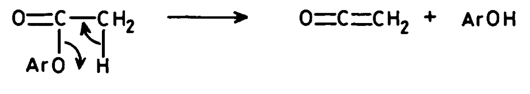
Benzyl Methyl Ether.—This gave very good first-order kinetics and the rate data are given in Table 1. N.m.r. analysis of the products showed the presence only of toluene, the product expected from the reaction given in (**IIIa**) (Scheme 1). Mass spectrometric–g.l.c. analysis confirmed toluene to be >95% of the product, and identified as minor components benzene, biphenyl, bibenzyl, ethylbenzene, and (probably) isopropylbenzene; these latter would be produced from minor radical reactions, which may be ruled out as responsible for the primary elimination by virtue of the reproducibility of the rate data, lack of scatter of the Arrhenius plot, invariance of rate with reagent quantity, and the magnitude of both the activation energies and log *A* values.

2-*Hydroxyethylbenzene.*—Although our analysis (**IIIa**) (Scheme 1) had led us to predict that toluene would be obtained from pyrolysis of 2-hydroxyethylbenzene we anticipated that dehydration to give styrene might be the dominant reaction.

[Dehydration did not accompany the related pyrolysis of 2-(2-hydroxyethyl)pyridine[6] but for that reaction nucleophilic attack by the more polar C=N bond would be expected to favour the reaction corresponding to that given in Scheme 1.] Surprisingly therefore, toluene constituted 90% of the reaction product and styrene only 10%. Other products formed in trace amounts (undetectable by Fourier transform n.m.r., but identified by m.s.–g.l.c.) were ethylbenzene, biphenyl, bibenzyl, and (probably) 2-methoxyethylbenzene; again minor radical processes could account for the formation of these. Very good reproducible first-order kinetics were obtained with this compound (Table 1), with no deviant points on the Arrhenius plot, indicating the absence of any significant radical component of the main reaction.

Phenyl Acetate.—Pyrolysis of phenyl acetate was first studied by Hurd and Blunck, who found rapid decomposition at 900 K into phenol and ketene.[7] They suggested that the mechanism given in Scheme 2 might be accompanied by a radical-chain mechanism (1). This conclusion was based upon the low reactivity of the compound, though this feature is in fact compatible with the six-centre electrocyclic mechanism, the π-electrons of the aromatic ring being involved. The radical-chain mechanism was apparently confirmed using CD_3COOPh by Barefoot and Carroll[8] who found no deuterium in the aromatic ring of the product. However, Nishida *et al.*[9] while confirming the absence of deuterium in the aromatic ring, found the yield of phenol and ketene to be pressure independent so discounting the radical-chain mechanism, and they concluded that a four-centre process (2) applies. This is thus analogous to the four-centre processes proposed to account for the formation of ketene in pyrolysis of the structurally similar acetic acid, acetyl bromide, and acetamide.[10]

$$\begin{aligned} &PhO\cdot + CH_3COOPh \longrightarrow PhOH + \cdot CH_2COOPh \\ &\cdot CH_2COOPh \longrightarrow CH_2CO + PhO\cdot \end{aligned} \qquad (1)$$



$$O{=}C(OAr){-}CH_2H \longrightarrow O{=}C{=}CH_2 + ArOH \qquad (2)$$

Our kinetic data indicate that some radical processes occur. In preliminary runs reproducibility could not be obtained and the reactions were not first order; the minimum rate coefficients at a given temperature also showed scatter on the Arrhenius plot. However, after carrying out a large number of runs at 775 K (high temperature is, in our experience, always more effective at suppressing surface catalysis) good, reproducible, first-order kinetics were obtained and these were unaffected by varying the amount of reagent. The rate coefficients were now 2—3-fold lower and these data gave an excellent Arrhenius plot. There was in each run an initial fast reaction, but after *ca.* 10% of the overall reaction had occurred, this fast reaction ceased, the subsequent reaction then giving first-order kinetics. The fast reaction is probably due to reactivation of the surface between runs, the catalysis ceasing once the surface becomes further deactivated by some of the initial reaction product; similar behaviour was observed previously for pyrolysis of 2-(2-hydroxyethyl)pyridine,[6] and 2-pyridyl acetate.[11]

