The Transition State in Ester Pyrolysis. Part 9.[1] On the 'Surface-catalysed' Mechanism for the Elimination

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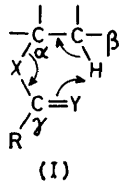
The 'surface-catalysed' mechanism of ester pyrolysis, recently proposed to account for the difference between observed alkene product distributions, and those predicted on the basis of alkene thermodynamic stability, is unsoundly based. Not only can all the known product patterns be accounted for primarily in terms of steric and statistical factors, the electronic contribution to thermodynamic stability being unimportant but, in addition, the classical demonstration of the supposed importance of the thermodynamic effect is shown to be experimentally incorrect.

Moreover where it has been examined the elimination pattern is the same in reactors with both active and deactivated surfaces which further rules out surface catalysis as an explanation of these patterns. Steric acceleration is emphasized as a factor governing the elimination pattern and is demonstrated by the marked increase in reactivity (per β-hydrogen) along the series: ethyl acetate < 3-methylbutyl acetate < 3,3-dimethylbutyl acetate.

THE mechanism of the pyrolysis of esters is now sufficiently well established [2] that it can be summarised as follows:



(I)

(i) The reaction is a cyclic semi-concerted process. (ii) The carbonyl oxygen (I; Y = O) and the β-hydrogen are approximately *cis*-coplanar, though deviations up to the staggered conformation are apparently permissible. (iii) The concerted nature of the process means that it is affected by all the functions which constitute the six-membered ring, as follows.

(*a*) The electron supply to the α-carbon. This carbon is partially positively charged in the transition state, so that increased electron supply gives an increased elimination rate.[3-7]

(*b*) The polarity of the C–X bond. Increasing electronegativity in X aids elimination and a reactivity series is therefore: acetates > thiolacetates > amides.

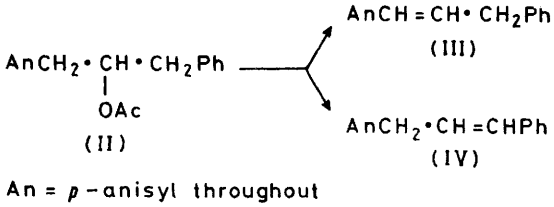
(*c*) The electron supply to the γ-carbon. This carbon is partially negatively charged in the transition state, hence increased electron withdrawal gives an increased elimination rate,[5,8-12] and reactivity series are: acetates < phenylacetates < carbamates < carbonates,[13] (phosphates) > carboxylates,[14] and chloroformates > formates.[15]

(*d*) The nucleophilicity of Y. The greater this is, the faster the elimination so that a reactivity series is thionacetates > acetates.[16]

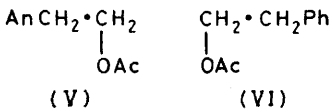
(*e*) The acidity and number of β-hydrogens.[4,11,17-21]

(*f*) Steric acceleration due to bulk in the ester which is relieved on forming the alkene.[12,20] In this paper we shall present additional evidence for this effect.

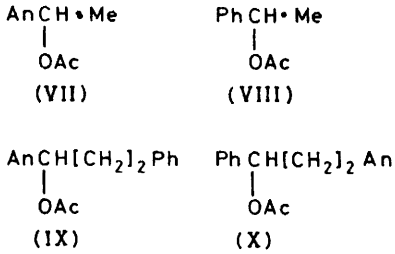
(*g*) The thermodynamic stability of the alkene product arising from both electronic and steric effects. This is perhaps the most often quoted effect governing the pyrolysis of esters, yet has been supported by only a single experiment.[22] De Puy and Leary pyrolysed an ester, which they believed to be pure 1-(*p*-anisyl)-3-phenylprop-2-yl * acetate (II) and obtained 1-(*p*-anisyl)-3-phenylpropene (III) and 1-phenyl-3-(*p*-anisyl)propene (IV) in the ratio of *ca.* 2.8 : 1. The product ratios were established by kinetic measurements on the bromo-derivatives of the alkenes; similar results were obtained with 1-(*p*-anisyl)-3-(*p*-chlorophenyl)prop-2-yl acetate.



We have long doubted the validity of this experiment because our kinetic studies of pyrolysis of the related pairs of esters (V) and (VI) showed that (VI) eliminates more readily than (V) by a factor of *ca.* 1.1.[3,20] By



contrast our kinetic studies of esters (VII) and (VIII) [3] reproduced precisely the reactivity difference (3.7-fold) between the related esters (IX) and (X) observed by De Puy and Leary from product studies. We shall show



below that pyrolysis of (II) gives a preponderence of (IV) rather than (III), *i.e.* elimination is subject to kinetic rather than thermodynamic control, so that the electronic contribution to thermodynamic stability is relatively insignificant.

* Although application of the IUPAC rules would lead to the numbering of the radical position in an alkyl radical as 1, for reasons of comparison with references 22 and 23, this rule has not been strictly followed.

Despite the wealth of consistent evidence relating to the pyrolysis mechanism, Wertz and Allinger have recently proposed that the alkene product ratios obtained in pyrolysis of esters are inconsistent with this mechanism. They lay particular emphasis on thermodynamic stability and proposed an alternative mechanism involving surface catalysis.[23] We shall show that this alternative mechanism is untenable.

