159. *The Kinetics of Anionotropic Rearrangement. Part VII. The Simultaneous Rearrangement and Hydrolysis of Propenylethynylcarbinyl Acetate. General Discussion of the Mechanism of Anionotropy and a Comparison of the Mobility of the Hydroxyl and the Acetoxyl Group.*

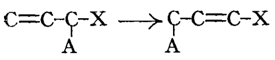
By Ernest A. Braude.

A detailed kinetic study has been made of the acid-catalysed rearrangement of propenylethynylcarbinol (I) and its acetate (III) in aqueous dioxan–hydrochloric acid. The features of the reaction closely resemble those previously established (Parts I and II, *J.*, 1944, 436,443) for the rearrangement of the carbinol in aqueous ethanol. Thus, (i) the rate of reaction is proportional to the concentration of carbinol or acetate, and of acid (at low acid concentrations); (ii) the rate constants decrease with increasing proportion (40 to 80% by vol.) of organic solvent; (iii) the energies of activation, when corrected for the temperature-dependence of the dielectric constant of the medium, are almost independent of the medium composition; (iv) the entropy of activation is positive. Furthermore, both the rate constants and the energies of activation for the carbinol and its acetate are nearly the same (though not identical), and the mobility of the hydroxyl and acetate groups are thus very similar under the conditions studied.

The acetate is hydrolysed simultaneously and at a rate comparable to that of its rearrangement. Nevertheless, the rearrangement and hydrolysis are independent reactions, hydrolysis being about four times as fast as rearrangement at 30° and about three quarters as fast at 95° (in 60% dioxan, 0·1M-HCl). The kinetic features of the hydrolysis are mainly the same as for rearrangement, but the energy of activation is lower by *ca.* 8 kg.-cals./mol. and the reaction constant *A* by a factor of *ca.* 10^6 than for the rearrangement, and the entropy of activation is negative. Also, solvent effects in this case are not temperature-independent and the isodielectric energies of activation are not independent of medium composition. In aqueous ethanol, both rearrangement and hydrolysis proceed at rates similar to those in aqueous dioxan, but liberation of the acetic acid is incomplete owing to the simultaneous hydrolysis and ethanolysis of the acetate.

Existing evidence for the mechanism of the anionotropy of carbinols and esters is reviewed. It is shown that the present results are in accord with the rearrangement mechanism of the type previously proposed (Parts I and II, *locc. cit.*) and subsequently elaborated (Parts III—VI, *J.*, 1946, 122, 128, 396; 1947, 1096). The first step is the fast reversible formation of the oxonium ion by transfer of a proton from the medium to the alkoxy-oxygen. This is followed by the rate-determining isomerisation, which involves the simultaneous detachment of an acetic acid molecule, migration of the electron pair, and reattachment of a water or acetic acid molecule at the γ-carbon atom. The third step is the reversible loss of a proton. The hydrolysis similarly involves the fast reversible formation of the oxonium ion followed by a slow bimolecular reaction with a water molecule, most probably accompanied by acyl–oxygen fission.

Some of the kinetic studies carried out in these laboratories on acid-catalysed rearrangements of the type shown below have been concerned with the effects of substituents in the three-carbon skeleton and variations in the unsaturated group X (Parts III—VI, *locc. cit.*). Another obvious extension of considerable interest is the variation of the migrating group (A). The present communication deals with a comparison of the mobility of the hydroxyl and the acetate group, as exemplified by the rearrangement of propenylethynylcarbinol (I) and its acetate (III).



$$\mathrm{C{=}C{-}\underset{A}{\overset{|}{C}}{-}X \longrightarrow \underset{A}{\overset{|}{C}}{-}C{=}C{-}X}$$

$$\text{(I.)}\quad \mathrm{Me{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}C{\vdots}CH \longrightarrow Me{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}C{\vdots}CH}\quad \text{(II.)}$$

$$\text{(III.)}\quad \mathrm{Me{\cdot}CH{:}CH{\cdot}CH(OAc){\cdot}C{\vdots}CH \longrightarrow Me{\cdot}CH(OAc){\cdot}CH{:}CH{\cdot}C{\vdots}CH}\quad \text{(IV.)}$$

