Electronic Effects of Polar Substituents in the Gas Phase Unimolecular Elimination of 4-Substituted Isobornyl Acetates

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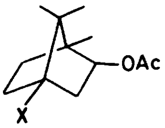
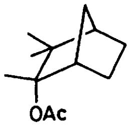
The rates of gas-phase elimination of a series of 4-substituted isobornyl acetates have been measured in the presence of propene between 209—370 °C and within a pressure range 37—153 Torr; a static system with seasoned vessels was used. The reactions are unimolecular, homogeneous, and obey a first-order rate law; electron-withdrawing substituents at C(4) cause a diminution in the elimination rate, such that ρ_I −0.69 in a Hammett treatment. The temperature dependence of the rate coefficients is illustrated for the Arrhenius equation for isobornyl acetate: $\log k/\text{s}^{-1} = (12.82 \pm 0.13) - (189.2 \pm 1.5)\ \text{kJ mol}^{-1}/2.303RT$. The results are consistent with a cyclic transition state in which C(2)–O cleavage is more advanced than that of C(3)–H. The major primary product of elimination of isobornyl acetate is bornylene, which partially isomerises to camphene and tricyclene under the reaction conditions. Bornylene also undergoes a retro-Diels–Alder reaction to yield the trimethylcyclopentadiene and ethylene.

THE semipolar or semi-concerted cyclic transition state in pyrolysis of esters [1-4] militates against the occurrence of neighbouring group participation and rearrangement reactions are infrequently encountered. A general review [4] describes only a few examples of rearrangements during pyrolysis and these involve special ring systems or experimental conditions that do not correspond to true gas-phase reactions. Thus, the reported examples of anchimeric assistance of a double bond in the gas phase [5,6] were found to be a consequence of surface catalysis during pyrolysis in stirred flow systems.[3] Further, in the gas-phase pyrolysis of bornyl and isobornyl acetates reported by Emovon [7] formation of bornylene, the product of *syn*-elimination, together with camphene and tricyclene was described. The latter products were considered to arise from participation of the C(1)–C(6) bond with the intervention of a quasi-non-classical transition state. Sato and his collaborators [8] also pyrolysed these bicyclic acetates and reported both rearrangement and stepwise reactions. Further examples of possible rearrangements have been described by Smith and Kelly.[4] More recently, a four-fold rate enhancement in the gas-phase pyrolysis of 2-(methylthio)ethyl acetate over ethyl acetate has been interpreted in terms of participation by the CH_3S substituent.[9]



(1) X = H
(2) X = Me
(3) X = Ph
(4) X = Cl
(5) X = OAc
(6) X = CN
(7) X = NO_2



(8)

These results prompted us to examine the pyrolysis of the 4-substituted isobornyl acetates (1)—(7) in order to ascertain whether rearrangement products arise from neighbouring group participation of the C(1)—C(6) bond, and also to examine the influence of C(4) substituents on the elimination.

EXPERIMENTAL

I.r. spectra of starting materials were determined with a Perkin-Elmer 257 spectrophotometer while a Perkin-Elmer 577 spectrophotometer was used in product analysis. Product identification and purity analysis were also determined with a Dupont 21-492B data system and 21-094B mass spectrometer and a Varian A60 n.m.r. spectrometer. ^{13}C N.m.r. spectra were recorded on a Varian XL 100 spectrometer and refer to *ca*. 0.1M solutions of substrate in $CDCl_3$.

M.p.s were recorded on a Kofler hot-stage apparatus and are uncorrected. Microanalytical determinations were carried out by the Microanalytical Department, University of Glasgow.

Quantitative g.l.c. analyses were carried out on columns consisting of (i) FFAP 7%–Chromosorb W.AW.DMCS. 80—100 mesh, and (ii) Carbowax 20M 15%–Chromosorb W.AW.DMCS. 80—100 mesh. Liquid esters were distilled several times until a purity >97.8% was indicated by g.l.c. analysis.

Camphene was acquired from Aldrich; bornylene was a gift from Professor C. J. W. Brooks and tricyclene was prepared according to a literature method.[10]

Isobornyl acetate was prepared from isoborneol by refluxing in acetic anhydride with a trace of pyridine. Other acetates were prepared from the corresponding alcohols by the same method and their ^{13}C chemical shifts are reported in Table 1.