RESULTS AND DISCUSSION

Steric Acceleration.—The importance of this factor is relevant to our argument below and in order to demonstrate its effects more rigorously we have pyrolysed 3,3-dimethylbutyl acetate and 3-methylbutyl acetate. The kinetic data (Table 1) taken along with those previously

TABLE 1

Pyrolysis of acetates

Ester	t/°C	10^3k/s^{-1}	log(A/s^{-1})	E/kcal mol^{-1}
3-Methylbutyl acetate	387.4	0.50	12.82	48.7
	404.7	1.34		
	421.3	3.12		
	438.7	7.29		
3,3-Dimethylbutyl acetate	387.2	1.01	12.35	46.4
	404.7	2.37		
	421.3	5.45		
	438.7	13.05		

obtained,[20] provide the relative rates per β-hydrogen given in Table 2. These not only demonstrate the marked increase in reactivity that accompanies bulk, but in particular the series from propyl acetate through to 3,3-dimethylbutyl acetate is one in which methyl substitution is made at a site remote from either α- or β-carbon so that electronic effects may be largely ruled out.

Thermodynamic Effects.—The ester (II) was prepared by the route given in Scheme 1. This is a low-yield route because the main product is 4,4′-dimethoxydiphenylethane, presumably because the methoxy-group

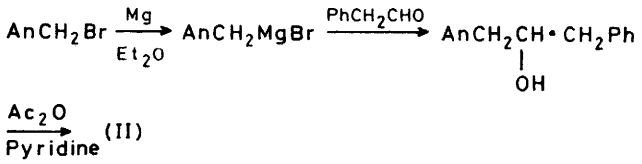
TABLE 2

Relative rates at 675 K for esters $RCH_2{\cdot}CH_2OAc$

R	10^3k/s^{-1}	$k_{rel.}$
Me	0.89	1
Et	1.06	1.19
Pr^i	1.12	1.26
Bu^t	2.12	2.38

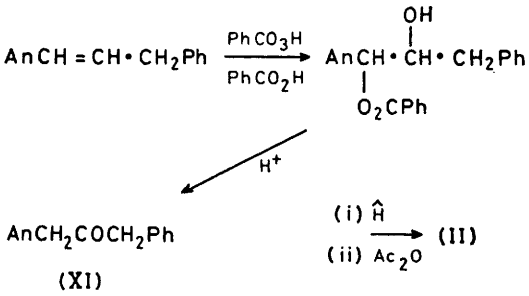
facilitates rapid nucleophilic substitution by the Grignard reagent upon unchanged arylmethyl bromide. We assume that this poor method is the reason for the adoption by De Puy and Leary, of a more complicated route to (II).

Pyrolysis of (II) through heated glass helices at temperatures in the range 390—430 °C gave (IV) and (III) *in a ratio of* 1.1 : 1.0. Not only is this result markedly different from that of De Puy and Leary, but confirms precisely the expectation based upon the kinetic results with (V) and (VI). *Thus the formation of alkenes is dominated not by thermodynamic stability, as previously considered, but rather, in the absence of dominating steric effects, by kinetic control.* The question then arises as to how De Puy and Leary could have obtained such erroneous results. Their work pre-dated the general advent of gas chromatography, and their analysis thus involved a kinetic method which they carefully checked and appears to us to be perfectly sound. We believe however that their ester (II) prepared as in Scheme 2, was not pure for the following reasons.



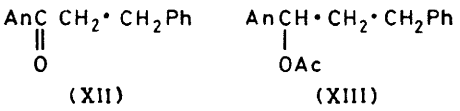
SCHEME 1

(i) This method presupposes that addition of perbenzoic acid is 100% stereospecific. If this is not the case, then the intermediate ketone will be contaminated with (XII) and hence (XIII) *which eliminates* ca. 4.0 *times faster than* (II). A simple calculation shows that only *ca.* 20% of (XII) as an impurity would produce the observed result (for 40% overall elimination) and moreover that the (III) : (IV) alkene ratio should decrease with increased proportion of elimination, exactly as observed by De Puy and Leary. They observed that



SCHEME 2

though the alcohol precursors of (II) and (XIII) had virtually the same m.p.s, a mixture of them had a reduced m.p. However this does not prove that the former was not contaminated with the latter in the first instance. We have repeated the preparation in Scheme 2, and obtained a mixture of ketone and original alkene. The ketone was not resolvable into isomers by g.l.c., but the n.m.r. of the reduced mixture (sodium borohydride) showed the presence of two tertiary protons,



giving a triplet (minor component, downfield) and a multiplet; these must, therefore, arise from a mixture of the alcohol precursors of (XIII) and (II) respectively.

(ii) Since the unchanged alkene and the desired ketone have almost identical b.p.s it is in addition possible for (II) to have been contaminated with the alkene (III) thereby producing an erroneously high yield of it in the decomposition product.

Thus the thermodynamic stability of the alkene pro-

duct is not nearly as important as previously considered, and this confirms our recent findings from pyrolysis of benzyldimethylcarbinyl acetate.[1] This logically follows from the fact that breaking of the β-C–H bond is rate determining, the mechanism being far removed from *E*1 in which the thermodynamic stability of the alkene would be of primary importance. Since the transition state for ester pyrolysis varies from E_i towards *E*1 along the series primary, secondary, tertiary esters, the importance of thermodynamic stability should increase along this series. It should also be noted that the effect of thermodynamic stability is in some cases more apparent than real, because of the need of the ester in the *cis*-coplanar transition state to adopt the conformation which is least sterically hindered; this then gives the thermodynamically most stable alkene but for entirely steric reasons.

The 'Surface-catalysed' Elimination Mechanism.— Wertz and Allinger have proposed that the majority of eliminations, *i.e.* all those not employing a carbon-deactivated surface, take place *via* a surface-catalysed mechanism, and one in which a carbocation is formed in a rapid pre-equilibrium involving the surface, followed by a rate-determining loss of a proton. According to their mechanism, the active surface stabilizes the free carbocation that is formed. Not only would this stabilization have to be very formidable since it would have to reduce the activation energy from *ca.* 670 kJ mol^{-1} to *ca.* 170 kJ mol^{-1}, but it would have to involve sites more polar than those found in a polar solvent. This is because a solvent may pack around a carbocation whereas the surface can approach one side only.

