The Mechanism of Thermal Eliminations. Part 22.[1] Rate Data for Pyrolysis of Primary, Secondary, and Tertiary β-Hydroxy Alkenes, β-Hydroxy Esters, and β-Hydroxy Ketones. The Dependence of Transition-state Structure for Six-centre Eliminations upon Compound Type

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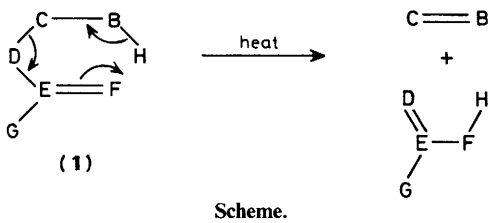
Rates of pyrolysis of but-3-en-1-ol, pent-4-en-2-ol, and 2-methylpent-4-en-2-ol, the corresponding methyl hydroxy esters *viz.* methyl 3-hydroxypropanoate, methyl 3-hydroxybutanoate, and methyl 3-hydroxy-3-methylbutanoate, and the corresponding methyl hydroxy ketones *viz.* 4-hydroxybutan-2-one, 4-hydroxypentan-2-one, and 4-hydroxy-4-methylpentan-2-one have been measured between 556.4 and 713.7 K. The relative 1°:2°:3° rates at 600 K are 1:2.0:3.47 for alkenes, (1):9.3:44.6 for the esters, and (1):7.0:21.6 for the ketones (the rates for the primary compounds in the latter two series being less accurate because of significant concurrent dehydration). The order of reactivity is ketones ≫ esters > alkenes, the relative reactivities at 600 K being 338:2.21:1 for 4-hydroxy-4-methylpentan-2-one, methyl 3-hydroxy-3-methylbutanoate, and 2-methylpent-4-enol, respectively. The reactivity of the ketones compared with the alkenes contrasts with the results for the structurally analogous acetates and vinyl ethers which eliminate with near identical rates and for which methyl substitution on the double bond produces substantially less rate modification. At 600 K 3-methylbut-3-en-1-ol is 8.4 times as reactive as but-3-en-1-ol, and phenyl 3-hydroxypropanoate is much less reactive than methyl 3-hydroxypropanoate. The results provide further evidence that within the spectrum of E_i transition states for six-centre eliminations there are two broad mechanistic categories. For reactions with more *E*1-like transition states, breaking of the C_α–X bond is the most important step, whereas for other reactions including those described here, nucleophilic attack of the double bond upon the β-C–H bond becomes the most important step. The higher nucleophilicity of the C=O bond *vs.* the C=CH_2 bond accounts for the difference in reactivity of ketones and alkenes, while the inductive effect of the methoxy group upon the nucleophilicity of the double bond appears to account for the lower reactivity of the esters compared to the ketones.

Many organic compounds are able to undergo thermal elimination according to a six-centre process depicted generally by the Scheme. We have previously shown that a spectrum of



(1)

Scheme.

transition states applies within the overall semi-concerted process,[2] depending both upon the atoms comprising the six-membered ring, and the nature of the groups attached at various points. Within the overall E_i process, some classes of compounds show some *E*1 characteristics, indicating that the transition states for these lie somewhat nearer to that for an *E*1 reaction (though of course still well removed from it). Compounds in this class are those for which the $C^{\delta+}$–$D^{\delta-}$ bond can readily polarise in the direction shown; alkyl substituents on C will substantially increase the elimination rate, and the 3°/2° rate ratio will be much greater than the 2°/1° rate ratio (for C being either 1°, 2°, or 3°). Aryl substituents at C give Hammett correlations (with σ^+-values) having negative ρ-values. Electron-withdrawing substituents at G increase the reaction rate, and aryl substituents there give Hammett correlations having positive ρ-values, the nucleophilicity of the E=F bond is relatively unimportant, and breaking of the B–H bond is less kinetically significant than is breaking of the C–D bond.

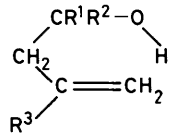
The other broad category of compounds is that in which the members have a relatively non-polar C–D bond, but by contrast a very polar B–H bond. For these compounds (which have been less thoroughly studied) nucleophilic attack by F (or the E=F bond) upon hydrogen should now be the most important step of the reaction. Alkyl substituents on C should have relatively little effect upon the reaction rate, and could even decrease it through reducing polarisation of the B–H bond in the direction required. By contrast, electron supply from G should produce a large rate increase, through raising the electron density on F. In order to provide further information on this category of reactions we have measured rates of elimination of 1°, 2°, and 3° derivatives of three types of compound which we expected to fall within this class *viz.* β-hydroxy alkenes (**2**), β-hydroxy esters (**3a**), and β-hydroxy ketones (**3b**). These provide a comparison, evident from their structure, with compounds *viz.* vinyl ethers (**4**), methyl carbonates (**5a**), and esters *e.g.* acetates (**5b**) which have E_i transition states with substantial *E*1 character.