4-Phenylisoborneol was obtained from 2-phenylisoborneol [11] by the method used by Morris and Murray [12] for 1-nitrocamphene. 4-Phenylisoborneol had m.p. 114—115 °C (lit.,[13] 115.5—116 °C), the derived acetate had m.p. 86—87° C (lit.,[13] 87 °C).

4-*Methylisoborneol* was prepared by the same general method [14] except that 1-methylcamphene was now stirred with a three-fold molar excess of trichloroacetic acid for 15 h at 80 °C. The acetate was obtained as an oil, $\nu_{max.}$ (film) 1 740 and 1 235 cm^{-1} (Found: C, 74.3; H, 10.7. $C_{13}H_{22}O_2$ requires C, 74.25; H, 10.55%).

4-Nitroisoborneol, prepared according to the literature method,[12] gave an *acetate* which was obtained as an oil, $\nu_{max.}$ (film) 1 730, 1 520, 1 230, and 820 cm^{-1} (Found: C, 59.95; H, 7.95; N, 6.05. $C_{12}H_{19}NO_4$ requires C, 59.7; H, 7.9; N, 5.8%).

TABLE 1

^{13}C Chemical shifts of 4-substituted isobornyl acetates (1)—(7)

4-Substituent	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8) †	C(9) †	C(10)
H[18]	48.60	80.76	38.79	45.10	27.09	33.80	46.91	19.90	20.14	11.37
Me	50.52 *	79.88	45.56	47.78 *	33.25	34.43	46.86 *	17.66	17.72	12.16
Ph	51.82 *	79.63	43.63	54.53 *	32.62	33.01	50.44 *	18.35	18.57	12.35
Cl	49.72 *	77.82	46.84	72.74	36.06	32.38	47.28 *	17.44	17.53	12.72
OAc	48.22 *	78.10	40.34	86.84	29.71	32.10	45.53 *	17.43	17.61	11.90
CN	51.67 *	77.84	42.47	43.92	31.83 †	32.39 †	49.84 *	18.18	18.48	11.57
NO_2	51.63 *	76.91	41.50	93.22	31.14 †	31.33 †	50.05 *	17.68	18.05	11.92

Acetate ^{13}C absorptions are between δ 169.70 and 170.29 p.p.m. for the eight acetate carbonyls and the corresponding methyl groups absorb between δ 20.91 and 21.15 p.p.m. Additionally the substituent at C(4) absorbs at the following positions in the compounds itemised: 4-CH_3, 15.69; 4-CN, 120.86; 4-Ph, 140.87, 127.83, 127.34, and 126.08 p.p.m.

Assignments indicated by †, *, or ‡ may be reversed.

4-Chlorisoborneol was prepared by the method of Houben and Pfankuch [14] and the *acetate* was obtained as an oil, $\nu_{max.}$ (film) 1 740 and 1 235 cm^{-1} (Found: C, 62.3; H, 8.5; Cl, 15.6. $C_{12}H_{19}ClO_2$ requires C, 62.45; H, 8.3; C, 15.35%).

exo-2,4-Dihydroxybornane was obtained by the method of Libman *et al.*[15] and Paukstelis *et al.*[16] The *diacetate* was obtained as a solid, m.p. 51—53 °C, $\nu_{max.}$ (Nujol) 1 730 and 1 245 cm^{-1} (Found: C, 65.95; H, 8.85. $C_{14}H_{22}O_4$ requires C, 66.1; H, 8.7%).

Isoborneol-4-carboxamide.—Camphene-1-carboxamide [17] (18.4 g, 0.103 mol) was heated at 80 °C for 15 h with trichloroacetic acid (76 g). The resulting solution was worked up as described previously [12] to give the trichloroacetate (29.4 g, 87.5%) as a very insoluble solid which was saponified overnight at room temperature with a solution consisting of methanol (170 ml) and sodium hydroxide (33 ml of a 30% aqueous solution). The resulting solution was filtered and the methanol partially evaporated; neutralisation was effected with dilute hydrochloric acid to give the highly insoluble isoborneol-4-carboxamide as a *solid* which was recrystallised from ethanol, m.p. 217—219 °C (Found: C, 67.2; H, 9.4; N, 7.15. $C_{11}H_{19}NO_2$ requires C, 66.95; H, 9.7; N, 7.1%).