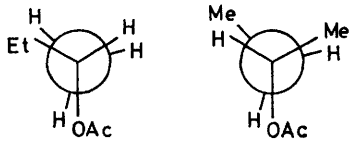
Their mechanism leads to more fundamental problems however. (i) They suggest that the β-hydrogen is removed either by the surface or by the counter ion lying on the surface. The first possibility can be discounted since it is known that in liquid-phase pyrolysis (undeactivated surface) xanthates and thionacetates are more reactive than acetates,[16] which would not be the case if the surface pulled off the β-hydrogen. This leaves the alternative which is that the hydrogen is pulled off by the acid counter (an)ion lying on the surface (presumably having been removed initially by interaction with the surface *). In this case the carbocation cannot be in contact with the surface and so cannot be stabilized. A further problem is that by an immense coincidence the surface would stabilize the carbocation (assuming it could somehow do this) by such an amount as to bring the nett polarity on the α-carbon down to *precisely* the same as that which is developed in the concerted process. The identical polarity is shown for example by the fact that the difference between a *p*-methoxyphenyl and phenyl group in stabilizing the α-carbocation in esters (IX) and (X) on an undeactivated surface [22] is exactly the same as their effects on esters (VII) and (VIII) (and also in the corresponding 1,2-diarylethyl esters [21]) in a reactor with a deactivated surface [3] (this latter accepted as such by Wertz and Allinger).

(ii) The kinetic isotope effect would be expected to be markedly different under the two sets of conditions whereas it is in fact the same.[4]

(iii) Wertz and Allinger have argued that the data of Sixma *et al.*[24] was obtained under surface-catalysed conditions. Yet using a deactivated surface we have been able to reproduce very closely the rate coefficients which they obtained.[20]

Wertz and Allinger based their proposals on the assumption that the alkene isomer distribution obtained in pyrolysis of some esters cannot be explained in terms of the normal mechanism. We do not believe this to be the case, though it is true that no such explanation has previously been given. We therefore discuss these results in detail below.

The Isomer Distribution in Ester Elimination.— Consider the data in Table 3. For 1-methylpropyl acetate (but-2-yl acetate) the 1- : 2-alkene ratio is slightly less than predicted and down the Table (to ester no. 5 †) the 1- : 2-alkene ratio decreases. At first sight, these differences appear to be due to increased thermodynamic stability of the alk-2-ene through increased electron supply to the 3-carbon. However, the results for esters (4) and (5) are too markedly different for this to be the correct explanation, and strongly indicate a steric effect. Models show that there are steric interactions between the terminal alkyl groups (and between these and the acetoxy-group); these are best relieved by formation of the alk-2-enes, the transition state (XIV) for which has lower-energy eclipsing interactions than that (XV) for alk-1-ene formation. This effect will thus become more important as the terminal groups become bulkier (and shows up kinetically as steric acceleration in the butyl acetates described above, even though these are less bulky).



(XIV) (XV)

Consider next esters (6)—(13) in Table 3. These tend to give *more* alk-1-ene than statistically predicted, and in *contradiction* of the prediction based on the thermodynamic stability. Again models indicate why. For ester (6) formation of alk-1-ene involves the transition state (XVI) which has lower-energy eclipsing interactions than that (XVII) for alk-2-ene formation. Likewise for ester (9) the transition state (XVIII) for

* We believe this probably accounts for the small surface effects that are observed in ester pyrolysis and which vary markedly with ester type. They are greatest for carbamates which have a lone pair of electrons easy to donate to the surface (or a hydrogen easy to bond with it). Since it is *known* that the surface interacts with these esters, it is improbable that the surface will conversely *donate* electrons to a carbocation.

† The very low k_1/k_2 ratio (0.32) reported by Wertz and Allinger for 4,4-dimethylpent-2-yl acetate (ester no. 5) seemed intuitively to us to be too low. We therefore repeated this work and obtained the higher value given in Table 3.

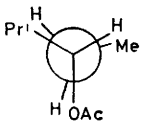
TABLE 3

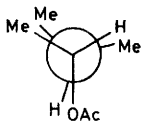
Pyrolysis of secondary and tertiary acetates

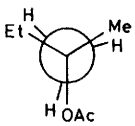
No.	Ester	Alk-1-ene (%)	Alk-2-ene (%)	k_1/k_2 Obs.	k_1/k_2 Calc.[a]	Ref.
1	$MeCH_2CH(OAc)Me$	57	15 *cis*, 28 *trans*	1.32	1.5	24—26
2	$EtCH_2CH(OAc)Me$	55	45 *cis* and *trans*	1.22	1.5	24
3	$Bu^nCH_2CH(OAc)Me$	54	17 *cis*, 29 *trans*	1.18	1.5	25, 27
4	$Pr^iCH_2CH(OAc)Me$	46	54 *cis* and *trans*	0.85	1.5	24
5	$Bu^tCH_2CH(OAc)Me$	33	67 *cis* and *trans*	0.49[b]	1.5	This work
6	$Me_2CHCH(OAc)Me$	80	20	4.0	3.0	25, 28
7	$MeEtCHCH(OAc)Me$	76	24 *cis* and *trans*	3.15	3.0	24
8	$Me_2CHCH(OAc)Pr$	73 *cis* and *trans*[c]	27	2.7	2.0	25
9	$MeCH_2C(OAc)Me_2$	76	24 *cis* and *trans*	3.15	3.0	24, 25, 29, 30
10	$EtCH_2C(OAc)Me_2$	72	28 *cis* and *trans*	2.56	3.0	29, 30
11	$Pr^iCH_2C(OAc)Me_2$	61.5	38.5 *cis* and *trans*	1.85[d]	3.0	This work
12	$Bu^tCH_2C(OAc)Me_2$	74	26 *cis* and *trans*	2.85[e]	3.0	23
13	$Me_2CHC(OAc)Me_2$	89	11	8.1	6.0	29, 30
14	$(MeCH_2)_2C(OAc)Me$	35	22 *cis*, 43 *trans*	0.54	0.75	24