The question of the relative anionotropic mobility of different groups was considered by Burton and Ingold (*J.*, 1928, 904) and Burton (*J.*, 1928, 1650), who concluded that the mobility of a system RA increases in the order $\mathrm{R{\cdot}OH < R{\cdot}OAc < CO_2R{\cdot}C_6H_4{\cdot}NO_2 < R{\cdot}Hal}$, *i.e.*, with increasing anionic stability of A and with increasing strength of the acid HA, and that the rearrangements can occur spontaneously in solvents of high dielectric constant. However, no authentic case of the rearrangement of a carbinol or acetate in the absence of hydrogen ion appears to have been described. (This statement is meant to apply to true rearrangements, resulting in an isomeric molecule, not to rearrangements consequent upon replacement reactions where different factors are involved; cf. Hughes, *Trans. Faraday Soc.*, 1941, **37**, 627; Balfe and Kenyon, *ibid.*, p. 721.) Propenylethynylcarbinol is not isomerised on standing with anhydrous acetic acid, and the plot of the rate constants in the presence of dilute aqueous acids against the acid concentration passes through the origin, indicating an immeasurably small "spontaneous" rate (Part I, *loc. cit.*). Other extensive investigations described in the earlier parts of this series with a large number of carbinols, including some extremely readily isomerised in the presence of dilute acid, have so far failed to reveal any examples of spontaneous oxotropic rearrangement. The conversion of certain arylpropenylcarbinols to the acetates of their rearranged isomers by prolonged treatment with boiling acetic anhydride (Burton and Ingold, *loc. cit.*) is almost certainly due to the free acetic acid present and produced in the reaction, since phenylpropenylcarbinol as well as its acetate are readily isomerised by dilute acetic acid (Part V, *loc cit.*, and unpublished work) and since the acetylation of the carbinol by pure acetic anhydride in the presence of pyridine proceeds without any isomerisation (Kenyon, Partridge, and Phillips, *loc. cit.*).* A very slow homogeneous rearrangement of γ-methyl-α-ethylallyl to α-methyl-γ-ethylallyl alcohol was originally claimed by Balfe and Kenyon (*loc. cit.*), but the evidence for this reaction is somewhat incomplete; it was stated later (Airs, Balfe, and Kenyon, *J.*, 1942, 18) that the change was accelerated by traces of acids and that the carbinol samples did in fact show an acid reaction when examined for rearrangement. Again, the acetates of propenylethynylcarbinol (this paper), divinyl- and propenylvinyl-carbinol (unpublished work), and phenylpropenylcarbinol (Kenyon, Partridge, and Phillips, *loc. cit.*) are all readily isomerised in the presence of dilute acid. The first two esters are recovered unchanged after prolonged treatment with boiling acetic anhydride. With the last two the isomerisation has been reported to take place slowly under these conditions (Kenyon, Partridge, and Phillips, *loc. cit.*; Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, 88), but no special precautions were apparently taken to ensure the absence of free acid, and no change was observed on heating with benzonitrile which has a dielectric constant similar to that of acetic anhydride.

The acid-catalysed rearrangement of propenylethynylcarbinol in aqueous alcohol under a wide variety of conditions has been extensively investigated (Parts I and II, *locc. cit.*). In view of the fact, however, that certain complications (see below) arise in the rearrangement of the acetate in aqueous-alcoholic solution, aqueous dioxan proved a more suitable solvent for the present work, and the kinetics of the rearrangement of the carbinol and of the acetate were determined in this medium. As previously, the reaction was followed by measuring the change in the intensity of the ultraviolet light absorption at 2230 A., where the rearranged isomers exhibit a maximum. Under the conditions examined, using mostly 0·1M-hydrochloric acid as catalyst, complete hydrolysis eventually occurred, which was followed by titration with dilute aqueous ammonia (see Experimental). The results may be briefly summarised as follows (Tables I—III).

(i) The rate of rearrangement of the carbinol is directly proportional to its concentration (*i.e.*, the reaction is of the first order with respect to the carbinol and the first order rate-constants, k, are independent of the carbinol concentration), almost directly proportional to the hydrochloric acid concentration (0·01—0·1M), and decreases with increasing dioxan concentration (40—80% by vol.) according to the relation $\log k = mD + n$, where D is the dielectric constant of the dioxan–water mixture and m and n are constants; m is almost independent of temperature between 30° and 60°. The Arrhenius equation is accurately obeyed between 30° and 80°, and isodielectric energies of activation, *i.e.*, Arrhenius parameters corrected for the temperature-dependence of the dielectric constant of the medium according to the method outlined in Part II (*loc. cit.*), are almost independent of solvent composition.

(ii) The rearrangement of the acetate shows exactly the same kinetic features as that of the carbinol. The rates of rearrangement are almost, though not quite, the same for the two compounds, the rate constants for the acetate being slightly higher in 60%, and slightly lower in 80% dioxan than for the carbinol. These small differences are real and are not to be ascribed to medium effects, the rate of rearrangement of the carbinol in the absence and the presence of an equimolar quantity of acetic acid being identical within experimental error. The value of m is somewhat larger (0·037) for the acetate than for the carbinol (0·026). The energies of activation and reaction constants A for the acetate and the carbinol are identical within experimental error.