In a previous study of the effects of phenyl groups upon the rate of elimination of β-hydroxy alkenes,[3] a 1-phenyl substituent was found to accelerate the reaction *ca.* 19-fold at 619 K. This was interpreted as indicating that cleavage of the C(1)–C(2) bond is the most important step of the reaction. Against this conclusion must be set the fact that though aryl substituents at C(1) gave a Hammett correlation with a negative ρ-factor, the magnitude of the latter was very small, being −0.11 at 600 K (statistically calculated—the original paper[3] gave the

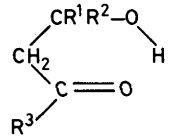
value incorrectly as −0.26). Furthermore the effects of methyl substituents at C(1) appeared to be very small, but these were determined over a rather limited temperature range. This suggested possible unreliability in the results, particularly since two studies by the same group[3,4] of the elimination of 3-phenylbut-3-en-1-ol yielded activation energies differing by 13 kJ mol^{-1}; rates differed by more than 40%, equivalent to a temperature error of >7 °C. We have therefore redetermined the elimination rates for the compounds with methyl groups substituted at C(1) using a wider temperature range and higher temperatures to ensure that surface catalysis (always likely to intrude at lower temperatures) was minimal. We have also measured the rates of elimination of 3-methylbut-3-en-1-ol in order to ascertain the effect of a methyl group at E in the Scheme *i.e.* G = Me, and thereby provide a direct comparison with the methyl ketones.

Some rate data have previously been obtained for hydroxy ketones,[5] but these were for pyrolysis in xylene, so that a direct comparison with the alkene data would not be justified. Gas-phase data were previously obtained for 2-methylpent-4-en-2-ol,[4] but at lower temperatures, whereas comparison with our data will show there was considerable incursion of some surface-catalysed elimination. Moreover the Arrhenius data quoted (E = 135.1 kJ mol^{-1}, log A = 11.63) markedly disagree with the values (127.2 kJ mol^{-1}, log A = 10.78) which may be calculated from the reported data.

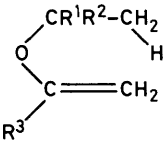
Some rate data have previously been reported for hydroxy esters,[6] but again the Arrhenius parameters given were not consistent with the kinetic data. Methyl esters were not studied so that a direct comparison with methyl ketones was not possible.



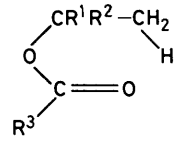
(**2**; R^1, R^2, R^3 = H, Me)



(**3**; R^1, R^2 = H, Me)
a; R^3 = OMe, OPh
b; R^3 = Me



(**4**; R^1, R^2, R^3 = H, Me)



(**5**; R^1, R^2 = H, Me)
a; R^3 = OMe
b; R^3 = Me

Table 1. Relative rates for elimination of (i) β-hydroxy alkenes $HOCR^1R^2CH_2CR^3{=}CH_2$; (ii) β-hydroxy esters $HOCR^1R^2CH_2COOR^3$; (iii) β-hydroxy ketones $HOCR^1R^2CH_2COR^3$

	R^1	R^2	R^3	$k_{rel.}$ (600 K)
(i)	H	H	H	1
	Me	H	H	2.00
	Me	Me	H	3.47
	H	H	Me	8.41
(ii)	H	H	Me	(1)
	Me	H	Me	9.3
	Me	Me	Me	44.6
(iii)	H	H	Me	(1)
	Me	H	Me	7.0
	Me	Me	Me	21.6

Results and Discussion

The β-hydroxy alkenes were very well behaved kinetically, giving kinetic plots first-order to 99% reaction, and excellent Arrhenius plots with no deviant points whatsoever. The tertiary hydroxy esters and hydroxy ketones were similarly well behaved, the primary and secondary compounds rather less so, and this was due to the incursion of some surface-catalysed dehydration, producing the corresponding alkenes. The dehydration arises from the electron-withdrawing nature of the group G–E=F in the Scheme and consequently is insignificant for the hydroxy alkenes and more important for the hydroxy ketones than for the hydroxy esters; it will also be more significant for the primary compounds relative to their rates of the main elimination given by the Scheme since this is slower. For the primary (and to a much lesser extent the secondary)

Table 2. Kinetic data for pyrolysis of β-hydroxy alkenes $HOCR^1R^2CH_2CR^3{=}CH_2$