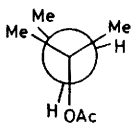
[a] Statistically predicted ratios. [b] Wertz and Allinger obtained an anomalously low value of 0.32 which they cited as supporting their surface-catalysed mechanism.[23] We were unable to reproduce this result on either an active one or a deactivated one. [c] This is described as alk-1-ene for the purposes of analogy, but is in fact an alk-3-ene. [d] At 400 °C. Wertz and Allinger obtained a lower value of 1.6 at 450 °C. However we find the value to decrease markedly with increasing temperature which probably accounts for their result. [e] May be affected by isomerisation—see ref. 23.

alk-1-ene formation is more favourable than that (XIX) for alk-2-ene formation. The formation of slightly less alk-1-ene from the ethyl-substituted esters (7) and (10)


(XVI)


(XVII)


(XVIII)


(XIX)

compared to the corresponding methyl substituted esters (6) and (9) is nicely self consistent and indicates that the two effects are here tending to cancel each other out. Similarly the decrease in k_1/k_2 along the esters (9)—(12) parallels that for esters (1)—(5) suggesting the same cause. The results for esters (6), (8), and (13) also show self-consistency in that the observed product ratios exceed the calculated ratio by the same factor (1.35). Steric effects predict the result for ester (14); the interaction between the ethyl groups is reduced considerably on forming the alk-2-ene, but only marginally on forming the alk-1-ene. Furthermore, ester (8) gives the alkene which is *least* expected if electronic contributions to thermodynamic stability were important.

For ester (15) in Table 4 the 2- : 3-alkene ratio is that statistically predicted, but as the terminal alkyl group becomes larger [esters (16)—(19)] it decreases. Steric compression in the ground state, which models indicate to be best relieved by formation of the *trans*-alk-3-ene (as observed), accounts for this result. This compression leads to steric acceleration (first proposed by Benkeser *et al.*[31]) which should be kinetically observable. This is confirmed by data in Table 1. Even for these esters [which are less bulky than (18) and (19) but were chosen for their simpler kinetics] marked acceleration parallels bulk in the terminal group.

TABLE 4

Pyrolysis of secondary aliphatic acetates

No.	Ester	Alk-2-ene (%)	Alk-3-ene (%)	k_2/k_3 Obs.	k_2/k_3 Calc.[a]	Ref.
15	$MeCH_2CH(OAc)CH_2Me$	40 *cis*, 60 *trans*		1.0	1.0	31
16	$EtCH_2CH(OAc)CH_2Me$	17 *cis*, 35 *trans*	15 *cis*, 33 trans	1.08	1.0	31
17	$Pr^nCH_2CH(OAc)CH_2Me$	12 *cis*, 35 *trans*[b]	53 *cis* and *trans*[b]	0.89	1.0	27
18	$Pr^iCH_2CH(OAc)CH_2Me$	12 *cis*, 33 *trans*	5 *cis*, 50 *trans*	0.82	1.0	31
19	$Bu^tCH_2CH(OAc)CH_2Me$	9 *cis*, 21 *trans*	5 *cis*, 65 *trans*	0.43	1.0	31

[a] Statistically predicted ratios. [b] These were incorrectly assigned in the original paper.

For unsaturated acetates (Table 5) the effect of thermodynamic stability could be of overriding importance (though it is not possible to rule out either relief of steric strain in the ground state or vinyl enhancement of β-hydrogen acidity as the important factors). Thus the 1,3-diene is produced in a much greater amount than

TABLE 5

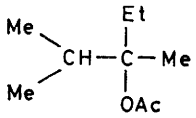
Pyrolysis of unsaturated acetates

No.	Ester	1,4-Diene (%)	1,3-Diene (%)	$k_{1,4}/k_{1,3}$ Obs.	$k_{1,4}/k_{1,3}$ Calc.[a]	Ref.
20	$CH_2{=}CHCH_2CH(OAc)Me$	26	74	0.35	1.5	28
21	$CH_2{=}CHCH_2C(OAc)(CH_3)_2$	50	50	1.0	3.0	28

[a] Statistically predicted ratios.

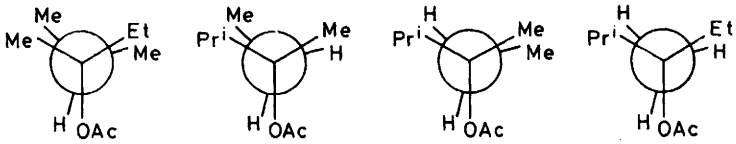
statistically predicted. Again [*cf.* esters (1) and (9), Table 3] the observed : calculated ratio is higher for the tertiary ester (0.33) than for the secondary one (0.234)—indeed the ratio of the ratios is closely similar, being 1.2 [esters (1) and (9)] and 1.4 [esters (20) and (21)]. These data also vitiate the surface-catalysed mechanism, because esters (1) and (9) were pyrolysed on undeactivated surfaces, whereas esters (20) and (21) were pyrolysed on a deactivated surface.

