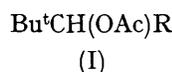


## Pyrolyses of Some Highly Branched Secondary Acetates

By G. Chuchani,\* G. Martin, and N. Barroeta, Chemistry Section, Instituto Venezolano de Investigaciones Científicas (I.V.I.C.), Apartado 1827, Caracas, Venezuela  
Allan Maccoll, Christopher Ingold Laboratories, University College, 20 Gordon Street, London WC1H 0AJ

Three highly branched secondary acetates were pyrolysed in a static system over the pressure range 25–300 mmHg and the temperature range 305–380 °C. The reactions in seasoned vessels were found to be homogeneous and unimolecular. The temperature-dependence of the rate constants is given by the Arrhenius equations: 3-acetoxy-2,2-dimethylbutane,  $\log k_1/s^{-1} = 12.5 \pm 0.22 - (44,060 \pm 600 \text{ cal mol}^{-1})/2.303RT$ ; 3-acetoxy-2,2-dimethylpentane,  $\log k_1/s^{-1} = 13.06 \pm 0.09 - (44,850 \pm 780 \text{ cal mol}^{-1})/2.303RT$ ; and 3-acetoxy-2,2,4-trimethylpentane,  $\log k_1/s^{-1} = 13.12 \pm 0.08 - (46,600 \pm 230 \text{ cal mol}^{-1})/2.303RT$ . Variation of the rate of reaction within the series is interpreted in terms of structural and electronic factors.

This paper describes a further investigation of the six-centred cyclic transition state<sup>1</sup> for the thermal decomposition of esters containing  $\beta$ -C-H bonds by a study of a series of highly branched secondary acetates (I) with R = Me, Et, and Pr<sup>i</sup>, and an interpretation of



the results in terms of steric and electronic effects. The formation of a mixture of alkenes and acetic acid, normally by a process of *cis*-elimination, has been discussed in terms of the alkyl-oxygen charge distribution caused by the inductive effect of  $\alpha$ - and  $\beta$ -substituents<sup>2</sup> and in terms of the acidity of the acid portion of the ester.<sup>3</sup> However, in the case of esters possessing certain structural features, Wagner-Meerwein rearrangements have been reported<sup>4</sup> as well as  $\alpha$ -elimination with a concerted migration.<sup>5</sup>

One approach would be to investigate the correlation, if any, between the pyrolysis rates of the present series of esters and the rates of unimolecular solvolysis and elimination of the corresponding halides in polar solvents.<sup>6</sup> This was not possible, since the appropriate halides have not so far been investigated under such conditions. It is, however, worth noting that the rates of hydrolysis of these acetates in 70% dioxan-water at 20 °C<sup>7,8</sup> fall in the order (I) R = Me > R = Et > R = Pr<sup>i</sup>. Steric effects appear to be important since the rate of hydrolysis is smaller, the closer the branching is to the acetoxy-group.

### RESULTS AND DISCUSSION

*Stoichiometry and Homogeneity.*—The equation describing the reactions studied was predominantly (I).



This implies that for long reaction times, the final pressure ( $P_f$ ) approaches twice the initial pressure ( $P_0$ ). The results for the acetate (I; R = Me) are in Table 1.

<sup>1</sup> C. D. Hurd and F. H. Blunck, *J. Amer. Chem. Soc.*, 1938, **60**, 2419.

<sup>2</sup> E. U. Emovon and A. Maccoll, *J. Chem. Soc.*, 1962, 335.

<sup>3</sup> E. U. Emovon, *J. Chem. Soc.*, 1963, 1246.

<sup>4</sup> E. U. Emovon, *J. Chem. Soc. (B)*, 1966, 588.

<sup>5</sup> H. Kwart and H. Ling, *Chem. Comm.*, 1969, 302.

<sup>6</sup> A. Maccoll and P. J. Thomas, *Nature*, 1955, **176**, 392.

The product was predominantly 3,3-dimethylbut-1-ene, although in clean glass vessels the presence of the isomers 2,3-dimethylbut-1-ene and 2,3-dimethylbut-2-ene was confirmed. This is consistent with the reported thermodynamic properties of the dimethylbutenes<sup>9</sup> which give

TABLE 1

Stoichiometry of the pyrolysis of 3-acetoxy-2,2-dimethylbutane

$t/^\circ\text{C}$	$P_0/\text{mmHg}$	$P_f/\text{mmHg}$	$P_f/P_0$
306.7	181.0	344.0	1.90
337.8	92.0	183.0	1.99
355.8	184.0	367.0	1.98
363.6	125.0	244.0	1.95

an equilibrium at 600 K, 0.2, 47.7, and 52.1% of the three olefins. A value of  $P_f/P_0$  close to two was also found for 3-acetoxy-2,2-dimethylpentane which yielded 95% of *trans*-4,4-dimethylpent-2-ene and 5% of the *cis*-compound. Under the conditions of the experiment, the *cis*- and *trans*-forms were found to isomerise, as shown in Table 2. Products other than acetic acid and