R^1	R^2	R^3	T/K	10^3k/s^{-1}	log (A/s^{-1})	E_a/kJ mol^{-1}	Corr. coeff.	k (600 K)/s^{-1}
H	H	H	635.7	1.60	10.672	163.90	0.999 99	2.51 × 10^{-4}
			658.2	4.61				
			680.3	12.1				
			703.1	31.5				
			713.7	47.2				
Me	H	H	635.7	3.11	10.828	162.22	0.999 98	5.02 × 10^{-4}
			658.2	9.07				
			680.3	23.6				
			703.1	59.7				
			713.7	89.2				
Me	Me	H	635.7	5.39	10.900	160.33	0.999 82	8.71 × 10^{-4}
			658.2	14.7				
			680.3	38.5				
			703.1	94.3				
			713.7	151				
H	H	Me	615.6	4.41	10.010	145.64	0.999 96	21.1 × 10^{-4}
			635.7	11.0				
			662.4	33.5				
			676.2	56.3				

Table 3. Kinetic data for pyrolysis of β-hydroxy esters $HOCR^1R^2CH_2COOR^3$

R^1	R^2	R^3	T/K	$10^3\ k$/s^{-1}	log (A/s^{-1})	E_a/kJ mol^{-1}	Corr. coeff.	k (600 K)/s^{-1}
H	H	Me	620.6	0.137	11.113	178.01	0.999 42	0.412×10^{-4}
			636.0	0.302				
			649.7	0.650				
			663.5	1.19				
			675.5	2.30				
H	Me	Me	608.2	0.65	10.900	164.43	0.997 76	3.84×10^{-4}
			620.6	1.04				
			636.0	2.50				
			649.7	4.58				
			633.5	9.50				
Me	Me	Me	608.2	2.88	11.182	159.85	0.999 67	18.4×10^{-4}
			626.1	6.69				
			636.0	11.5				
			649.7	21.5				
			663.5	39.4				

Table 4. Kinetic data for pyrolysis of β-hydroxy ketones $HOCR^1R^2CH_2COR^3$

R^1	R^2	R^3	T/K	$10^3\ k$/s^{-1}	log (A/s^{-1})	E_a/kJ mol^{-1}	Corr. coeff.	k (600 K)/s^{-1}
H	H	Me	595.1	12.6	11.098	149.06	0.992 06	13.6×10^{-3}
			601.3	13.0				
			615.6	25.2				
			626.1	46.2				
			636.4	79.6				
			643.9	108				
H	Me	Me	556.4	11.0	11.097	139.19	0.992 21	95.0×10^{-3}
			567.1	17.2				
			573.4	26.2				
			575.7	29.4				
			580.2	40.8				
			587.3	49.1				
Me	Me	Me	556.4	35.8	11.128	133.91	0.999 54	294×10^{-3}
			567.1	61.9				
			576.0	98.3				
			580.6	118				

compounds, a larger number of kinetic runs than usual were required to produce a minimum rate set giving a satisfactory Arrhenius line; runs giving the minimum rate set were all good first-order. Rate data are given in Tables 1—4. The relative rates ($k_{rel.}$) for the primary β-hydroxy esters and the β-hydroxy ketones are parenthesised because there is some uncertainty in the accuracy of these values due to the concurrent dehydration (see Table 1). The relative rates for the β-hydroxy alkenes differ slightly from those (*viz.* 1:2.97:5.16) obtained in a less rigorous study by Smith and Yates,[4] but both sets agree in showing that the 3°/2° rate ratio is less than the 2°/1° rate ratio. The data for the tertiary hydroxy alkene, 2-methylpent-4-en-2-ol (**2**; R^1, R^2 = Me, R^3 = H), indicate that the rates for this compound obtained by Smith and Yates[4] were accelerated *ca.* 2-fold by surface catalysis. The relative rates of the tertiary and secondary hydroxy ketones (3.09) agree quite well with the value (3.64) which may be calculated from the rate data for pyrolysis in xylene,[5] though the latter gave increased rate coefficients (6—11-fold) in comparison with our data due to the accelerating effect of the solvent, which for example has been observed in pyrolysis of carbamates.[7,8] The relative rates for the tertiary and secondary hydroxy esters (4.8) is close to the value (4.3) which may be calculated from the literature rate data[6] which were obtained using apparatus with only ±1 °C temperature control.

1. *The Primary:Secondary:Tertiary Rate Ratio.*—All three sets of data indicate that the 3°/2° rate ratio is less than the 2°/1° rate ratio, and this pattern is also evident in the rate data for pyrolysis of β-hydroxy alkynes, the 1°:2°:3° ratio at 623 K being 1:2.0:2.5.[9] The spread of alkyl substituent effects is substantially different from those (statistically corrected to account for the different number of β-hydrogens) which have previously been obtained for compounds with a more *E*1-like transition state (Table 5),[10] and is consistent with C(1)–C(2) bond-breaking being of secondary importance. The conclusion of Smith and Yates regarding hydroxy alkene pyrolysis (see Introduction) must now be modified. The ρ-factor for 1-aryl substituents in hydroxy alkenes, and upon which they based their conclusion, is 6—8 times smaller than the values which have been obtained for compounds in Table 5.[11–13] (The transition state for the compounds becomes increasingly *E*1-like down the table and the ρ-factors increase in this direction.) For hydroxy alkynes a 1-phenyl group activates only 19-fold (at 623 K),[9] the same as in hydroxy alkenes, this value being substantially smaller than values found for compounds in Table 5.