The transition states for the four possible eliminations in pyrolysis of 2,3-dimethylpent-3-yl acetate [32] (XX) are given in (XXI)—(XXIV) along with the observed and calculated alkene yields. [Attention was drawn to the



(XX)

importance of steric effects in governing the direction of elimination,[32] but the discussion appeared ambiguous and contradictory.] The repulsive interactions clearly



	(XXI)	(XXII)	(XXIII)	(XXIV)
Obs. yield (%)	6	5	28	61
Calc. yield (%)	17	17	17	51

decrease from (XXI) to (XXIV) so that the corresponding alkene yields increase in this direction. This result points to the relative unimportance of thermodynamic stability which would lead one to expect a high yield of the product from transition state (XXI).

Wertz and Allinger believed that some of the results for pyrolysis of cycloalkyl acetates (Table 6) were anomalous and can only be accounted for in terms of the surface-catalysed mechanism. In fact all of the isomer distributions follow from the normal elimination mechanism.

Esters (22)—(24) show that in general, formation of the *exo*-cyclic alkene is unfavourable (statistically it should be obtained in 60% yield). It is now evident that this is unlikely to be due to the instability of the *exo*-cyclic alkene, but due rather to the greater number of eclipsing interactions (either between adjacent pairs of ring C–H bonds, or between the double bond and the adjacent C–H bonds). Again steric effects are seen to be of particular or even sole importance, for eclipsing interactions in ester (22) are removed to a greater extent on forming the *endo*-cyclic alkene than is the case for esters (23) and (24). Consequently the yield of *endo*-cyclic alkene is greatest for ester (22). Moreover, this reasoning predicts that elimination from ester (22) should be *sterically accelerated* which is in fact the case, elimination occurring 3.4—5.2 times faster than from ester (23).

The elimination pattern is significantly altered on going to the *cis*-1,2-dimethylcyclopentyl- and *cis*-1,2-dimethylcyclohexyl-esters (25) and (27). Both give significantly greater amounts of the *exo*-cyclic product which can again be accounted for in steric terms. The adjacent methyl groups sterically interact, especially in ester (25) where they are eclipsed. Removal of this eclipsing may be regarded as paramount (and more important than reduction of other eclipsing interactions in the cycloalkyl ring) and is best achieved by conversion of the 1-methyl group into methylene, giving the *exo*-cyclic alkene. It is significant that the change in *exo*- : *endo*-cyclic product ratio (relative to the unmethylated analogue) is greatest for the cyclopentyl ester (25) which has the most eclipsed ground state. For the *trans*-cyclopentyl ester (26) there is no methyl–methyl interaction, so that formation of the *exo*-cyclic alkene is not sterically favoured, and the *exo* : *endo* product ratio becomes comparable to that for ester (22). It should also be noted that the eclipsing interactions in cyclopentane are sufficient to cause substantial puckering, and this will be greater in the presence of substituents. Consequently the formation of 5—10% of 1,2-dimethylcyclopentene from ester (26) is unlikely to involve a *trans*-elimination; models indicate that the puckering can be sufficient to place the acetoxy-group and β-hydrogen *gauche* to each other, thereby permitting a *cis*-elimination mechanism. For *trans*-1,2-dimethylcyclohexyl acetate, ester (28), the acetoxy-group being less bulky than the two methyl groups, must occupy the axial position. This has two consequences: (i) the 1-acetoxy-group and the 2-hydrogen are *trans* to each other so no 1,2-dimethylcyclohexene can be produced. (ii) The methyl groups lie *gauche* to each other and conversion of one of them to methylene will be sterically accelerated. Consequently a much higher yield of *exo*-cyclic alkene is obtained compared to the *trans*-cyclopentyl ester (26).

The cyclononyl and cyclodecyl acetates, esters (29) and (30), have sufficient flexibility to permit elimination of either the *cis* or *trans* β-hydrogen in a normal *cis*-elimination. Elimination of the latter (to give the *trans*-alkene) does *not* therefore indicate that a different

mechanism applies, as has been suggested.[44] For ester (29), elimination of the *trans*-β-hydrogen requires interaction of the hydrogens on C-2 and C-7, so this is unfavourable. On the other hand, elimination of the *cis*-β-hydrogen requires a conformation in which most of the C–H bonds in the ring are eclipsed; ring opening therefore dominates. For ester (30) the reverse situation applies. Elimination of the *cis*-β-hydrogen involves interaction of the hydrogens on C-3 and C-7, whereas elimination of the *trans*-β-hydrogen does not. Moreover, in the transition state for the latter, most of the C–H bonds in the ring are staggered. Thus *trans*-product formation without ring opening is primarily obtained.

A *trans*-elimination mechanism is also *not* involved in elimination from *trans* 2-methylcyclohexyl acetate, ester (32) (*cf.* ref. 44). Both acetoxy and methyl groups will occupy equatorial positions so that there are *cis*-β (*gauche*) hydrogens on either side of the acetoxy-group. A 1 : 1 product ratio should be obtained but steric effects cause 1-methylcyclohexene to predominate. Formation of this latter from the *cis*-ester (31) can only be achieved by having the more bulky acetoxy-group in the sterically unfavourable axial position. As a result formation of 1-methylcyclohexene is much less for the *cis*- compared to the *trans*-isomer.

The importance of steric effects rather than thermodynamic effects as a whole is also shown by the products of pyrolysis of esters (33) and (34), because proportionally *less* of the alkene which is resonance stabilised is formed in each case. Formation of these latter require transition states in which there is eclipsing between the ring C–H and α-C–Me bonds. Moreover there is eclipsing in these alkene products, which is greatest for the cyclohexyl derivative (and compounded by the fact that the α-Me–ring C–H bond distance is shorter in this product). Consequently less of this alkene is formed from ester (34) than from the corresponding cyclopentyl ester (33).