(iii) The hydrolysis of the acetate is of the first order with respect to the ester, the rate constants are somewhat less than directly proportional to the acid concentration, and decreased by increasing dioxan concentration as before. The solvent effects are similar to those reported by Harned and Ross (*J. Amer. Chem. Soc.*, 1941, **63**, 1993) for the hydrolysis of methyl acetate in aqueous dioxan. Unlike in the rearrangement, however, values of m are strongly temperature-

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* Burton (*loc. cit.*) also states that *p*-chlorophenylvinylcarbinol itself undergoes rearrangement, on the grounds that a mixture of the two isomers was apparently obtained from the condensation products of *p*-chlorophenylmagnesium iodide and acraldehyde. Since the decomposition of the Grignard complex was carried out under acid instead of neutral conditions such a result would not be unexpected (cf. Braude, Jones, and Stern, *J.*, 1947, 1087) and does not constitute any evidence for spontaneous rearrangement.

dependent, increasing from 0·017 at 30° to 0·036 at 80°. Also, the value of $E_{[D]}$ (calculated by equation 8, Part II, *loc. cit.*) is higher for 60% than for 80% dioxan, about 8 k.-cals./mol. lower than for the rearrangement. The rates of rearrangement and hydrolysis are of the same order of magnitude but their ratio clearly depends on the conditions chosen, particularly the temperature. Hydrolysis is about four times as fast as rearrangement at 30°, about equally fast at 60°, and about three-quarters as fast at 95°. (An upper limit to the temperature-range of measurements

TABLE I.

Rearrangements of propenylethynylcarbinol and its acetate in aqueous dioxan–hydrochloric acid.

$c_{\text{ROH or ROAc}}$ = carbinol or acetate concentration (g.-mol./l.); c_A = hydrochloric acid concentration (g.-mol./l.); c_S = dioxan concentration (% v/v); k_R, k_H = first-order rate constants of rearrangement and hydrolysis, respectively.

	Conditions.			Carbinol.	Acetate.	
Temp.	$c_{\text{ROH or ROAc}}$.	c_S.	c_A.	10^4k_R.	10^4k_R.	10^4k_H.
			The effect of carbinol or acetate concentration.			
60·0°	0·05	60	0·1	24·5	27·2	33·4
	0·1	60	0·1	22·6	26·0	33·2
	0·2	60	0·1	24·0	26·6	34·6
			The effect of acid concentration.			
60·0	0·1	60	0·01	1·80	2·40	4·2
	0·1	60	0·05	11·6	13·1	18·5
	0·1	60	0·1	22·6	26·0	33·2
	0·1	60	0·1 *	22·8	—	—
			The effect of solvent composition.			
60·0	0·1	40	0·1	68	78	85
	0·1	60	0·1	22·6	26·0	33·2
	0·1	80	0·1	11·0	9·1	14·4
			The effect of temperature.			
30·0	0·1	60	0·1	0·360	0·46	1·68
	0·1	80	0·1	0·150	0·136	0·95
40·0	0·1	60	0·1	1·64	1·80	4·83
	0·1	80	0·1	0·73	0·62	2·40
50·0	0·1	60	0·1	6·4	7·5	13·2
	0·1	80	0·1	3·1	2·56	5·8
60·0	0·1	60	0·1	22·6	26·0	33·2
	0·1	80	0·1	11·0	9·1	14·4
80·0	0·1	60	0·1	226	228	222
	0·1	80	0·1	143	110	90
95·0	0·1	60	0·1	760	780	570
	0·1	80	0·1	460	290	220

* In the presence of 0·1M-acetic acid.

TABLE II.

Variations of solvent effects with temperature.

$$m = \log k_{60} - \log k_{80}/(D_{60} - D_{80}).$$

Temp.	30°	40°	50°	60°	80°
Carbinol rearrangement	0·026	0·026	0·025	0·026	0·019
Acetate rearrangement	0·036	0·034	0·038	0·038	0·030
Acetate hydrolysis	0·017	0·022	0·028	0·030	0·036

TABLE III.

Arrhenius parameters, isodielectric energies of activation, and entropies of activation.

	Solvent.	$E_{\text{Arr.}}$ (kg.-cal./mol.).	$\log A_{\text{Arr.}}$ (sec.$^{-1}$).	$E_{[D]}$ (kg.-cal./mol.).	$\Delta S_{30°}$ (kg.-cal./deg.-mol.
Carbinol rearrangement	60% Dioxan	26·9	14·2	29·2	6·4
	80% ,,	28·6	15·0	29·6	10·0
Acetate rearrangement	60% ,,	26·7	14·2	29·9	6·4
	80% ,,	28·2	14·6	29·6	8·2
Acetate hydrolysis	60% ,,	19·8	9·7	23·3	−14·0
	80% ,,	19·7	9·3	20·6	−16·0

is set, of course, by the boiling point of the solvent.) The inverted sequence of rates above *ca.* 80° is important in confirming the fact, already indicated by the simple first-order kinetics, that rearrangement of the acetate is *not* consequent upon its hydrolysis to the carbinol, but that the two reactions are kinetically independent of one another.