Since a radical reaction occurs, and can be suppressed, the residual elimination must be an electrocyclic one in view of its kinetic order, reproducibility, and typical log A value. The four-centre process (2) is evidently preferred over the normally more favourable six-centre process by the nucleophilicity of the ArO group, and retention of aromaticity in the transition state. At high enough temperatures the six-centre process shown in Scheme 2 probably takes place, but we can be certain that rates of elimination by this mechanism are much less than we have obtained.

Ethyl Phenyl Ether.—We noted previously that good first-order kinetics could not be obtained with this compound.[12] Further runs were carried out at higher temperatures at which incursion of surface-catalysed reactions could be expected to be less significant. However, acceptable first-order kinetics were unobtainable, and the Arrhenius data given in Table 2 are very approximate values (and may refer in part to a four-centre process in view of the results for phenyl acetate). We may nevertheless be certain that the rate of elimination at 600 K by the mechanism given in Scheme 1 cannot be greater than the value calculated in Table 2.

3,4-*Dihydro*-3H-*pyran*.—This compound was also well behaved kinetically and gave good first-order kinetics, confirming the previous observations.[4] The kinetic data are given in Table 1 and plotted in the Figure with, for comparison, the correlation line and data points given by Wellington; these latter do not correspond with each other. Our elimination rates are lower, suggesting that his data may have been slightly affected by surface catalysis. Our activation energy and log A values are also both less than his[4] (219.33 kJ mol^{-1} and 14.526 s^{-1}, respectively).

The main features of the results are as follows.

(i) *Mechanism of Eliminations*.—The log (A/s^{-1}) values for isochroman-3-one, benzyl methyl ether, and 2-hydroxyethylbenzene are 14.305, 11.212, and 12.921, respectively. These values are within the range expected for unimolecular six-centre eliminations and provide strong support for the mechanisms proposed in Schemes 1 and 2 for these compounds. The values are in each case larger than for the corresponding non-aromatic compounds but the reason for this is not evident. The significantly greater value for isochroman-3-one reflects, as it does for the pyrans, the fact that the ground state is already constrained into the geometry required in the transition state. The Arrhenius values for 2-hydroxyethylbenzene contain a contribution from the elimination which gives styrene. This four-centre process will have slightly higher parameters so the true values for the six-centre process are probably a little lower than the values given in Table 2. The errors are not significant to the subsequent discussion.

(ii) *Comparison of Elimination Rates of Compounds* (**I**) *and* (**II**).—Rate coefficients for elimination from the simplest members of each series are shown in Table 2.[13–17] The reactivities are closely similar though compounds (**II**) appear to be slightly the less reactive, arising from higher activation energies. This in turn may be attributed to the lower polarities in the transition states for compounds (**II**) owing to the absence of the polar X–H bond. The higher activation energies for compounds (**II**) are offset by higher log (A/s^{-1}) arising from their favourable ground-state geometry. Rate data for the two sets of compounds show consistency in that the lower reactivity of vinyl ethers to β-hydroxyalkenes is paralleled by the lower reactivity of 3,4-dihydro-2*H*-pyrans compared with 3,6-dihydro-2*H*-pyrans; the rate difference is *ca.* six-fold in each case.

(iii) *Comparison of Elimination Rates of Compounds* (**I**) *with* (**IIIa**) *and* (**II**) *with* (**IIIb**).—Replacement of the double bond by a benzene ring would be expected to result in a decrease in reactivity and this is the case. The rate-reduction factors are 150 (allyl methyl ether:benzyl methyl ether) and *ca.* 2 800 (but-3-enol:2-hydroxyethylbenzene). The large difference in these values (which arises because but-3-enol is more reactive than methyl allyl ether, whereas 2-hydroxyethylbenzene in less re-