4-*Cyanoisobornyl Acetate.*—Isoborneol-4-carboxamide (18.3 g, 0.092 mol) was heated with acetic anhydride (29 g, 0.27 mol) containing two drops of pyridine at 130 °C for 120 h. The cooled solution was poured into cold aqueous $NaHCO_3$ solution and stirred for 3 h to hydrolyse excess of acetic anhydride. The solid acetate was taken up in ether, washed with dilute hydrochloric acid, water, brine, and dried ($MgSO_4$). After removal of $MgSO_4$ by filtration the solvent was evaporated to give the crude acetate (18 g) as a light brown solid. This was chromatographed on alumina using as eluent, 30% ether in light petroleum (b.p. 40—60 °C). This gave crystals of 4-*cyanoisobornyl acetate* (12 g), m.p. 62—63 °C, $\nu_{max.}$ (Nujol) 2 225, 1 730, and 1 240 cm^{-1} (Found: C, 70.7; H, 8.45; N, 6.65. $C_{13}H_{19}NO_2$ requires C, 70.55; H, 8.65; N, 6.35%).

The pyrolysis experiments were performed in a static system, and the reaction vessel was at all times seasoned by the product of allyl bromide decomposition.[19,20] The kinetic measurements were made by titration of acetic acid produced in the reaction against a solution of 0.05M-sodium hydroxide.

The esters were injected directly into the reaction vessel through a silicone rubber septum.[21] Some of these substrates of low m.p. were kept in liquid form by gentle warming in order to introduce them into the reaction vessel through injection. The temperature of these reactions was kept constant within ±0.2 °C as indicated by a calibrated platinum–platinum–13% rhodium thermocouple. Measurements at different points along the reaction vessel showed no temperature gradient.

RESULTS AND DISCUSSION

The products of pyrolysis of 4-substituted isobornyl acetates (1)—(7) in the presence of a chain inhibitor (propane) consisted of a mixture of $C_{10}H_{15}X$ hydrocarbons, together with their derivatives, and acetic acid. For a normal elimination the theoretical stoicheiometry requires that the final pressure, P_f, be twice the initial pressure, P_0. However the average experimental results of P_f/P_0 after ten half lives and at four different temperatures were the following: isobornyl acetate, 2.91; 4-methylisobornyl acetate, 3.12; 4-phenylisobornyl acetate, 3.03; 4-acetoxyisobornyl acetate, 3.31; 4-chloroiosbornyl acetate, 2.33; 4-cyanoisobornyl acetate, 2.72; and 4-nitroisobornyl acetate, 2.16. The higher value of P_f/P_0 is due to formation of other than the normal elimination products of substituted bornylene and its isomers. The other products were mainly substituted trimethylcyclopentadienes and ethylene formed by retro-Diels–Alder reaction of the bornylene.

The homogeneity of these eliminations was examined by comparing the rate of pyrolysis in a packed vessel with a surface-to-volume ratio of 6.14 times greater than the normal vessel. For each ester decomposition, packing had no significant effect on the rate coefficient as long as the vessel was seasoned with allyl bromide.

The rate coefficients were determined by a titrimetric method, and the *k* values were found to be the same at different percentages of decomposition at each working temperature. The velocity of elimination is independent of the initial pressure and the first-order plots are linear up to 50% decomposition. The effect of temperature on the rate coefficients for elimination is given in Table 2.