(iv) The acetate is readily hydrolysed by 0·1M-potassium hydroxide without any rearrangement (see Experimental).

The rearrangement and hydrolysis of the acetate in aqueous ethanol have also been studied (Table IV). With regard to the rearrangement, the results are exactly parallel with those obtained for aqueous dioxan. Just as with the carbinol, the rate constants are only slightly higher in the ethanolic media, thus once more exemplifying the fact that the rates of rearrangement are not directly governed by the dielectric constant of the solvent. With regard to the hydrolysis, it is found that only partial liberation of acetic acid occurs and that the extent of hydrolysis decreases with increasing ethanol content, but is practically independent of the concentrations of acid and ester. The equilibria reached correspond closely to those attained in the esterification of acetic acid under the same conditions (Table V) and must be due to either (i) initially complete hydrolysis of the acetate and subsequent re-esterification of the acetic acid by the solvent, or (ii) simultaneous hydrolysis and ethanolysis of the acetate. If all the acetic acid were liberated as such, it would be subsequently esterified by the ethanol in the solvent to the same extent and at the same rate as if it had been originally present. If, on the other hand, water and ethanol molecules attack the ester simultaneously, they will do so in much the same ratio as they react with ethyl acetate or acetic acid, and the same equilibria will occur again.

A distinction between the two alternatives can be derived, however, from the fact that satisfactory first-order rate constants are obtained by applying the ordinary equation $k = 2{\cdot}3 \times \log[(x_\infty - x_0)/(x - x_0)]/t$, where x_∞ is the titre at equilibrium, and that the rate constants thus calculated are very similar to those previously obtained in aqueous dioxan media where hydrolysis was complete. If the formation of acetic acid and ethyl acetate is simultaneous, the reaction will exhibit first-order kinetics as expressed by the above equation, and the rate constant k will be the sum of the separate rate constants for hydrolysis and ethanolysis, *i.e.*, $k = k_{\text{Hydrolysis}} + k_{\text{Ethanolysis}}$. If, on the other hand, the formation of ethyl acetate were

TABLE IV.

Rearrangement of propenylethynylcarbinyl acetate in aqueous ethanol–hydrochloric acid.

c_{ROAc} = acetate concentration; c_A = acid concentration (both in g.-mol./l.); c_S = ethanol concentration (% v/v); k_R, k_H = first-order rate constants for rearrangement and hydrolysis, respectively; Δ_H = fraction hydrolysed; $k_{\text{Hydrolysis}} = k_H \times \Delta_H$; $k_{\text{Ethanolysis}} = k_H - k_{\text{Hydrolysis}}$; temp. = 60·0° throughout.

c_{ROAc}.	c_S.	c_A.	10^4k_R.	10^4k_H.	Δ_H.	$10^4k_{\text{Hydrolysis}}$.	$10^4k_{\text{Ethanolysis}}$.
			The effect of acetate concentration.				
0·05	60	0·1	33	101	0·41	41·5	59·5
0·1	60	0·1	33	95	0·40	38	57
0·2	60	0·1	31	91	0·39	35·5	55·5
			The effect of solvent composition.				
0·1	60	0·1	33	95	0·40	38	57
0·1	80	0·1	14	59	0·25	15	44
			The effect of acid concentration.				
0·1	60	0·01	3·5	9·1	0·42	3·8	5·3
0·1	60	0·05	16	51	0·41	21	30
0·1	60	0·1	33	95	0·40	38	57

TABLE V.

The esterification of acetic acid in aqueous ethanol.

c_{AcOH}, c_A = concentrations of acetic and hydrochloric acids (g.-mol./l.); c_S = concentration of ethanol (% v/v); Δ_E = fraction esterified; $k_{\text{Esterification}} = k \times \Delta_E$; $k_{\text{Hydrolysis}} = k - k_{\text{Esterification}}$; temp. = 60·0° throughout.

c_{AcOH}.	c_S.	c_A.	10^4k(min.$^{-1}$).	Δ_E.	$k_{\text{Esterification}}$.	$k_{\text{Hydrolysis}}$.
0·1	60	0·1	120	0·54	65	55
0·1	60	0·1[1]	130	0·62	80	50
0·1	60	0·1[2]	135	0·62	84	51
0·1	80	0·1	160	0·74	118	42

[1] In the presence of 0·1M-propenylethynylcarbinol.

[2] In the presence of 0·1M-hex-3-en-5-yn-2-ol (II).

consecutive upon the liberation of acetic acid, the reaction would not, in general, exhibit first-order kinetics, and in any case the first step would have to proceed at a rate considerably greater than that of the second step to result in the measured overall rate of reaction. This would lead to a rate of hydrolysis unexpectedly large by comparison with the rate of hydrolysis of the ester in aqueous dioxan. The "consecutive" reaction scheme can thus be excluded, and hence hydrolysis and ethanolysis must occur simultaneously. The rate constants of partial hydrolysis (Table IV) are very similar to those previously determined for aqueous dioxan media where hydrolysis was complete, and are again practically independent of the acetate concentration, almost directly proportional to the acid concentration, and decreased by increasing ethanol concentration. The rates of ethanolysis are somewhat higher than those of hydrolysis.