Table 1. Rate data for pyrolysis

Compound	T/K	10^3k/s^{-1}	E/kJ mol^{-1}	log (A/s^{-1})	Correlation coefficient
Isochroman-3-one	662.1	0.716	221.07	14.305	0.998 99
	662.6	0.710			
	674.0	1.61			
	684.8	2.83			
	698.9	5.82			
	710.1	10.9			
Benzyl methyl ether	719.5	0.440	200.49	11.212	0.999 42
	729.6	0.733			
	742.6	1.33			
	754.1	2.05			
	766.8	3.56			
2-Hydroxyethylbenzene	719.5	0.124	231.75	12.921	0.999 89
	730.5	0.219			
	742.6	0.423			
	754.1	0.737			
	766.8	1.34			
Phenyl acetate	716.3	0.0398	221.79	11.78	0.999 96
	740.3	0.134			
	751.3	0.227			
	765.5	0.446			
	781.0	0.864			
3,4-Dihydro-2*H*-pyran	615.5	0.652	209.01	13.556	0.999 98
	636.4	2.50			
	637.0	2.62			
	652.5	6.71			
	666.4	14.7			
2-Methyl-3,4-dihydro-2*H*-pyran	637.0	9.63	191.5[a]	12.7[a]	0.999 99
	649.9	19.7			
	666.2	47.0			
Chroman-1-one	766.8	0.665			

[a] These values are approximate only, in view of the restricted temperature range employed arising from the small sample of compound available (see Experimental section).

Table 2. Kinetic data for elimination from compounds (**I**)—(**VI**)

Type	Compound	10^6k/s^{-1} at 600 K	E/kJ mol^{-1}	log (A/s^{-1})	Ref.
(I)	Ethyl vinyl ether	43.2	185.92	11.826	13
	Methyl allyl ether	86.0	174.05	11.09	14
	But-3-enol	251	163.90	10.672	15
(II)	3,4-Dihydro-2*H*-pyran	22.8	209.01	13.556	16
	3,6-Dihydro-2*H*-pyran	155	208.1	14.31	17
(IIIa)	Ethoxybenzene	<2	201	10.7	16
	Benzyl methyl ether	0.570	200.49	11.212	16
	2-Hydroxyethylbenzene	0.055	231.75	12.921	16
(111b)	Chroman	no data but less reactive than isochroman			2
	Isochroman	no kinetic data, eliminates at >773 K			2
(IV)	Vinyl acetate	<1	*ca.* 182	*ca.* 10.4	18
	Allyl formate		no data		
	But-3-enoic acid	1 130	170.54	11.9	19
(V)	3,4-Dihydro-2*H*-pyran-2-one		no data		
	3,6-Dihydro-2*H*-pyran-2-one	*ca.* 200[a]	*ca.* 160[a]	*ca.* 12.6[a]	20
(VIa)	Phenyl acetate	0.029	221.79	11.78	16
	Phenylmethyl formate		no data		
	Phenylacetic acid		forms anhydride[b]		21
(VIb)	Chroman-1-one	*ca.* 0.05			16
	Isochroman-3-one	11.4	221.07	14.305	16

[a] See text. [b] This also eliminates normally, but is too insoluble in chlorobenzene for accurate kinetic studies by our method.

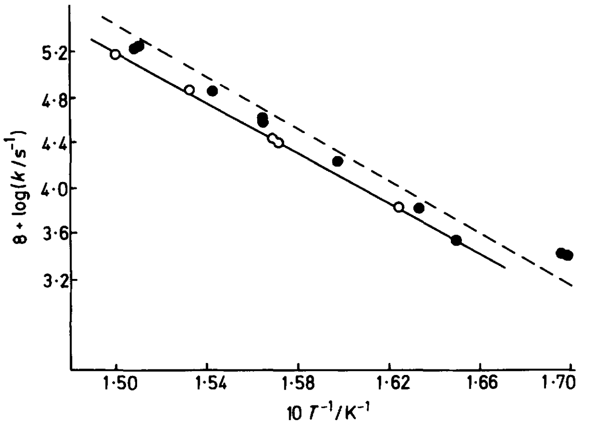


Figure. Arrhenius plot for pyrolysis of 3,4-dihydro-2*H*-pyran: ○, data points and correlation line, this work; ●, data points and quoted correlation line, ref. 4

active than benzyl methyl ether) is consistent with the different mechanisms for the two reactions (Scheme 1). Electrons from the ring are donated to an X–H bond in one case, and received from it in the other; this is discussed further under (viii). The approximate reactivity difference between ethyl vinyl ether and ethoxybenzene (> 20-fold) is consistent with the overall pattern.