Pyrolysis of menthyl acetate, ester (35), in which all of the substituents on cyclohexane are equatorial, gives mainly (±)-*p*-menth-3-ene, but here again it is unlikely that this is due to thermodynamic stability arising from resonance. Models show that this alkene has fewer eclipsing interactions between the isopropyl group and the cyclohexene ring than in *trans*-*p*-menth-2-ene, and so should be the favoured product.

TABLE 6

Pyrolysis of cycloalkyl esters

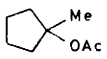
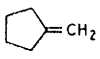
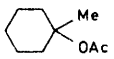
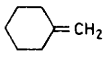
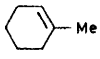
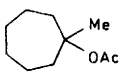
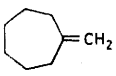
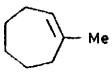
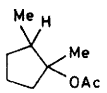
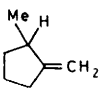
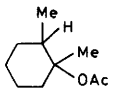
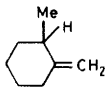
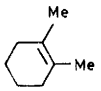
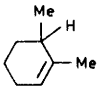
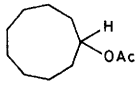
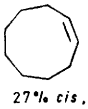
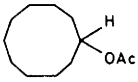
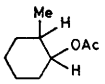
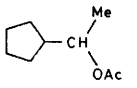
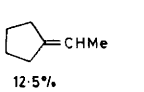
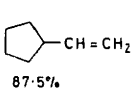
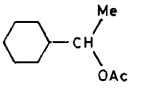
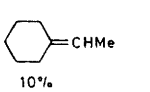
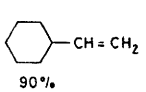
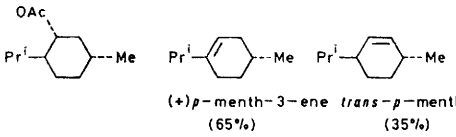
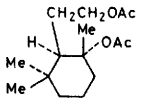
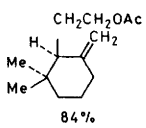
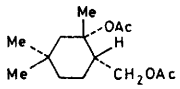
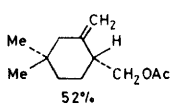
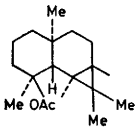
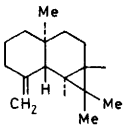
No	Ester	Products			Ref.
22		 0–16%	 84–100%		25, 33
23		 24%	 76%		24, 25, 26*d*, 29, 34
24		 24%	 76%		35
25	 *cis*	 20–30%	 40–50%	 25–30%	25
26	*trans*	1–4%	5–10%	85–90%	
27	 *cis*	 45%	 28%	 26%	25
28	*trans*	55%	0%	45%	
29		 27% *cis*, 1·5% *trans*	Nona-1,8-diene		36
30		 *trans*			37

TABLE 6 (*Continued*)

No.	Ester	Products			Ref.
31	 *cis*	 25%	 75%		38
32	*trans*	55%	45%		
33		 12·5%	 87·5%		39
34		 10%	 90%		39
35	 (+)-*p*-menth-3-ene (65%)	*trans*-*p*-menth-2-ene (35%)			40
36		 84%			41
37		 52%			42
38					43

The product from pyrolysis of ester (36) also has a logical explanation. The 1- and 3-methyl groups must be axial in order that the three other and bulkier groups may be equatorial. This causes a substantial steric interaction (compounded by buttressing of the CH_2CH_2-OAc group) which is best relieved by formation of the *exo*-cyclic alkene. A similar explanation accounts for the product from pyrolysis of ester (37), the reduced steric crowding requiring less *exo*-cyclic alkene formation, precisely as observed. Formation of the *exo*-cyclic alkene from ester (38) also arises from the need to reduce the methyl–methyl repulsions enforced by the molecular structure.

Thus the seemingly contradictory product patterns obtained in ester pyrolysis, in fact, follow from straightforward steric effects, and explanations involving 'surface-catalysed' mechanisms are unnecessary. In some eliminations, rearrangement products are obtained (see Table IV, ref. 23) and Wertz and Allinger conceded that the product distributions were far removed from those expected for equilibriation of a fully formed intermediate carbocation. They reconciled this with their mechanism by arguing that the positive charge on the α-carbocation would be substantially delocalised by the surface. This explanation is also unnecessary. The symmetry of the ester function leads to the expectation that migration, aided in some cases by neighbouring-group participation, will take place. This requires that the product distribution will be highly dependent on ester type, precisely as observed though evidently overlooked by Wertz and Allinger; their mechanism requires the product pattern to be independent of ester type.

Finally, we have shown that the transition state becomes slightly more *E*1-like and correspondingly less E_i-like as the ester reactivity increases.[4] It follows that in this direction, thermodynamic stability should become more important so that less terminal alkenes, and more *trans*-relative to *cis*-alkene should be obtained. Both of these predictions are observed along the increased reactivity series derived from butan-2-ol *viz*: acetate < chloroacetate < dichloroacetate < trifluoroacetate,[26d] and acetate < carbonate.[45] Likewise ester (35) gives more (±)-*p*-menth-3-ene along the reactivity series: acetate < benzoate < carbonate. Again these results rule out the surface-catalysed mechanism because the alkene distribution is not independent of ester type.

EXPERIMENTAL

1,3,3-*Trimethylbutyl Acetate* (4,4-*Dimethylpent*-2-*yl Acetate*).—This ester, b.p. 152 °C at 760 mmHg was obtained by acetylation of 4,4-dimethylpentan-2-ol (Aldrich) with pyridine and acetic anhydride.