2. *The Effects of Substituents G Attached to the Double Bond.*—The above analysis indicates that the transition states for hydroxy alkene, hydroxy alkyne, hydroxy ester, and hydroxy ketone elimination are significantly different from those for elimination from the compounds listed in Table 5. Another feature which distinguishes the two broad classes of compounds is the effect of substituents G in the Scheme. For the compounds listed in Table 5 (except vinyl ethers, the mechanism of which is borderline) electron withdrawal by G decreases the rate (and *vice versa*), and for this reason the elimination rates increase regularly down the Table. However,

Table 5. Rate ratios (statistically corrected for the number of β-hydrogens) for pyrolysis of various compounds at 600 K

Compound	Pr^i/Et	Bu^t/Pr^i
Vinyl ethers	5	11.8
Thioacetates	8.5	51
2-Alkoxypyridines	9	61
Acetates	14.4	77
Phenyl acetates	16.1	80
Benzoates	18.1	83
Phenyl carbonates	19.9	84
Trifluoroacetates	23.6	90

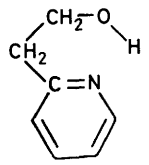
for the other broad category of compounds (*i.e.* those with a less *E*1-like transition state) electron supply by G *increases* the rate (and *vice versa*), and the electronic effect of substituents here is considerably greater than in the former category. The increase in rate must arise through increasing the nucleophilicity of the double bond or of F.[14,15] Thus a 3-methyl group increases the elimination rate of hydroxy alkenes 8.4-fold (Table 2), which may be contrasted with the trivial effect of methyl at the corresponding position in compounds of the former class *e.g.* the near identity of elimination rates in acetates and formates.[13,16] Increase in the nucleophilicity of the double bond now also explains the observation of Smith and Vorhees[3] that a 3-phenyl group increased the reaction rate 9.4-fold whilst 3-aryl substituents gave a Hammett correlation (requiring σ^+-values) with a relatively large negative ρ-factor of −0.49 at 600 K (the value of −0.59 at 619 K given in the original paper took into account data for the *meta* bromo compound which gave anomalous Arrhenius parameters). By contrast, aryl substituents in the corresponding position of compounds with more *E*1-like transition states require σ^0-values in Hammett correlations which give positive ρ-factors.[8,17,18]

In the compounds with more *E*1-character in the transition states, changing the group G from Me to MeO [*i.e.* acetates (**5b**) to methyl carbonates (**5a**)] produces a substantial rate increase (*ca.* 18-fold), due to the $-I$ effect of the methoxy oxygen aiding C_α–O bond breakage. By contrast, in the β-hydroxy compounds, changing Me to MeO produces the opposite, and much larger effect *e.g.* methyl 3-hydroxy-3-methylbutanoate (**3a**; R^1, R^2 = Me, R^3 = MeO) is 153 times less reactive than 4-hydroxy-4-methylpentan-2-one (**3b**; R^1, R^2, R^3 = Me). Whilst this superficially accounts for the generally lower reactivity of hydroxy esters to hydroxy ketones, it is nevertheless surprising that the $+M$ effect of the methoxy group fails to outweigh its $-I$ effect (as would normally be the case in favourable conjugating situations) and thereby increase the nucleophilicity of the double bond. We suggest that the inductive effect in the methoxy group lowers the nucleophilicity of the double bond to the extent that the transition state is altered slightly towards the *E*1 direction; this would also account for the larger 3°:2°:1° ratios found for the hydroxy esters. The lower reactivity of phenyl compared with methyl 3-hydroxypropanoate (**3a**; R^1, R^2 = H, R^3 = OPh or OMe) appears also to be derived from inductive effects.

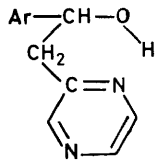
3. *Nucleophilicity of the Double Bond.*—For compounds with the less *E*1-like transition state, nucleophilic attack by the double bond (or the group F) should have greater kinetic significance. Thus the hydroxy ketones are substantially more reactive than the corresponding hydroxy alkenes, *e.g.* at 600 K 4-hydroxy-4-methylpentan-2-one (**3b**; R^1, R^2, R^3 = Me) is 338 times as reactive as 2-methylpent-4-en-2-ol (**2**; R^1, R^2 = Me, R^3 = H). By contrast the analogous ester, t-butyl acetate (**5**; R^1, R^2, R^3 = Me), is only 4 times as reactive as the corresponding alkene t-butyl vinyl ether (**4**; R^1, R^2 = Me, R^3 = H). The importance of this nucleophilicity also nicely accounts for the greater reactivity of hydroxy alkynes[9] compared with hydroxy alkenes, and the variation in rate ratio along the series: 1° (1.83), 2° (1.75), 3° (1.33) since the importance of nucleophilic attack diminishes in this direction.