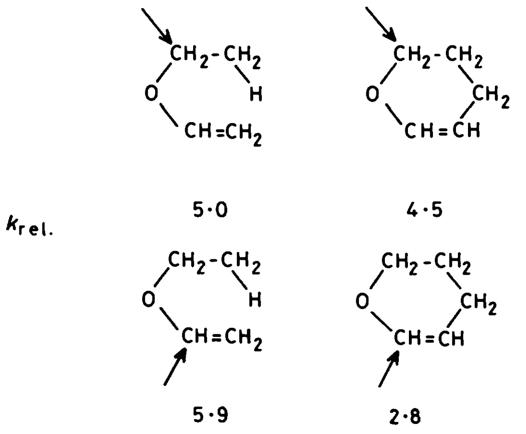
For compounds (**IIIb**) the retro-Diels–Alder elimination has been shown to occur but at high temperatures (500—650 °C)[2] confirming that the presence of the benzene ring lowers the reactivity. Thus isochroman gave 80% benzocyclobutene, along with other products (especially in a static reactor where subsequent decompositions are more likely). By contrast no oxygen-containing analogue of benzocyclobutene was obtained from the decomposition of chroman which is therefore less reactive, so the pattern noted in compounds (**I**) and (**II**) is again found.

(iv) *Comparison of Elimination Rates of Compounds* (**IV**) *with* (**V**).—Rate coefficients for the simplest members of each series are shown in Table 2. Just as β-hydroxyalkenes are more reactive than vinyl ethers, so β,γ-alkenoic acids are more reactive than vinyl acetate. The rate difference (at least 100-fold) is much greater here. No data are available for either 3,4-dihydro-2*H*-pyran-2-one or 3,6-dihydro-2*H*-pyran-2-one though the rate of elimination of the 4,6,6-trimethyl derivative of the latter has been measured.[20] Elimination in toluene between 253 and 332 °C gave E 37.5 kcal mol^{-1} and log A 12.64 s^{-1}, hence k (600 K) 95 × 10^{-3} s^{-1}. The accelerating effect of toluene is unlikely to be greater than two-fold (*cf.* the effect of solvents on the elimination rates of allyl ethers)[14] whilst the effect of a 4-methyl group can be estimated very roughly from the comparable effect in thermal decomposition of β,γ-alkenoic acids as *ca.* 30-fold.[22] If we may assume that the effect of a methyl group at the 6-position in 3,6-dihydro-2*H*-pyran-2-one is approximately the same as at the allylic position of allyl ethers, then from the data of Cookson and Wallis (who found a three-fold acceleration[23]) we estimate the effect of two methyls as nine-fold. Thus a reasonable estimate of the rate coefficient for elimination from 3,6-dihydro-2*H*-pyran at 600 K is *ca.* 200 × 10^{-6} s^{-1}, which is less than for but-3-enoic acid. The reactivity of compounds (**V**) relative to (**IV**) appears then to parallel the behaviour of compounds (**II**) relative to (**I**). It seems reasonable to assume that just as vinyl acetate undergoes the elimination shown in Scheme 2 *ca.* 10^3 times slower than does but-3-enoic acid, so 3,4-dihydro-2*H*-pyran-2-one will be less reactive than the 3,6-dihydro isomer by a comparable factor.

Similar treatment of the data predicts that allyl formate should undergo the elimination shown and with a rate coefficient of *ca.* 500 × 10^{-6} s^{-1} at 600 K.