1,1,3-*Trimethylbutyl Acetate* (2,4-*Dimethylpent*-2-*yl Acetate*).—This ester, b.p. 84 °C at 60 mmHg was obtained by acetylation of 2,4-dimethylpentan-2-ol (Koch Light) with acetic anhydride and *N*,*N*-dimethylaniline.

3-*Methylbutyl Acetate*.—This was a commercial sample (Koch-Light), redistilled before use.

3,3-*Dimethylbutyl Acetate*.—This ester, b.p. 150 °C at 760 mmHg, n_D^{20} 1.406 4, was obtained by acetylation of 3,3-dimethylbutanol (Aldrich) as above.

1-*Phenyl*-3-(p-*anisyl*)*propene and* 1-(p-*Anisyl*)-3-*phenylpropene*.—These were both prepared as described by De Puy and Leary.[18]

1-(p-*Anisyl*)-3-*phenylprop*-2-*yl Acetate*.—The Grignard reagent from *p*-methoxybenzyl chloride was treated with an excess of phenylacetaldehyde in the usual way. Work up gave white crystals of 4,4-dimethoxydiphenylethane, m.p 126 °C (lit.,[43] 126 °C) as the main product, together with a small quantity of a yellow oil. Fractional distillation of this gave 1-(p-*anisylmethyl*)-2-*phenylethyl acetate* [1-(p-*anisyl*)-3-*phenylprop*-2-*yl acetate*] (10%), b.p. 170 °C at 0.5 mmHg (Found: C, 76.1; H, 7.08. $C_{18}H_{20}O_3$ requires C, 76.2; H, 7.11%), τ (CCl_4) 2.84 (s, C_6H_5), 3.11 (q, C_6H_4OMe), 4.76 (m, *J* 6.5 Hz, CH), 6.30 (s, OCH_3), 7.19 (d, *J* 6.5 Hz, CH_2), 7.25 (d, *J* 6.5 Hz, CH_2), and 8.35 (s, $OCOCH_3$).

Kinetic Studies.—These were carried out using the stainless-steel reactor system (with deactivated surface) in the manner previously described.[44] Excellent first-order kinetics (Table 1) were obtained to beyond 95% reaction, and rate coefficients (which were independent of a 5-fold change in initial pressure) could be duplicated to within ±1%.

Product Studies.—1,3,3-Trimethylbutyl acetate was pyrolysed on glass helices at temperatures between 395 and 505 °C by the standard method [18,19] and also in the stainless-steel reactor possessing a deactivated surface.[44] The alkenes were separated both on a 9 ft × 4.5 mm column packed with 5% Carbowax 20M adsorbed on 100—120 mesh Chromosorb operated at 70 °C and a flow rate of 50 ml min^{-1} N_2 and also on a 20 ft × 2.1 mm column packed with 5% silicone oil adsorbed on 100—120 mesh Chromosorb G operated at 50 °C and a flow rate of 15 ml min^{-1} N_2. On both columns the alk-1-ene eluted first followed by the unresolved *cis*/*trans* mixture of the alk-2-ene. Both columns gave a 1-/2-alkene ratio of 0.49 ± 0.02 *under all conditions*. The independence of the value of surface types also argues persuasively against the surface-catalysed mechanisms.

1,1,3-Trimethylbutyl acetate was pyrolysed on glass helices as described above, the products being separated on the silicone oil column operated at 35 °C.

1-(*p*-Anisyl)-3-phenylprop-2-yl acetate was pyrolysed on glass helices as described by De Puy and Leary.[18] The alkenes produced were successfully resolved by g.l.c. using a 20 ft × 2.1 mm column packed with 5% OV17 adsorbed on 100—120 mesh Chromosorb G operated at 260 °C and 15 ml min^{-1} N_2. The retention times were 2 100 and 2 170 s for 1-phenyl-3-(*p*-anisyl)propene and 1-(*p*-anisyl)-3-phenylpropene respectively, the respective peak ratios being 1.1 : 1.0, *i.e.* the thermodynamically least-stable product was produced in the greatest amount. The retention times were checked with authentic samples of the alkenes, and the identity of the peaks was also confirmed by using mass spectroscopy–g.l.c. analysis.

[8/2214 *Received*, 28*th December*, 1978]

REFERENCES

[1] Part 8, R. Taylor, *J. Chem. Research*, 1978, (*S*) 267; (*M*) 3526.
[2] For the most recent review, see R. Taylor, 'The Chemistry of the Functional Groups,' Supplementary Volume B: Acid derivatives, ed. S. Patai, Wiley, London, 1979, pp. 859—915.
[3] R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4817.
[4] H. B. Amin and R. Taylor, *J.C.S. Perkin II*, 1978, 1090.
[5] H. B. Amin and R. Taylor, *J.C.S. Perkin II*, 1978, 1095.