The rate of elimination of but-3-en-1-ol (**2**; R^1, R^2, R^3 = H) is close to that of 2-(2-hydroxyethyl)pyridine (**6**) ($10^4k/s^{-1}$ at 600 K = 2.8),[2] the greater nucleophilicity of the C=N bond probably being counterbalanced here by the loss of aromaticity on going to the transition state. The importance of the nucleophilicity of the double bond is also shown by the finding that the 2-(2-hydroxy-2-phenylethyl)pyrazine derivative (**7**; Ar = Ph) is less than half as reactive as the corresponding pyridine compound (**8**; Ar = Ph) (in diglyme at 443 K).[19,20] Furthermore the greater nucleophilicity of the C=N bond means that O–H bond breaking should be more important here, hence in pyrolysis of (**7**) and (**8**) substituents in the aryl ring gave a zero or *positive* Hammett ρ-factor[19,20] which contrasts with the *negative* value of −0.11 obtained in the corresponding 1-arylbut-3-en-1-ols.[3] In the pyrazine ring of compounds (**7**) a 5-methyl substituent reduced the rate whilst 6- and 3-methyl substituents increased the rate, the latter by the greater amount.[20] These results parallel exactly those for pyrolysis of ethoxypyridines[21] and the same explanations apply.

Substitution of a phenyl group in the terminal position of the double bond giving 4-phenylbut-3-en-1-ol (**9**) produces a 4.4-fold decreased in reactivity.[3] This evidently arises from the loss of conjugation with the aryl group upon formation of products; an exactly parallel effect (7.5-fold rate decrease) is found in the pyrolysis of the corresponding alkenoic acids.[22]



(**6**)



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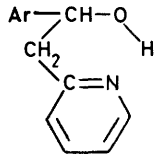

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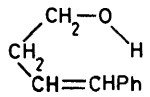
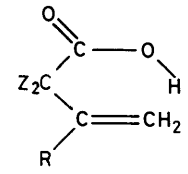


(**9**)

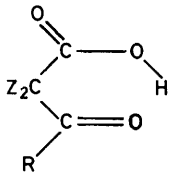
4. *Effects of Methyl Groups at D.*—A literature search shows that there is a common effect for methyl substitution at D, namely acceleration of the elimination rate by factors of *ca.* 1.5, 1.5, 2.0, and 3.0, respectively for hydroxy alkenes,[4] hydroxy alkynes,[9] hydroxy ketones,[5] and hydroxy esters.[6] This may reflect increased nucleophilicity of the double bond through greater electron supply. Since the effect is common to all four classes of compounds, hyperconjugative stabilisation of the forming double bond may be ruled out as an explanation as it cannot apply to the ketones or esters. Steric acceleration may be responsible. This has been found to be important in ester pyrolysis[14,18,23] and has been proposed as important in the pyrolysis of β-hydroxy esters.[24] In this latter (theoretical) study it was claimed that steric strain release is the *predominant*

controlling factor in the retroaldol reaction. The substituent data show this explanation to be inadequate; in particular it is unable to account for the large differences in reactivity between the hydroxy esters and hydroxy ketones, which do not have alkyl groups substituted at D.

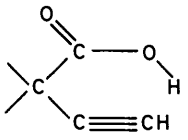
5. *The Mechanism of Pyrolysis of Related Compounds.*— Compounds which are related to those above are, for example, alkenoic acids (**10**) and β-oxo acids (**11**). The hydrogen for elimination in these is more acidic, so that nucleophilic attack upon this could be expected to be more important. No direct comparison of the reactivities of (**10**) and (**11**) is available, but the β-oxo acids are certainly the more reactive.[14] It is tempting to speculate that by analogy with the hydroxy alkenes *vs.* hydroxy alkynes, so alkynoic acids (**12**) will be more reactive than alkenoic acids (**10**), probably by a larger factor. A corresponding prediction regarding the methyl half ester of malonic acid (**13**) is more difficult because it appears that in the



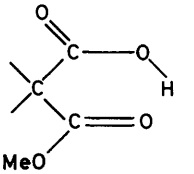
(**10**; Z = H, Me)



(**11**; Z = H, Me)



(**12**)



(**13**)

acids the conjugative effect of the methoxy group now outweighs its inductive effect. For example in the acids (**10**; Z = Me), methoxy (R = OMe) activates *ca.* 10^2 more than phenyl (R = Ph),* whilst in the acids (**10**; Z = H), phenyl (*i.e.* R = Ph) activates *ca.* 3 times more than methyl (R = Me)[14,25,26] so overall the methoxy group is considerably more activating than methyl. Methyl activates by a factor which has been given as 30-fold at 773 K[27] and also as 20-fold at 500 K.[15] (The higher value should be obtained at the lower temperature, and the discrepancy probably reflects the difficulty associated with obtaining accurate kinetic data for very reactive compounds in the gas phase.) The value is independent of whether Z is H or Me indicating, as proposed earlier,[14] that the rate acceleration is not a steric effect.