(v) *Comparison of Elimination Rates of Compounds* (**IV**) *with* (**VIa**) *and* (**V**) *with* (**VIb**).—The general pattern noted in (ii)—(iv) is continued here. Thus phenyl acetate is (for the six-centre process shown) at least 25-fold less reactive than vinyl acetate, and isochroman-3-one is at least 10-fold less reactive than the corresponding 3,6-dihydro-2*H*-pyran-2-one. Isochroman-3-one is *ca.* 250-fold more reactive than chroman-1-one, and phenylacetic acid was evidently more reactive than phenyl acetate, though accurate rates could not be obtained because of experimental difficulties arising from its low solubility.

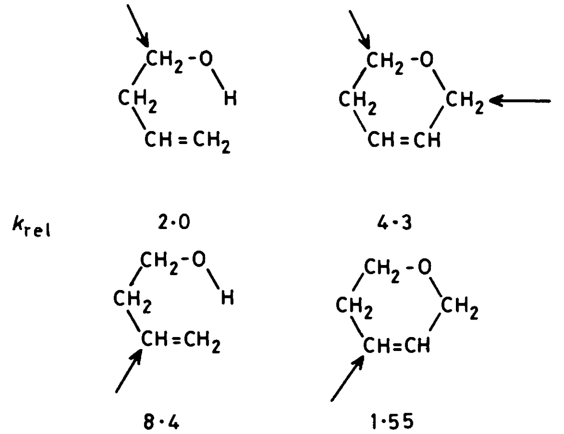
(vi) *Substituent Effects in* 3,4-*Dihydro*-2H-*pyran and Vinyl Ethers, and Polarities of Transition States*.—Frey *et al.* showed that a 2-alkoxy group accelerates elimination in 3,4-dihydro-2*H*-pyran 15—20-fold.[24] This is qualitatively consistent with the results for vinyl ethers where substituents at the α-carbon (which corresponds to the 2-position in the pyran) accelerate the reaction.[13,25] The effects of α-alkoxy groups in vinyl ethers are not known so to provide a more direct comparison we have obtained some rate data for pyrolysis of 2-methyl-3,4-dihydro-2*H*-pyran (Table 1). The 2-methyl substituent accelerates *ca.* 4.5-fold at 600 K, only marginally less than the (statistically corrected) value of 5.0 obtainable from comparison of the rates of elimination of ethyl- and isopropyl vinyl ethers.[13] The polarities of the respective transition states are thus closely similar. Confirmation comes from the 2.76-fold acceleration of the pyran elimination at 600 K, by a 6-methyl group.[26] This is quite close to the 5.9-fold acceleration produced by a methyl group at the corresponding position in isopropyl 1-methylvinyl ether.[25] (The effect here is enhanced in the vinyl ether because the transition state for elimination of isopropyl ethers is more polar than for ethyl ethers.[13]) The effects of the methyl subsituent are shown in Scheme 3.



Scheme 3. Activating effects, at 600 K, of methyl substituents in vinyl ethers and 3,4-dihydro-2*H*-pyrans

The similarity in behaviour of the two sets of compounds implies that α-alkoxyethyl vinyl ethers (acetaldehyde acetals) ought to be reasonably stable.

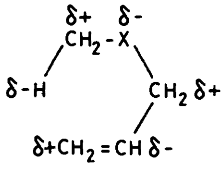
(vii) *Substituent Effects in* 3,6-*Dihydro*-2H-*pyrans and* β-*Hydroxyalkenes, and Polarities of Transition States*.—Frey *et al.* measured the effects of the methyl substituent in 3,6-dihydro-2*H*-pyrans[27] and found the activating effects to be 1.55-fold and 4.3-fold at the 4- and 2,6-positions, respectively. They suggested[17] that the polarisation of the 1,2-bond was probably in the direction $C^{\delta+}$–$O^{\delta-}$, and their results are consistent with electron deficiency at the 2-, 4-, and 6-positions, which would arise from the electron movements given in Scheme 1 (assuming, by analogy with elimination from β-hydroxyalkenes that bond breaking slightly precedes bond formation). The charge distribution in the transition state for β-hydroxyalkenes is known from a range of substituent effects studies.[15,28] Thus a methyl substituent at the 1-position (≡ to the 2-position in 3,6-dihydro-2*H*-pyran) produced a two-fold rate increase at 600 K,[15] whilst a 1-phenyl group increased the elimination rate 19-fold, and 1-aryl substituents gave a Hammett correlation with ρ −0.11.[15,28] In the β-hydroxyalkenes the 3-position (≡ to the 4-position of 3,6-dihydro-2*H*-pyran) is also electron deficient, confirmed by the 8.4- and 9.4-fold rate increases produced by methyl[15] and phenyl[28] respectively, and substituents in the latter give a Hammett correlation with ρ −0.49.[15,28] The methyl substituent effects are shown in Scheme 4.