[6] H. B. Amin and R. Taylor, *J.C.S. Perkin II*, 1979, 228.
[7] G. G. Smith, K. K. Lum, J. A. Kirby, and J. A. Posposil, *J. Org. Chem.*, 1969, **34**, 2090.
[8] G. G. Smith, D. A. K. Jones, and D. F. Brown, *J. Org. Chem.*, 1963, **28**, 403; G. G. Smith and D. A. K. Jones, *ibid.*, p. 3896.
[9] H. B. Amin and R. Taylor, *J.C.S. Perkin II*, 1975, 1802.
[10] G. G. Smith, D. A. K. Jones, and R. Taylor, *J. Org. Chem.*, 1963, **28**, 3547.
[11] R. Taylor and M. P. Thorne, *J.C.S. Perkin II*, 1976, 799.
[12] R. Taylor, *J.C.S. Perkin II*, 1978, 1255.
[13] R. Taylor, *J.C.S. Perkin II*, 1975, 1025.
[14] C. E. Higgins and W. D. Baldwin, *J. Org. Chem.*, 1961, **26**, 846.
[15] E. S. Lewis and W. C. Herndon, *J. Amer. Chem. Soc.*, 1961, **83**, 1955, 1961; E. S. Lewis, W. C. Herndon, and D. C. Duffey, *ibid.*, 1961, **83**, 1959; E. S. Lewis and K. Witte, *J. Chem. Soc.* (*B*), 1968, 1198; W. A. Sheppard, *J. Org. Chem.*, 1962, **27**, 3756; N. Barroeta, V. de Santis, and M. Rincon, *J.C.S. Perkin II*, 1974, 911.
[16] P. C. Oele, A. Tinkelberg, and R. Louw, *Tetrahedron Letters*, 1972, 2375.
[17] H. Kwart and J. Slutsky, *J.C.S. Chem. Comm.*, 1972, 1182.
[18] R. Taylor, *J.C.S. Perkin II*, 1972, 165.
[19] D. Y. Curtin and D. B. Kellom, *J. Amer. Chem. Soc.*, 1953, **75**, 6011; C. H. De Puy, R. W. King, and D. H. Froemsdorf, *Tetrahedron*, 1959, **7**, 123; A. T. Blades and P. W. Gilderson, *Canad. J. Chem.*, 1960, **38**, 1401, 1407; E. A. Halevi, *Progr. Phys. Org. Chem.*, 1963, **1**, 109.
[20] S. de Burgh Norfolk and R. Taylor, *J.C.S. Perkin II*, 1976, 280.
[21] G. G. Smith, F. D. Bagley, and R. Taylor, *J. Amer. Chem. Soc.*, 1961, **83**, 3647.
[22] C. H. De Puy and R. E. Leary, *J. Amer. Chem. Soc.*, 1957, **79**, 3705.
[23] D. H. Wertz and N. L. Allinger, *J. Org. Chem.*, 1977, **42**, 698.
[24] J. C. Scheer, E. C. Kooyman, and F. L. J. Sixma, *Rec. Trav. chim.*, 1963, **82**, 1123.
[25] D. H. Froemsdorf, C. H. Collins, G. S. Hammond, and C. H. De Puy, *J. Amer. Chem. Soc.*, 1959, **81**, 643.
[26] (*a*) J. P. W. Hartman, J. Van Steenis, and P. M. Heertjes, *Rec. Trav. chim.*, 1946, **65**, 781; (*b*) W. O. Haag and H. Pines, *J. Org. Chem.*, 1959, **24**, 877; (*c*) R. Borkowski and P. Ausloos, *J. Amer. Chem. Soc.*, 1961, **83**, 1053; (*d*) C. H. De Puy, C. A. Bishop, and C. N. Goeders, *ibid.*, p. 2151; (*e*) D. B. Bigley and C. M. Wren, *J.C.S. Perkin II*, 1972, 1744.
[27] E. E. Royals, *J. Org. Chem.*, 1958, **23**, 1822.
[28] K. K. Lum and G. G. Smith, *Internat. J. Chem. Kinetics*, 1969, **1**, 401.
[29] W. J. Bailey and W. F. Hale, *J. Amer. Chem. Soc.*, 1959, **81**, 647.
[30] R. Onesta and G. Castelfranchi, *Chimica et Industria*, 1959, **41**, 222.
[31] R. A. Benkeser, J. J. Hazdra, and M. L. Burrows, *J. Amer. Chem. Soc.*, 1959, **81**, 5374.
[32] A. Cuenca and G. Chuchani, *Internat. J. Chem. Kinetics*, 1977, **9**, 379.
[33] W. J. Bailey and W. F. Hale, *J. Amer. Chem. Soc.*, 1959, **81**, 651.
[34] R. A. Benkeser and J. J. Hazdra, *J. Amer. Chem. Soc.*, 1959, **81**, 228.
[35] A. T. Blomquist and G. Denning, Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, March 1961.
[36] A. T. Blomquist and P. R. Taussig, *J. Amer. Chem. Soc.*, 1957, **79**, 3505.
[37] A. T. Blomquist and A. Goldstein, *J. Amer. Chem. Soc.*, 1955, **77**, 1001.
[38] W. S. Briggs and C. Djerrassi, *J. Org. Chem.*, 1968, **33**, 1625.
[39] J. R. van der Briz and E. C. Kooyman, *Rec. Trav. chim.*, 1952, **71**, 837.
[40] J. P. Wibaut, H. C. Beyerman, and H. B. Leenwen, *Rec. Trav. chim.*, 1951, **71**, 1027; N. L. McNiven and J. Read, *J. Chem. Soc.*, 1953, 2067.
[41] G. Ohlaff and G. Schade, *Chem. Ber.*, 1958, **91**, 2017.
[42] A. Brenner and H. Schinz, *Helv. Chim. Acta*, 1952, **35**, 1333.
[43] G. Büchi, M. Schack van Wittenau, and H. Schechter, *J. Amer. Chem. Soc.*, 1959, **81**, 1968.
[44] G. G. Smith and F. W. Kelly, *Progr. Phys. Org. Chem.*, 1971, **9**, 150.
[45] D. B. Bigley and C. M. Wren, *J.C.S. Perkin II*, 1972, 1744.
[46] L. B. Howard, G. E. Hilbert, R. Weibe, and V. L. Gaddy, *J. Amer. Chem. Soc.*, 1932, **54**, 3628.
[47] R. Taylor, *J. Chem. Soc.* (*B*), 1968, 1397.