Finally, for purposes of comparison, a few measurements were made with the rearranged isomer of propenylethynylcarbinyl acetate, 2-acetoxyhex-3-en-5-yne (IV). As might be expected, hydrolysis proceeds without any de-rearrangement and is somewhat slower than for propenylethynylcarbinyl acetate (Table VI).

TABLE VI.

Hydrolysis of 2-*acetoxyhex*-3-*en*-5-*yne* (IV).

Concentration of acetate and hydrochloric acid 0·1M throughout; temp. = 60·0°. For meaning of symbols, see Table I.

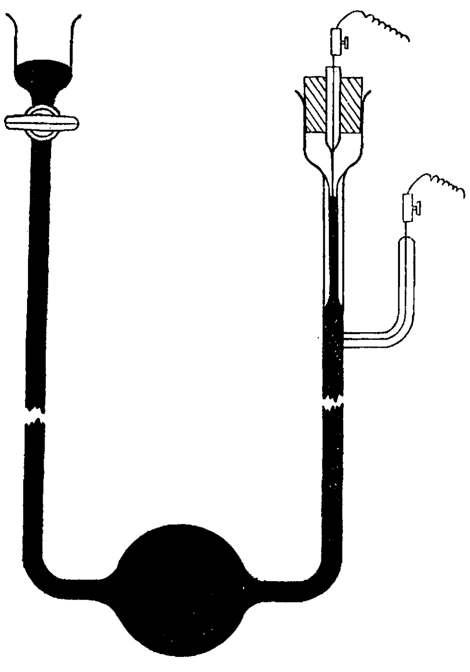
Solvent.	Δ_H.	$10^4 k_H$(min.$^{-1}$).	$10^4 k_{Hydrolysis}$.
60% Dioxan	1·0	22·8	22·8
80% ,, ...	1·0	16·4	16·4
60% EtOH .:................................	0·41	22·2	9·1
80% ,, ...	0·24	27·3	6·6

EXPERIMENTAL.

Materials.—Propenylethynylcarbinol (I) (Heilbron, Jones, and Weedon, *J.*, 1945, 81) had b. p. 75°/30 mm., $n_D^{21°}$ 1·4645, $\epsilon_{2230 A.} < 10$. Its acetate (III), prepared from the carbinol (20 g.), acetic anhydride (22 g.), and pyridine (20 g.) at room temperature, treatment with water after 3 days, and isolation with ether, had b. p. 71°/18 mm., $n_D^{20°}$ 1·4476, $\epsilon_{2230 A.} < 10$ (Jones and McCombie, *J.*, 1942, 733, give b. p. 110°/100 mm., $n_D^{20\cdot5°}$ 1·4463, $\epsilon_{2230 A.} < 1500$). A 0·1M-solution of the acetate in initially 0·1M-potassium hydroxide in 60% aqueous dioxan, after being kept for 24 hours at 30°, required < 0·1 ml. of 0·01M-hydrochloric acid for neutralisation, and the solution showed $\epsilon < 20$ at 2230 A. 2-Acetoxyhex-3-en-5-yne (IV) had b. p. 91—93°/55 mm., $n_D^{16°}$ 1·4570 (Jones and McCombie, *J.*, 1943, 261, give b. p. 101—103°/70 mm., $n_D^{18\cdot5°}$ 1·4576).

Kinetic Measurements.—The rearrangements were followed by the spectrophotometric technique previously described (Parts I, III, and V, *locc. cit.*). Measurements at and above 80° were carried out in a thermostat containing light oil and controlled by the all-mercury thermoregulator shown in the figure, which is essentially a contact-thermometer of large and variable bulb capacity. This regulator is easier to fill, empty, and clean than the conventional toluene–mercury type, more constant when used over prolonged periods, especially at elevated temperatures, and available over a much wider temperature range. 25 Ml. of reaction medium were used for each run. 1-Ml. samples were withdrawn and diluted to 50 ml. with 90% ethanol containing 1 ml. of 0·1M-potassium hydroxide, and the light absorption intensity of the resulting solution determined at 2230 A.

The hydrolyses of the acetate were followed by titrating 1-ml. samples diluted with 20 ml. of water with 0·01M-aqueous ammonia, using neutral-red–methylene-blue (five drops of a 0·1% solution in 70% aqueous ethanol) as "flash-indicator" (cf. Skrabal and Rückerl, *Monatsh.*, 1928, **50**, 369): the ammonia solution is run in continuously with constant shaking until the *first* colour change from blue to green is observed. The solution rapidly regains its blue colour on standing, partly owing to the rapid alkaline hydrolysis of unchanged acetate. With practice, end-points readings consistent to 0·05 ml. can nevertheless be obtained.