Scheme 4. Activating effects, at 600 K, of methyl substituents in β-hydroxyalkenes and 3,6-dihydro-2*H*-pyrans

(viii) *Charge Distribution in Transition State for Allyl Ether Pyrolysis.*—3,6-Dihydro-2*H*-pyrans may be considered as derivatives of either β-hydroxyalkenes or allyl ethers (Scheme 1). Given that the transition-state polarities and resultant electron movements are established for β-hydroxyalkenes and 3,6-dihydro-2*H*-pyrans, then the electron movements for allyl ethers should be as shown in Scheme 1. Thus hydrogen is transferred as an incipient anion, rather than the incipient cation which is more generally the case for eliminations. The carbon of the methyl group should therefore be electron deficient (as are the carbons at the comparable positions in the other two classes of compounds). This is supported by methyl or phenyl substituents at this carbon increasing the elimination rates by (statistically corrected) factors of 2.3 and 5.5, respectively.[14] It is also supported by the 8.9-fold relative rate of elimination of diallyl ether compared with allyl methyl ether (after correction for the differing number of allyl groups and β-hydrogens.[14,29] The vinyl group here conjugatively stabilises the adjacent electron-deficient methylene carbon. The 1-carbon of the allyl ethers should also be electron deficient in the transition state and hence a 1-phenyl substituent produces a 4.7-fold (statistically corrected) rate increase.[11] This latter result confirmed an earlier semi-quantitative study which showed also that electron removal from the 2-carbon increased the reaction rate,[23] indicating the 2-carbon to be electron rich in the transition state as required by the proposed mechanism.

(ix) *Elimination from Compounds containing Nitrogen or Sulphur.*—We are unaware of any data for elimination from cyclic compounds containing sulphur or nitrogen in place of oxygen. It seems reasonable to assume however that reactivities may be estimated from the rate data for open-chain compounds using the relationships deduced in this paper. There are few data for open-chain compounds but values of $10^3\ k/s^{-1}$ (at 600 K) of 0.086, 0.039, and 1.99 have been given for allyl methyl ether,[14] allyl methylamine,[30] and allyl methyl sulphide.[31] The difference in reactivity of the first two compounds is consistent with development in the transition state of negative charge on the heteroatom [see (VII)] since oxygen can better accommodate this. The higher reactivity of the sulphur compounds may reflect the substantially weaker C–S bond together with the ability of sulphur to accept electrons into its *d*-orbitals. The reactivities of allyl alkyl sulphides have been measured by Martin *et al.*[31] who assumed that the hydrogen atom is transferred as a partial *cation i.e.* the methyl group carbon atom becomes electron rich in the transition state. They found that adjacent double or triple bonds, phenyl, and SR groups all produced a rate increase which they attributed to conjugative electron withdrawal. However, each of these groups is better at *supplying* electrons conjugatively and moreover alkyl groups *increased* the reaction rate. This latter is unlikely to be due to steric acceleration, since the neopentyl group produced a rate increase comparable with that by other alkyl groups. It could be argued that alkyl groups are behaving here as electron acceptors as they do in carbon acids in the gas phase when adjacent to saturated sp^3 carbon.[32] However there is no evidence that electron withdrawal occurs by alkyl groups in eliminations. Further consideration of the effects of substituents in pyrolysis of alkyl allyl sulphides must await the accumulation of further rate data. In particular it needs to be demonstrated that the low activation energies and log *A* values observed for some of the compounds[31] are not due to surface catalysis.