TABLE 2

Yields of isomeric 4,4-dimethylpent-2-enes formed after 16 h at 360 °C

Starting olefin	$P_0/\text{mmHg}$	<i>cis</i> (%)	<i>trans</i> (%)	Unidentified (%)
<i>cis</i>	149	58.5	41.5	0.0
<i>trans</i>	141	4.1	94.3	1.6
Equilibrium mixture*		34.0	66.0	0.0

\* These values are calculated by the method of Van Krevelen (see G. J. Janz, 'Estimation of thermodynamic properties of organic compounds,' Academic Press, New York, 1958).

2,4,4-trimethylpent-2-ene were observed in the pyrolysis products of 3-acetoxy-2,2,4-trimethylpentane. This olefin, when pyrolysed in a seasoned vessel, formed a product identical with that observed as a minor product in the ester pyrolysis, namely 2,4,4-trimethylpent-1-ene. This is produced in very small amounts (*ca.* 3%) together with smaller amounts of decomposition products

<sup>7</sup> M. S. Newman and S. Hishida, *J. Amer. Chem. Soc.*, 1962, **84**, 3582.

<sup>8</sup> S. Sarel, L. Tsai, and M. S. Newman, *J. Amer. Chem. Soc.*, 1956, **78**, 5420.

<sup>9</sup> D. R. Stull, E. F. Westrum, jun., and G. C. Sinke, 'The Chemical Thermodynamics of Organic Compounds,' Wiley, New York, 1969.

such as isoprene, one of the isomers of dimethylpentene and trimethylpentene. These minor products do not, however, substantially affect the stoichiometry represented by (I).

The homogeneity of the reactions was checked by using vessels of surface: volume ratio 4.0 and 6.8 times greater than that of the unpacked vessel. Packing had no significant effect on the rate constants for the decompositions, although it did affect the isomeric olefin

been factored out<sup>10</sup> by considering the 'rate per  $\beta$ -hydrogen available' in the calculation of relative rates.

The fact that a uniform structural change is accompanied by a maximum in relative reactivity clearly indicates the importance of opposing effects along the series. The nature of these effects has been previously explained<sup>11</sup> in discussing the results of a series of esters studied by a flow technique. The present results indicate that the same principles can be extended to

TABLE 3

Olefin composition in the pyrolysis of 3-acetoxy-2,2,3-trimethylpentane

$t/^\circ\text{C}$	$S/V$	% Reaction	A* (%)	B* (%)	C (%)	D (%)	E (%)	F (%)	G (%)	H (%)	I (%)
382.2	1	100	0.03	0.00	0.12	0.07	0.00	99.8	0.00	0.00	0.00
383.2	1	100	0.12	0.00	0.33	0.18	0.00	99.4	0.00	0.00	0.00
382.2	1	100	0.00	0.00	0.62	0.18	0.90	98.2	0.00	0.00	0.00
357.9	4	81	0.11	0.04	0.51	0.22	0.67	97.9	0.00	0.00	0.50
243.2	6.8	59	0.09	0.00	0.18	0.35	1.65	96.3	0.00	0.00	1.41

\* A and B = unidentified; C = isoprene; D = dimethylpentene; E = 2,4,4-trimethylpent-1-ene; F = 2,4,4-trimethylpent-2-ene; G, H, and I = unassigned trimethylpentenes.

composition. It was concluded that the reactions studied were effectively homogeneous.

*Effect of Inhibitor on the Rates.*—The presence of cyclohexene (a free-radical inhibitor) showed no significant effect on the rates within experimental error (Table 4).

*Kinetics of the Elimination Reaction.*—The first-order rate constants for the decomposition of these esters are

TABLE 4

Effect of cyclohexene on rates

$t/^\circ\text{C}$	$P_0/\text{mmHg}$	$P_c/\text{mmHg}$	$10^4 k_1/s^{-1}$
(I; R = Me)			
347.0	171.0		10.86
347.0	219.0	40.0	10.90
347.0	102.0	116.0	10.76
347.0	60.0	157.0	10.75
(I; R = Et)			
337.4	172.0		10.19
337.4	152.0	45.0	10.23
337.4	121.0	105.0	9.91
337.4	51.0	103.0	10.30
(I; R = Pr <sup>1</sup> )			
382.2	125.0		37.83
382.2	139.0	23.0	37.20
382.2	54.5	40.0	37.96
382.2	60.0	102.0	37.36

independent of initial pressure over the range 25–300 mmHg and the first-order logarithmic plots are satisfactorily linear up to at least 60% decomposition. The temperature-dependence of the rate constants is shown in Table 5. From the experimental results, the Arrhenius equations given in Table 6 were obtained by means of a least-squares procedure. The errors are given as standard errors.