In view of the simultaneous reactions occurring with the acetate, measurements were as far as possible made on the first third of the reactions. Except at the lower temperatures, however, the rates of rearrangements and hydrolyses do not differ appreciably, and no drift was observed in the first-order rate constants, which were reproducible to ± 2%. Activation energies were computed graphically, the points for 95°, which fell somewhat below the straight plot, being neglected. Isodielectric energies of activation were calculated from $E_{[D]} = E_{\text{Arr.}} + 2{\cdot}3RT_1T_2mb$ for the rearrangements and from $k_{[D]} = k$ antilog $[(t - 30)\ mb]$ for the hydrolyses (Part II, *loc. cit.*). The values of b used were 0·18 and 0·08 for 60% and 80% dioxan, respectively (Part V, *loc. cit.*). The averaged values, 0·026 in the carbinol rearrangement and 0·036 in the acetate rearrangement, were used for m (cf. Table II). Values of $A_{\text{Arr.}}$ were calculated from the equation log $A_{\text{Arr.}} = 0{\cdot}657\ E_{\text{Arr.}} \times \log(k_{60^\circ}/c_A) - 1{\cdot}78$.

Some typical runs are reproduced below :

Rearrangements and hydrolyses in 0·1M-hydrochloric acid, 60% (v/v) aqueous dioxan. Carbinol or acetate concentration 0·1M ; ϵ = molecular extinction coefficient at 2230 A. ; x = number of ml. of 0·01M-NH_4OH required to neutralise 1 ml. of reaction mixture.

Carbinol.			Acetate.				
Time (mins.).	ϵ.	10^4k_R (min.$^{-1}$).	Time (mins.).	ϵ.	10^4k_R (min.$^{-1}$).	x.	10^4k_H (min.$^{-1}$).
			Temp. 30·0°.				
0	0	—	0	0	—	10·0	—
1050	490	0·366	1065	620	0·46	11·65	1·68
2400	1,120	0·374	2415	1,350	0·45	13·3	1·65
3830	1,680	0·365	3855	2,050	0·44	14·6	1·65
5270	2,200	0·352	5285	2,650	0·43	16·0	1·73
6760	2,760	0·356	6775	3,160	0·41	16·85	1·70
∞	13,000 *	—	∞	13,000 *	—	20·0 *	—
		Mean 0·360			Extrapolated 0·46		Mean 1·68
			Temp. 60·0°.				
0	0	—	0	0	—	10·0	—
117	3,070	23·0	126	3,750	26·9	13·4	33·0
243	5,400	22·0	252	6,240	26·0	15·7	33·4
317	6,800	23·3	327	7,600	26·8	16·7	33·9
393	7,500	21·8	394	8,300	25·8	17·2	32·5
466	8,650	23·4	485	9,200	25·3	18·4	33·4
4000	13,000	—	4000	13,000	—	20·0	—
		Mean 22·7 †			Mean 26·2 †		Mean 33·2
			Temp. 95·0°.				
0	0	—	0	0	—	10·0	—
2	1,800	741	2·0	1,950	810	—	—
3	2,700	772	2·25	—	—	11·1	563
4	3,400	758	3·0	2,700	770	—	—
5	4,100	758	3·25	—	—	11·7	573
6	4,900	787	4·0	3,350	745	—	—
60	13,000	—	4·25	—	—	12·2	578
		Mean 763 †	5·0	3,950	770	—	—
			5·25	—	—	12·6	570
			6·0	4,700	785	—	—
			6·25	—	—	12·9	548
			60	13,200	—	19·9	—
					Mean 780		Mean 570

* Assumed.

† These values are slightly different from those given in Table I, which are averaged from several runs.

Rearrangement and hydrolysis of propenylethynylcarbinyl acetate in 0·1M-HCl, 60% (v/v) aqueous ethanol at 60°. Acetate concentration = (*a*) 0·1M, (*b*) 0·2M. ϵ and x as in preceding table.