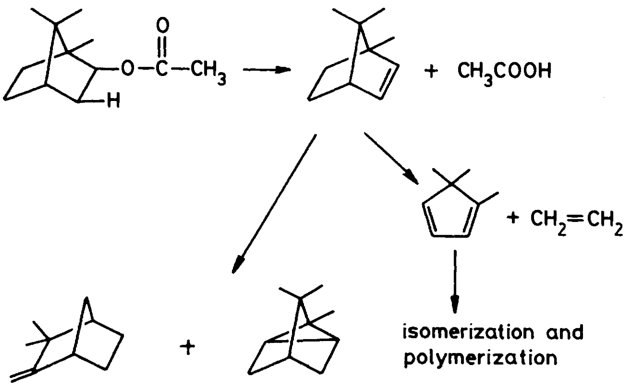
TABLE 2

The effect of temperature on rate coefficient

Isobornyl acetate				
Temperature (°C)	321.8	329.2	340.5	344.1
$10^4k/s^{-1}$	1.58	2.53	5.07	6.30
Temperature (°C)	350.0	359.4	368.9	
$10^4k_1/s^{-1}$	8.92	15.36	26.19	
4-Methylisobornyl acetate				
Temperature (°C)	310.2	319.1	328.8	340.1
$10^4k_1/s^{-1}$	1.01	1.80	3.31	6.59
Temperature (°C)	344.2	350.0	359.5	370.0
$10^4k_1/s^{-1}$	8.47	11.79	20.27	36.21
4-Phenylisobornyl acetate				
Temperature (°C)	289.8	300.1	310.2	319.9
$10^4k_1/s^{-1}$	0.53	1.06	2.05	3.78
Temperature (°C)	332.3	344.1		
$10^4k_1/s^{-1}$	8.05	16.08		
4-Acetoxyisobornyl acetate				
Temperature (°C)	310.0	320.9	325.1	329.8
$10^4k_1/s^{-1}$	0.48	0.99	1.30	1.75
Temperature (°C)	341.1			
$10^4k_1/s^{-1}$	3.53			
4-Chloroisobornyl acetate				
Temperature (°C)	325.9	330.0	339.1	344.1
$10^4k_1/s^{-1}$	1.45	1.86	3.30	4.60
Temperature (°C)	349.3	359.5	370.3	
$10^4k_1/s^{-1}$	6.21	10.85	20.85	
4-Cyanoisobornyl acetate				
Temperature (°C)	336.4	344.2	350.3	360.1
$10^4k_1/s^{-1}$	1.43	2.29	3.33	5.92
Temperature (°C)	369.7			
$10^4k_1/s^{-1}$	10.21			
4-Nitroisobornyl acetate				
Temperature (°C)	318.6	329.1	339.8	344.1
$10^4k_1/s^{-1}$	0.45	0.88	1.73	2.25
Temperature (°C)	350.0	359.5		
$10^4k_1/s^{-1}$	3.20	5.57		

The results listed in Table 2 give, by using the least-squares procedure and 0.8 confidence limits, the Arrhenius parameters given in Table 3.

The $C_{10}H_{16}$ hydrocarbons formed in the pyrolysis of isobornyl acetate (Table 4) are bornylene, tricyclene, and camphene together with trimethylcyclopentadienes and ethylene. Because of the formation of the latter two compounds by a retro-Diels–Alder decomposition of bornylene, Herndon and Manion [22] seriously questioned the rearrangement reactions proposed by Emovon.[7] In order to evaluate whether rearrangement reactions of the products of pyrolysis take place, each of the $C_{10}H_{16}$ bicyclic compounds was introduced into the reaction vessel in the presence of acetic acid and propane inhibitor as an approximate condition of the pyrolysis experiments. The results are given in Table 5, and show that the product distribution of bornylene is very similar to that obtained from the pyrolysis of isobornyl acetate (Table 4). It also appears that the greater the temperature of decomposition the more is favoured the formation of camphene and trimethylcyclopentadienes. These facts imply strongly that tricyclene and camphene are merely products of isomerization processes, while trimethylcyclopentadienes and ethylene are products of retro-Diels–Alder addition of bornylene. Consequently the schematic representation of the pyrolysis of isobornyl acetate is as given in the Scheme.



SCHEME Product formation from pyrolysis of isobornyl acetate

The occurrence of rearrangement *via* neighbouring group participation from the C(1)–C(6) bond is therefore put in serious doubt, a view already expressed by Herndon and Manion.[22] It has also recently been shown by labelling experiments that no Wagner–Meerwein rearrangement is involved in the formation of either norbornene or nortricyclene [23] although there is more heterolytic character in the transition state for pyrolysis of alkyl halides than for acetates.[24]

The relative reactivities for the gas-phase thermal decomposition of 4-substituted isobornyl acetates are given in Table 3. These data show that electron-withdrawing substituents decrease the rate of elimination with respect to isobornyl acetate; thus a plot of log k *versus* σ_I values [25] for the polar substituents OAc, Cl, CN, NO_2 yields an approximate straight line (Figure), characterised by slope (≡ ρ_I) of -0.698 (r 0.903, intercept 0.043). Thus the effect of substituent on the elimination rate is not dramatic. However, considered with hydrogen, the isobornyl acetates with weakly inductive substituents do not conform to this behaviour but rather the rates of elimination, expressed as log *k*, increase in the sense indicated by the linear free energy steric parameter E_s.[26] The geometric disposition of the C(4) substituent fixed in a rigid bicyclic framework and the intramolecular nature of the elimination make the rate data for (1)—(3) difficult to explain in terms of a mechanism involving steric acceleration. However it has recently been noted that pyrolysis of 2-alkyl-substituted ethyl acetates showed that the elimination rates were susceptible to steric acceleration, the values for log k_{rel} showing a linear correlation with E_s.[27]