(VII) X = O, S, NH

Experimental

Preparations.—Benzyl methyl ether and phenyl acetate were prepared by standard procedures, and fractionally distilled before use as also were commercial samples of 2-hydroxyethylbenzene, dihydrocoumarin (chroman-1-one), and 3,4-dihydro-2*H*-pyran. For benzyl methyl ether, n_D^{20} was 1.5010, lower than the literature[33] value of 1.5022; the latter sample may have been contaminated with some benzyl chloride precursor, since this has a higher refractive index. 2-Methyl-3,4-dihydro-2*H*-pyran, b.p. 58—62 °C at 150 mmHg, $\delta(CDCl_3)$ 6.3 (1 H, d, OCH=), 4.6 (1 H, m, =CH), 3.9 (1 H, m, CH), 2.0 and 1.7 (4 H, m, CH_2CH_2), 1.3 (3 H, d, CH_3) was made from glutaraldehyde and methylmagnesium chloride by the literature method.[34] This reaction fails if methylmagnesium iodide is used, presumably because iodine is insufficiently electronegative to facilitate the necessary ring closure. The overall yield in this preparation was only 5%, insufficient for a full kinetic study so that the kinetic data reported in Table 1 are regarded as approximate only.

Product Analysis.—The products from pyrolysis of isochroman-3-one,[3] 3,4-dihydro-2*H*-pyran,[4] and phenyl acetate[7] were confirmed. Passing phenyl acetate through a column of heated helices at 775 K (non-deactivated surface) gave in addition some toluene and a peak, *m*/*e* 118, with fragmentation pattern corresponding to benzo[*b*]furan. The latter is a product of dehydration though the mechanism of its formation is obscure. We detected neither cresols nor phenoxyphenols reported by Barefoot and Carroll.[8]

The product from pyrolysis of benzyl methyl ether showed only toluene in the n.m.r., but m.s.–g.l.c. analysis showed additional minor products, *m*/*e* 78, 104, 106, 120, 154, and 182, attributed to benzene, styrene, ethylbenzene, n- or iso-propylbenzene, biphenyl, and bibenzyl, respectively. The product from 2-hydroxyethylbenzene showed the presence of styrene in the n.m.r. to the extent of 10% of the amount of toluene; only trivial amounts of other products were evident. M.s.–g.l.c. analysis confirmed the existence of styrene and toluene, and gave additional peaks at *m*/*e* 78, 106, 136, 154, and 182; the peak at 136 (fragments at 77, 91, 105, and 121) is probably due to methyl 2-phenylethyl ether, the other peaks were assigned as above.

M.s.–g.l.c. analysis of the product from pyrolysis of chroman-1-one (775 K; heated helices) showed peaks which gave *m*/*e* 91 (toluene), 104 (styrene), 106 (ethylbenzene), 108 (cresol, probably *ortho*), 118 (benzo[*b*]furan), 132 (possibly indanone), and 146 (coumarin). Benzo[*b*]furan and coumarin were the main components, and their presence was confirmed by separate mass spectral analysis and by 360 MHz n.m.r. spectroscopy. Coumarin gave doublets at δ 6.41 and 7.74 (J 9.5 Hz), the latter doublet showing secondary splitting, J 0.65 Hz. However, in the mixture of products the doublets appeared at δ 6.27 and 7.47, confirmed by addition of authentic coumarin. Benzo[*b*]furan gave doublets at δ 6.675 and 7.535 (J 0.2 Hz) with secondary splitting J 0.1 Hz).

Kinetic Studies.—These were carried out in the stainless steel static reactor system according to the method described previously.[35] Isochroman-3-one is a solid and was therefore injected into the reactor as a solution in chlorobenzene in the usual way, chlorobenzene being stable under the pyrolysis conditions. The stoicheiometry of each elimination was 2.0 ± 0.1, and rates showed no variation for a four-fold change in the reagent quantity.

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