	Time (mins.).	ϵ.	10^4k_R (min.$^{-1}$).	Time (mins.).	x.	10^4k_H (min.$^{-1}$).
(*a*)	0	0	—	0	10·0	—
	61	2,400	33·8	41	11·3	95
	119	4,300	33·3	53	11·65	100
	217	6,650	33·1	85	12·2	95
	235	7,000	32·7	125	12·75	93
	405	9,450	32·1	162	13·1	92
	1440	13,000	—	370	13·9	—
			Mean 33	1440	14·0	—
						Mean 95
(*b*)	0	0	—	0	10·0	—
	62	2,300	31·3	57	13·1	89
	141	4,700	31·7	101	14·65	90
	217	6,350	30·8	146	15·85	95
	365	8,700	30·2	253	16·9	85
	468	9,800	29·8	370	17·5	—
	1580	13,000	—	520	17·8	—
			Mean 31	1580	17·8	—
						Mean 90

Reaction Products.—Propenylethynylcarbinyl acetate (4 g.) was mixed with 60% aqueous dioxan, 0·1M-hydrochloric acid (50 ml.) at 60°. After 50 hours, the solution was neutralised to phenolphthalein with 1M-potassium hydroxide (Required: 34·0 ml. Calc. for complete hydrolysis: 34·0 ml.), diluted to 120 ml., saturated with sodium chloride, and extracted four times with 20 ml. of ether. Repeated fractionation of the combined ether extracts yielded hex-3-en-5-yn-2-ol (II) (2·3 g. Calc. for complete hydrolysis: 2·8 g.), b. p. 79—80°/30 mm., $n_D^{19°}$ 1·4770, $\epsilon_{2230\,\mathrm{A.}}$(max.) = 13,000 [Jones and McCombie, *J.*, 1943, 261, give b. p. 70°/18 mm., $n_D^{22°}$ 1·4791, $\epsilon_{2230\,\mathrm{A.}}$(max.) = 13,500].

DISCUSSION.

The Mechanism of Anionotropy.—The kinetic features of the rearrangement of the acetate of propenylethynylcarbinol are in all respects analogous to those encountered with the carbinol itself, and substitution of the acetoxyl for the hydroxyl as migrating group does not, therefore, appear to result in a change of mechanism. It will be opportune, at this stage, to summarise the main arguments leading to the mechanism proposed in the earlier parts of this series for propenylethynyl and a large number of other carbinols. The reaction exhibits specific hydrogen-ion catalysis and the rate is proportional to the concentration of carbinol and, at low acidities and constant solvent composition, of hydrogen ion; more generally, the rate is proportional to the concentration of carbinol and to the proton-donating properties of the medium as measured by the indicator ratio $[BH^+]/[B]$, where B is a neutral base such as the carbinol itself or an indicator, *e.g.*, *p*-nitroaniline (Part II, *loc. cit.*, and Part VIII, in the press). Since its availability is essential to the reaction under the conditions now considered, a proton must combine with either the carbinol or a fission product of it, either before or during the rearrangement. There are two plausible types of mechanism:

$$\text{(I.)}\quad R{\cdot}OH + H^+ \underset{\text{(i)}}{\rightleftharpoons} R{\cdot}OH_2^+ \underset{\text{(ii)}}{\rightleftharpoons} R'{\cdot}OH_2^+ \underset{\text{(iii)}}{\rightleftharpoons} R'{\cdot}OH + H^+$$

$$\text{(II.)}\quad R{\cdot}OH + H^+ \underset{\text{(i)}}{\rightleftharpoons} R^+ + H_2O \underset{\text{(ii)}}{\rightleftharpoons} R'^+ + H_2O \underset{\text{(iii)}}{\rightleftharpoons} R'{\cdot}OH + H^+$$

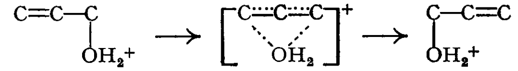
In (I), (i) a proton is transferred from the solvent to the carbinol molecule to form the oxonium ion, (ii) the oxonium ion rearranges by detachment of a water molecule at one point of the carbon skeleton and attachment at another, with simultaneous redistribution of electrons in R, (iii) the rearranged oxonium ion loses a proton. In (II), the first step (i) is the fission of the carbinol molecule by reaction with a proton to form the positive carbonium ion (R^+) and water, followed by (ii) the redistribution of electrons in the carbonium ion to R'^+ and (iii) recombination of R'^+ with a water molecule to give the rearranged carbinol and a proton. The essential difference between (I) and (II) is that the latter involves the free carbonium ion, whereas the former only involves the oxonium ion as intermediate.

In the mechanisms (I) and (II), either or both steps (i) and (ii), if sufficiently slow, can determine the overall reaction rate, and it is thus necessary to consider to what extent other evidence is compatible with any or all of these steps proceeding at rates comparable to the overall rate of reaction. Considering mechanism (II) first, the first step (i) cannot be fast since it has been shown that when R·OH is optically active, racemisation proceeds at the same rate as rearrangement (Parts I and V, *locc. cit.*; Kenyon, Partridge, and Phillips, *J.*, 1937, 207), and since the positive carbonium ion, if formed, would racemise instantaneously (Wallis and Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 3838). In any case, step (ii) which represents merely the redistribution of electrons in the ion R^+, is bound to be very fast, and hence step (i) cannot be fast as well, if mechanism (II) were applicable. However, the remaining possibility of step (II) (i) being slow can also be ruled out on two grounds. First, kinetic analysis shows (cf. Parts II and VIII, *locc. cit.*) that a slow reaction with a proton and the production of an *unstable* intermediate will lead to the measured rate constant being proportional to the stocheiometric acid concentration and not to the indicator ratio $[BH^+]/[B]$, as it actually is. Secondly, it is shown in the present work that the values of the kinetic parameters for the rearrangement of a carbinol and its acetate are nearly the same, and this is most unlikely if the electrophilic attack of a proton on the hydroxyl and acetate groups respectively were rate-determining, since the electron availability at the alkoxy-oxygen atom will be different in the two cases.