TABLE 3

Kinetic parameters for pyrolyses of 4-substituted isobornyl acetates at 340 °C, together with activation parameters

Substituent	$10^4k_1/s^{-1}$	Relative rate	E_a/kJ mol^{-1}	log (A/s^{-1})	log k_{rel}
4-H	5.01	1.00	189.2 (±1.5)	12.82 (±0.13)	0.000
4-H [a]	4.59	—	175.8	11.64	
4-CH_3	6.50	1.30	186.7 (±1.3)	12.72 (±0.12)	0.113
4-C_6H_5	12.76	2.55	181.5 (±1.6)	12.57 (±0.15)	0.406
4-CH_3CO	3.35	0.69	190.9 (±3.8)	12.79 (±0.34)	−0.175
4-Cl	3.53	0.71	191.8 (±2.1)	12.89 (±0.18)	−0.162
4-CN	1.78	0.36	192.6 (±0.9)	12.66 (±0.08)	−0.450
4-NO_2	1.75	0.35	191.5 (±1.2)	12.56 (±0.11)	−0.457

[a] From ref. 7.

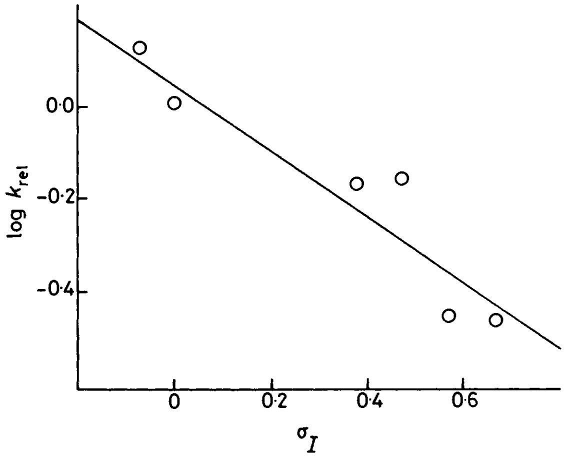
In the case of the isobornyl acetates with electron-withdrawing substituents *i.e.* (4)—(7), together with (1), the bond-breaking and -making steps may be considered as part of a cyclic mechanism.[28] The relative timings of the steps may not be in complete concert, however it is possible to place certain limits on particular events in the transition state for elimination. Thus with the known propensity of the norbornan-2-yl cation and its derivatives for rearrangement [29] it is apparent that heterolysis of the C(2)–O bond is not advanced to such an extent as to permit products of Wagner–Meerwein rearrangement to arise from an electron-deficient centre C(2) since such products have been shown, for (1), to originate from secondary reactions of bornylene. If heterolysis of the *exo*-C(3)–H bond were alone crucial in the rate-determining step then the rate of elimination of (7) would be expected to be fastest since the electron-withdrawing nature of the nitro-group would have an acidifying effect on this proton, as has been found in the base-catalysed proton exchange rates of the related 4-substituted bornanones.[30]

TABLE 4

Yields of products from isobornyl acetate pyrolysis [a] at several temperatures

Product	Temperature (°C) 320	340	370
Bornylene	22.3	23.6	24.8
Tricyclene	14.8	12.2	9.4
Camphene	50.1	52.8	55.4
Trimethylcyclopentadienes	12.7	11.8	11.2

[a] Ethylene is obtained in about the same proportion as the trimethylcyclopentadienes.