The pertinent information in relation to reactivity has been collected in Table 7 where the statistical effect has

highly branched acetates such as those studied here. Table 7 shows that both the activation energy and the frequency factor increase in going from R = Me to

TABLE 5

Variation of rate constants with temperature

$t/^\circ\text{C}$	306.6	315.7	325.0	335.8	347.0	355.5	363.6
No. of runs	10	14	12	11	18	16	17
$10^4 k_1/s^{-1}$	0.813	1.62	2.63	5.40	10.73	16.3	25.7
(I; R = Et)							
$t/^\circ\text{C}$	312.2	320.5	329.2	337.4	345.5	353.5	359.6
No. of runs	9	12	11	12	13	11	10
$10^4 k_1/s^{-1}$	2.04	3.66	6.17	10.14	16.4	26.3	37.3
(I; R = Pr <sup>1</sup> )							
$t/^\circ\text{C}$	322.2	332.5	342.2	353.2	364.6	372.6	382.2
No. of runs	10	13	11	11	10	12	11
$10^4 k_1/s^{-1}$	1.03	2.01	3.72	7.14	14.3	21.5	37.5

TABLE 6

Arrhenius parameters for pyrolysis of (I)

R	$\log_{10} A/s^{-1}$	$E_a/\text{cal mol}^{-1}$
Me	$12.54 \pm 0.22$	$44,060 \pm 600$
Et	$13.06 \pm 0.09$	$44,850 \pm 780$
Pr <sup>1</sup>	$13.12 \pm 0.08$	$46,600 \pm 230$

TABLE 7

Kinetic parameters for pyrolysis of (I) at 360 °C

R	$10^4 k_1/s^{-1}$	Relative rate per $\beta$ -hydrogen	$E_a/\text{cal mol}^{-1}$	$\log A/s^{-1}$
Me	6.84	1.00	44,061	12.537
Et	12.0	2.63	44,854	13.063
Pr <sup>1</sup>	3.22	1.41	46,597	13.122

R = Pr<sup>1</sup>. These effects can be explained as follows. The methyl substitution at the  $\beta$ -carbon results in an ever increasing difficulty in attaining planarity in the

<sup>10</sup> D. M. Bishop and K. J. Laidler, *J. Chem. Phys.*, 1965, **42**, 1688.

<sup>11</sup> J. C. Scheer, E. C. Kooyman, and F. L. J. Sixma, *Rec. Trav. chim.*, 1963, **82**, 1123.

transition state and hence in a larger energetic demand. On the other hand the formation of a cyclic transition state with appreciable rehybridisation in the 'double-bond-forming' carbon atoms may give rise to a decrease in the steric interaction among the alkyl groups, thus increasing the entropy in relation to the ground state. The magnitude of this entropy change is expected to be larger the more crowded the ground state.

#### EXPERIMENTAL

The acetates were prepared from the corresponding alcohols as described.<sup>12</sup> They were fractionated and the fraction of 99.8% purity, as determined by v.p.c., was used. However, once the ester of 2,4,4-trimethylpentan-3-ol was distilled, it was treated with phenyl isocyanate and again fractionated in order to attain maximum purity. The olefins and starting materials were determined quanti-

<sup>12</sup> S. Sarel and M. S. Newman, *J. Amer. Chem. Soc.*, 1956, **78**, 5416.

tatively by the method of internal standard in a Perkin-Elmer F-11 gas chromatograph provided with flame-ionization detector. Dinonyl phthalate 20%—Celite 60—80 mesh and di-isodecyl phthalate 5%—Chromosorb G A.W. D.M.C.S. 60—80 mesh were used as columns for ester analysis, while the above two columns along with bis-(2-methoxyethyl) adipate 5%—Chromosorb G A.W. D.M.C.S. 80—100 mesh were used for the olefins. The product analysis was also carried out in a gas chromatograph (Perkin-Elmer 900) coupled to a mass spectrometer (Hitachi-Perkin-Elmer RMU-6H) and complemented by i.r. and n.m.r. spectrometry.

The esters were pyrolysed in vessels which had been seasoned by the products of decomposition of allyl bromide<sup>13,14</sup> in a static system and were followed manometrically.

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<sup>13</sup> A. Maccoll, *J. Chem. Soc.*, 1955, 965.

<sup>14</sup> A. Maccoll and P. J. Thomas, *J. Chem. Soc.*, 1955, 979.