The greater importance of nucleophilic attack in the acids is also reflected by the larger negative ρ-factors for the effects of aryl substituents at R in (**10**) compared with (**2**); values of *ca.* −1.1 and −2.7 apply to (**10**) for Z = Me and H, respectively.[25,†]

A further parallel between the series is provided by the effects of methyl groups Z in (**10**)[27] and (**11**)[28] which produce similar though larger acceleration of 2.8- and 2.5-fold per methyl group respectively. In this connection it is possible that the smaller effects of aryl substituents R noted in (**10**) for Z = Me compared with Z = H is a manifestation of the well known 'tool of increasing electron demand'.[29] Thus greater electron supply to the double bond by the methyl group results in less demand for electron supply from the aryl groups, and a smaller ρ-factor.

Experimental

But-3-en-1-ol, pent-4-en-2-ol, and *3-methylbut-3-en-1-ol* were supplied by the Aldrich Chemical Co.

2-Methylpent-4-en-2-ol. Acetone (11.6 g, 0.2 mol) in dry ether was added dropwise to the Grignard reagent formed from allyl bromide (17.5 g, 0.145 mol) and magnesium (5 g, 0.21 mol) in dry ether (50 ml), and the mixture was heated under reflux during 1 h. Hydrolysis and normal work-up gave 2-methylpent-4-en-2-ol (4.2 g, 29%), b.p. 115 °C; n_D^{20} 1.4266 (lit.,[30] 119.5 °C; n_D^{17} 1.4277).

Methyl 3-hydroxypropanoate. This was prepared from β-propiolactone and methanol on a 0.2 mol scale according to the literature method.[31] Fractional distillation gave methyl 3-hydroxypropanoate (15.6 g, 75%), b.p. 66 °C at 9 mmHg; n_D^{20} 1.4224 (lit.,[32] 71 °C at 13 mmHg; n_D^{20} 1.4225).

Phenyl 3-hydroxypropanoate. Attempted preparation of this compound by a base-catalysed reaction between β-propiolactone and phenol as for the previous preparation failed. Work-up and fractional distillation yielded phenol, phenyl propenoate (b.p. 40 °C at 0.4 mmHg; n_D^{20} 1.5212), and phenyl 3-phenoxypropanoate (b.p. 130 °C at 0.1 mmHg; n_D^{20} 1.5490), the identities of the latter two compounds being confirmed by n.m.r. and g.l.c.–mass spectral analysis. The former two compounds are probably produced from the latter during fractional distillation (the work-up procedure would have removed phenol). Formation of phenyl 3-phenoxypropanoate may occur through acyl oxygen cleavage of the lactone to give phenyl 3-hydroxypropanoate followed by nucleophilic substitution of OH by OPh.

The title compound was successfully prepared by the sulphuric acid-catalysed reaction between β-propiolactone and phenol on a 0.5 mol scale, according to the literature method.[32] Normal work-up with fractional distillation gave phenyl 3-hydroxypropanoate (29.0 g, 35%) b.p. 90—92 °C at 0.25 mmHg (lit.,[32] 90—92 °C at 0.2 mmHg). Earlier *and* later fractions showed the presence of phenyl propenoate which suggests that the ester dehydrates readily (though see *Product Studies*).

Methyl 3-hydroxybutanoate. The Reformatsky reaction using acetaldehyde and methyl bromoacetate failed to give the required product, substantial recovery of the latter reagent resulting from two attempts. Catalytic (PtO_2) reduction of methyl acetoacetate gave very pure methyl 3-hydroxybutanoate, b.p. 47 °C at 3.9 mmHg; $n_D^{23.5}$ 1.4194 (lit.,[33] 67 °C at 13 mmHg; n_D^{25} 1.4195).

Methyl 3-hydroxy-3-methylbutanoate. Various attempts to make this compound in usable quantities using the Reformatsky reaction between acetone and methyl bromoacetate or methyl chloroacetate failed (totally using the latter). By-products included methyl hydroxyacetate, unchanged methyl halogenoacetate, and a fraction b.p. 30 °C at 80 mmHg which was probably methyl 3-methylbut-2-enoate produced by

* The accuracy of this value is in some doubt,[26] and its calculation assumed that rates of concerted reactions are not enhanced by solvents. However, increases of up to 25-fold have been observed for carbamate pyrolysis, and in the latter reaction nitrobenzene (the solvent used in pyrolysis of the methoxy acid) increased the rate over 4-fold.[7]