Plot of log k_{rel} *versus* σ_I in the pyrolysis of 4-substituted isobornyl acetates

A thorough study of the electronic effects of substituents on pyrolysis rates in acyclic systems has been reported by Taylor's group.[31,32] Thus it is found that among convenient leaving groups the transition state for elimination is about the least polar for acetate with the β-carbon–hydrogen bond not more than one third

TABLE 5

Product distribution of the bicyclic $C_{10}H_{16}$ compounds (and trimethylcyclopentadienes) after equilibration of bornylene, tricyclene, and camphene under the reaction conditions

	Temperature (°C)	Bornylene	Tricyclene	Camphene	Trimethylcyclopentadienes
Bornylene	340	24.4	8.6	48.8	1.73 [a]
	370	21.2	9.1	49.1	20.0 [a]
Tricyclene	340		93.5	6.2	
	370		92.4	7.4	
Camphene	340		99.7		
	370		99.3		

[a] Ethylene is formed in the same proportion.

broken in the transition state;[28] additionally the charge developed at C$_\alpha$ in the transition state for elimination is just over 50% greater than that developed at C$_\beta$. It was also found that electron-withdrawing groups on aryl rings substituted at C$_\beta$ bring about a modest increase in the rate of pyrolytic elimination.[2] This is in contrast to the behaviour of electron-withdrawing substituents at C(4) *i.e.* at C$_\gamma$ in the present work. The results are reconcilable if one considers that our substituent exerts a composite effect, acting on both C(3) and also on the more remote site C(2), presumably by a field effect. Since bond breaking at C(2) is more advanced in the transition state it is reasonable to infer that the effect of the substituent is more keenly felt at this position, thereby over-riding the countervailing influence of the substituent at C(3).

In accord with the observed rate sequence for isobornyl acetates with electron-withdrawing substituents at C(4) it is noted that C(2) chemical shifts (Table 1) are progressively displaced to higher field in these cases. The C(2) chemical shifts may imply a greater concentration of electron density at C(2) for the more strongly electron-withdrawing substituents with attendant greater ease of heterolysis of the acetate group.

The observation of a negative ρ value in the present work is surprising since negative values have been found for *inter alia* 1-arylethyl acetates, where the aryl group is bonded to the acetoxy-bearing carbon, whereas ρ is positive, and of smaller magnitude in *inter alia* 2-arylethyl acetates [28] (see however ref. 9).

A referee, citing ref. 33, has suggested that the present results are better accommodated, as regards the sign and magnitude of ρ, by considering a rearrangement to give the tertiary acetate (8) which serves as the immediate olefin-forming precursor. However the mechanism given [33] has the features that concerted substitutions are occurring at C(1) and C(2) with retention of configuration at both sites. Moreover, the acetate in our system is in an *exo*-configuration and such a mechanism is therefore further excluded.

Alternative modes of rearrangement *via* electron-deficient intermediates mediated by the bornyl carbocation or the bornyl radical would almost certainly lead to products of elimination rather than to an isomeric acetate. The latter entity, the bornyl radical, has been observed to undergo Wagner–Meerwein rearrangement although camphene was not among the products.[34] Thus while a rearrangement, having occurred, has the feature of accommodating the observed ρ value in accord with precedent, the mechanism of its execution is difficult to sustain.

A further disadvantage with the mechanism involving prior rearrangement to (8) is that (8) provides no direct pathway to bornylene; this and trimethylcyclopentadiene, a product (which subsequently isomerises) of retro-Diels–Alder reaction of bornylene, account for *ca.* 35% of the product. The data in Table 5 also show that bornylene is a primary product, being formed neither from tricyclene nor from camphene under reaction conditions. The formation of tricyclene from rearranged acetate is possible by a ' concerted ' 1,3-elimination, in the event, unlikely based on precedent from solution reactions,[35] that *endo*-rearranged acetate is formed.

The same referee cited different product yields [7] obtained from pyrolyses of isobornyl acetates, benzoates, xanthates ' at the same temperature ' as providing proof of a rearrangement prior to elimination. However Emovon does not quote the temperature at which he obtained the product yields (we find a small but significant variation with temperature, Table 4) and Bunton,[36] whose data are collated by Emovon,[7] pyrolysed xanthates at 300 °C and benzoates at 350 °C and explicitly stated that ' the temperature difference may make comparison misleading '.

Accordingly, we find the case for a major part of the pyrolysis taking place *via* a rearrangement prior to elimination uncompelling and with the data available prefer the mechanism as described in the earlier part of this paper.

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REFERENCES

[1] D. J. Kramer and G. G. Smith, *Int. J. Chem. Kinet.*, 1974, **6**, 849.

[2] S. de Burgh Norfolk and R. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, 1976, 280.