† Our view regarding a possible steric explanation for the magnitude of these ρ-factors was misrepresented in this paper. In ref. 14 we suggested that steric effects could modify the ρ-factor through inhibiting conjugation (thereby making analysis of electronic effects *via* Hammett correlations unreliable here) and this now appears to have been confirmed.[25] In ref. 25 this view is wrongly attributed to Bigley and Thurman[27] whilst we were stated to have *dismissed* this proposal. Our belief was that the substituent effects observed at the β-position of βγ-unsaturated acids could be entirely electronic, as has been confirmed for the effects of alkyl groups at this site.[15]

dehydration of the required product. A final attempt according to the literature method,[34] but using a 4-fold excess of acetone, gave a small yield of the required product, b.p. 116 °C at 80 mmHg. Purification of this product is difficult because it tends to codistil with unchanged methyl bromoacetate, and these mixtures were coloured yellow or red (probably due to traces of polymer from methyl 3-methylbutenoate). Very careful fractional distillation at the lowest possible temperature yielded methyl 3-hydroxy-3-methylbutanoate (indicated to be pure by g.l.c.), b.p. 25 °C at 1 mmHg (lit.,[34] 70 °C at 12 mmHg); δ($CDCl_3$) 1.28 (6 H, s, Me_2), 2.51 (2 H, s, CH_2), 3.68 (3 H, s, OMe), and 3.82 (1 H, s, OH). On standing this product turned *blue* which is rather surprising. The colour must be due to the formation of a trace impurity since there was no detectable change in the n.m.r.; the colour faded after a week or so. Reanalysis of a sample which had been allowed to stand during *ca.* three years showed that it had hydrolysed to the acid in what may be a self-catalysed reaction; no other hydroxy ester showed this behaviour.

4-*Hydroxybutan*-2-*one and* 4-*hydroxy*-4-*methylpentan*-2-*one.* These were purchased from Aldrich Chemical Co., and were redistilled before use; the former compound contained many impurities and required very careful fractional distillation to purify it.

4-*Hydroxypentan*-2-*one.* Acetaldehyde (11 g, 0.25 mol) was passed as a vapour into an oxygen-free flask containing acetone (94 ml), methanol (6 ml), and potassium hydroxide (0.34 g) during 3 h. Oxalic acid was added to just neutralise the product, the precipitate removed by filtration, and the residue concentrated and fractionally distilled to give 4-hydroxypentan-2-one, b.p. 29 °C at 3 mmHg.

Kinetic Studies.—The general method and apparatus used has been described previously.[35] Kinetic runs were first-order to at least 90% reaction (99% in the case of the alkenols). Rate coefficients were independent within experimental error of a 4-fold change in the initial conentration and such changes did not alter the first-order form of the reaction kinetics. Nevertheless this test for homogeneity is unreliable in our experience and proved to be so here since scatter was observed on the Arrhenius plots, as noted in the discussion. We therefore used only minimum rate coefficients which fell upon a good straight line, our experience of gas-phase eliminations being that such data are generally due to reactions which are free of heterogeneous components. Although good first-order kinetics can be obtained when the latter are present, *reproducible* kinetics (±2% or better) are never obtained. The Arrhenius lines finally obtained indicated that in runs giving deviant points the rates were increased by up to 30%.

Product Studies.—Although product studies have been carried out previously with hydroxy alkenes, hydroxy ketones, and hydroxy esters we carried out additional checks with the latter two classes because of the unexpectedly large difference in rates between them, and the scatter on the Arrhenius plots for the primary and secondary compounds. Product runs were mostly carried out by passing the sample down a column of helices heated to the same temperature as that used in the kinetic runs; the throughput time was adjusted by the rate of flow of the argon carrier gas such that approximately 90% of the sample was decomposed. Products were analysed by n.m.r. together with g.l.c.–mass spectrometry where this was considered necessary.

4-Hydroxy-4-methylpentan-2-one gave only acetone as product. 4-Hydroxypentan-2-one gave the expected acetone and acetaldehyde, together with *ca.* 5% of *trans*-pent-3-en-2-one; δ($CDCl_3$) 6.88 (1 H, dd, *J* 17 and 7 Hz, =*H*CCOMe), 6.00 (1 H, dd, *J* 17 and 2 Hz, =*H*CMe), and 1.80 (3 H, dd, *J* 7 and 2 Hz, *Me*CH=). 4-Hydroxybutan-2-one gave mainly acetone and formaldehyde together with but-3-en-2-one (*m*/*z* 70%); δ($CDCl_3$) 6.34—5.84 (overlapping second-order multiplets); the n.m.r. spectrum also showed peaks at δ 4.97—4.76 (m) but these could not be assigned.