[3] I. Matin, J. A. Hernandez A, A. Rotinov, and G. Chuchani, *J. Phys. Chem.*, 1979, **83**, 3070.

[4] G. G. Smith and F. W. Kelly, *Prog. React. Kinet.*, 1971, **8**, 75, and references cited therein.

[5] M. Hanack, H. H. Schneider, and H. Schneider-Bernlohr, *Tetrahedron*, 1967, **23**, 2195.

[6] R. W. Thies and L. E. Schick, *J. Am. Chem. Soc.*, 1974, **96**, 456.

[7] E. U. Emovon, *J. Chem. Soc. B*, 1966, 588.

[8] T. Sato, K. Murata, A. Nishimura, T. Tsuchiya, and N. Wasada, *Tetrahedron*, 1967, **23**, 1791.

[9] G. Chuchani, I. Martin, J. A. Hernandez A, A. Rotinov, G. Fraile, and D. B. Bigley, *J. Phys. Chem.*, 1980, **84**, 944.

[10] R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *J. Am. Chem. Soc.*, 1976, **89**, 1442.

[11] N. C. Deno, J. J. Jaruzelski, and A. Schrieshein, *J. Am. Chem. Soc.*, 1955, **77**, 3044.

[12] D. G. Morris and A. M. Murray, *J. Chem. Soc.*, *Perkin Trans. 2*, 1975, 734.

[13] S. S. Nametkin, A. S. Kichina, and D. N. Kursanov, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 1065 (*Chem. Abstr.*, 1930, **24**, 841).

[14] J. Houben and E. Pfankuch, *Liebigs Ann. Chem.*, 1933, **501**, 219.

[15] J. Libman, M. Sprecher, and Y. Mazur, *Tetrahedron*, 1969, **25**, 1679.

[16] J. V. Paukstelis and B. W. Macharia, *Tetrahedron*, 1973, **29**, 1955.

[17] S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. G. Morris, *J. Am. Chem. Soc.*, 1972, **94**, 4615.

[18] Compare ^{13}C spectrum of isobornyl acetate in F. Bohlmann, R. Zeisberg, and E. Klein, *Org. Magn. Reson.*, 1975, **7**, 426.

[19] A. Maccoll, *J. Chem. Soc.*, 1955, 965.

[20] A. Maccoll and P. J. Thomas, *J. Chem. Soc.*, 1955, 979.

[21] M. R. Bridge, D. H. Davies, A. Maccoll, R. A. Rose, and O. Banjoko, *J. Chem. Soc. B*, 1968, 805.

[22] W. C. Herndon and J. M. Manion, *Tetrahedron Lett.*, 1968, 6327.

[23] J. L. Holmes, D. L. McGillivray, and D. Yuan, *Can. J. Chem.*, 1979, **57**, 2621.

[24] A. Maccoll, *Chem. Rev.*, 1969, **69**, 33.

[25] M. Charton, *Prog. Phys. Org. Chem.*, 1981, **13**, 119.

[26] S. H. Unger and C. Hansch, *Prog. Phys. Org. Chem.*, 1976, **12**, 91.

[27] G. Chuchani, I. Martin, and I. Avila, *Int. J. Chem. Kinet.*, 1979, **11**, 561.

[28] R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1972, 165.

[29] J. A. Berson in ' Molecular Rearrangements Part 1,' ed. P. de Mayo, Interscience, New York, London, 1963.

[30] F. C. Brown, E. Casadevall, P. Metzger, and D. G. Morris, *J. Chem. Res.*, 1977, (*S*) 335; (M) 3588.

[31] G. G. Smith, F. D. Bagley, and R. Taylor, *J. Am. Chem. Soc.*, 1961, **83**, 3647.

[32] R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1730 and references cited.

[33] R. Taylor in ' Chemistry of Functional Groups, Acid Derivatives,' Supplement B, Part 1, Wiley, Chichester, 1979, vol. 13, ch. 15, pp. 901—904.

[34] J. A. Berson, C. J. Olsen, and J. S. Walia, *J. Am. Chem. Soc.*, 1960, **82**, 5000.

[35] S. Winstein, *J. Am. Chem. Soc.*, 1965, **87**, 381; H. L. Goering and C. B. Schewens, *ibid.*, 1965, **87**, 3516.

[36] C. A. Bunton, K. Khaleeluddin, and D. Whittaker, *Nature*, 1961, **190**, 715.