Methyl 3-hydroxy-3-methylpropanoate gave only acetone and methyl acetate as products. Methyl 3-hydroxybutanoate gave acetaldehyde and methyl acetate and a trace of *trans*-methyl but-2-enoate (*m*/*z* 100%). Methyl 3-hydroxypropanoate gave methyl acetate together with a small amount of methyl propenoate. Phenyl 3-hydroxypropanoate formed only phenyl acetate as a detectable product and the extent of decomposition was much less than that of methyl 3-hydroxypropanoate under identical conditions, showing it to be less reactive. In kinetic runs the phenyl ester appeared to be marginally the more reactive, but the runs were not good first-order, and we believe that surface catalysis accounted for the discrepancy.

In general, product analysis of kinetic runs indicated that the by-products were produced in particular from runs which gave anomalously high rates indicating that these dehydration side reactions were surface catalysed.

References

1 Part 21, N. Al-Awadi and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1589.
2 R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1983, 809; M. A. Hossaini and R. Taylor, *ibid.*, 1982, 187, and earlier papers in each series.
3 G. G. Smith and K. J. Vorhees, *J. Org. Chem.*, 1970, **35**, 2182; *ibid.*, 1971, **36**, 1755.
4 G. G. Smith and B. L. Yates, *J. Org. Chem.*, 1965, **30**, 2067.
5 B. L. Yates and J. Quijano, *J. Org. Chem.*, 1969, **34**, 2506.
6 B. L. Yates, A. Ramirez, and O. Velasquez, *J. Org. Chem.*, 1971, **36**, 3579.
7 S. J. Ashcroft and M. P. Thorne, *Can. J. Chem.*, 1972, **50**, 3478.
8 R. Taylor and M. P. Thorne, *J. Chem. Soc., Perkin Trans. 2*, 1976, 799.
9 A. Viola, J. H. MacMillan, R. J. Proverb, and B. L. Yates, *J. Am. Chem. Soc.*, 1971, **93**, 6967.
10 R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1179.
11 R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Am. Chem. Soc.*, 1962, **84**, 4817.
12 H. B. Amin and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1090, 1095; *ibid.*, 1979, 229.
13 R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1025.
14 R. Taylor, 'The Chemistry of the Functional Groups, Supplementary Volume B. Acid Derivatives,' ed. S. Patai, Wiley, London, 1979, p. 862.
15 D. B. Bigley, R. H. Weatherhead, and R. B. May, *J. Chem. Soc., Perkin Trans. 2*, 1977, 745.
16 A. T. Blades and H. S. Sandhu, *Int. J. Chem. Kinet.*, 1971, **3**, 187; E. Gordon, S. J. W. Price, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1957, 2813.
17 G. G. Smith, D. A. K. Jones, and R. Taylor, *J. Org. Chem.*, 1963, **28**, 3547; H. B. Amin and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1802; *ibid.*, 1978, 1095.
18 R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1255.
19 Y. Houminer and R. L. Williams, *J. Org. Chem.*, 1983, **48**, 2622.
20 Y. Houminer, *J. Org. Chem.*, 1980, **45**, 999.
21 N. Al-Awadi, J. Ballam, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1175.
22 D. B. Bigley and R. W. May, *J. Chem. Soc. (B)*, 1967, 558.
23 R. Taylor and G. G. Smith, *Tetrahedron*, 1963, **19**, 937; S. de Burgh Norfolk and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1976, 280; R. Taylor, *ibid.*, 1979, 1730; G. G. Smith, L. Mütter, and L. P. Todd, *J. Org. Chem.*, 1977, **42**, 44.
24 Y. Houminer, J. Kao, and J. I. Seeman, *J. Chem. Soc., Chem. Commun.*, 1984, 1608.
25 A. Al-Borno and D. B. Bigley, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1311.
26 A. Al-Borno and D. B. Bigley, *J. Chem. Soc., Perkin Trans. 2*, 1982, 15.
27 D. B. Bigley and J. C. Thurman, *J. Chem. Soc. (B)*, 1968, 436.
28 K. J. Pedersen, *J. Phys. Chem.*, 1934, **38**, 559.

29 Leading references are given in H. C. Brown, 'The Non-Classical Ion Problem,' Plenum, New York, 1977.
30 'Dictionary of Organic Compounds,' 4th Edn., Eyre and Spottiswoode, London, 1965.
31 T. L. Gresham, J. E. Jansen, F. W. Shaver, J. T. Gregory, and W. L. Beears, *J. Am. Chem. Soc.*, 1948, **70**, 1004.
32 T. L. Gresham, J. E. Jansen, F. W. Shaver, R. A. Bankert, W. L. Beears, and M. G. Prendergast, *J. Am. Chem. Soc.*, 1949, **71**, 661.
33 N. Mori, S. Omura, N. Kobayashi, and Y. Tsuzuki, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 2149.
34 S. Searles, E. K. Ives, and S. Nukima, *J. Org. Chem.*, 1959, **24**, 1770.
35 N. Al-Awadi and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1581.

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