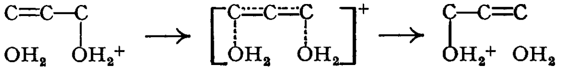
In mechanism I, step (i) which represents a simple proton transfer is intrinsically likely to be fast (cf. Day and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 686,705) and the slow reaction is in any case ruled out on the same grounds as a slow step (II) (i). On the other hand, step (I) (ii) is intrinsically likely to be slow, and the fast reaction is ruled out by the fact that racemisation and rearrangement proceed at the same rate. Moreover, mechanism (I), with a fast step (i) and a slow step (ii), accounts for the similarity in the values of the kinetics parameter for the carbinol and its acetate (see below) and is therefore compatible with all the evidence so far cited. It is also compatible with other evidence not, however, excluded by mechanism (II), particularly the fact that the energies of activation are largely independent of the dielectric constant of the medium provided the necessary corrections be applied (Part II, *loc. cit.*), as would be expected for a reaction involving no bi-ionic step. The rate constants are increased and the energies of activation decreased the more electron-donating or electron-repelling R (Parts III—VI, *locc. cit.*); this is to be expected since both steps in (I) require electron accession at the point of reaction.

The rate-determining step (I) (ii) may now be considered in more detail. It can be formulated intra- or inter-molecularly; in the former case (I*a*) the water molecule detached from one carbon atom becomes reattached at the other, but in the latter case (I*b*) a different water or another solvent molecule becomes attached :

(I*a*.)



(I*b*.)



Both modes of reaction have been observed experimentally. Thus, the rearrangement proceeds in completely anhydrous dioxan (Part V, *loc. cit.*, and Part VIII, in the press) where it must be intramolecular, as well as in aqueous ethanol where it is at least partly intermolecular since the ethyl ethers of the rearranged carbinols are formed roughly in proportion to the molar fraction of ethanol in the medium and since etherification proceeds as a consequence of and at the same rate as rearrangement (Parts II and V, *locc. cit.*; Heilbron, Jones, and Weedon, *J.*, 1945, 81). Whether the intra- or the inter-molecular reaction occurs will depend on the concentrations of carbinol and water (or alcohol) in the medium and on the relative probabilities of approach of the "internal" and of an "external" water molecule to the carbon atom concerned. If the approach of an "external" molecule were a prerequisite for the reaction, the rate would decrease with decreasing water concentration when the latter is sufficiently small, whereas in fact the rate increases with decreasing water concentration in that region (Parts II and IX, *loc. cit.*). The intra- and the inter-molecular reaction probably occur side by side under suitable conditions, and the change-over from one to the other will not be discernible by the kinetic criteria so far applied. Retention of optical activity, which can be used as a criterion for the intramolecular nature of *uncatalysed* rearrangements (Kenyon, Partridge, and Phillips, *loc cit.*; Balfe and Kenyon, *Trans. Faraday Soc.*, 1941, **37**, 721), is inapplicable in the hydrogen-ion-catalysed reaction since the migrating positive charge will destroy any asymmetry produced by the orientated approach of the migrating water molecule on one side of the γ-carbon atom.

Earlier discussions of the mechanism of anionotropy (Burton and Ingold, *J.*, 1928, 904; Burton, *J.*, 1928, 1650; 1929, 455; Kenyon, Partridge, and Phillips, *loc. cit.*; Balfe and Kenyon, *loc. cit.*) have centred about two mechanisms, (III) and (IV), analogous to (I) and (II), but not involving hydrogen-ion :

$$\text{(III.)}\quad \text{R·OH} \xrightarrow{\text{slow}} \text{R'·OH}$$

$$\text{(IV.)}\quad \text{R·OH} \overset{\text{slow}}{\rightleftharpoons} \text{R}^+ + \text{OH}^- \xrightarrow{\text{fast}} \text{R'}^+ + \text{OH}^- \rightleftharpoons \text{R'·OH}$$

However, no authentic case of the rearrangement of a carbinol or acetate in the absence of hydrogen ion appears to have been observed (see above). There is no *a priori* reason why the uncatalysed rearrangements should not occur under suitable conditions when the carbon–oxygen link is sufficiently weakened by $\beta\gamma$-unsaturation in the alkyl group R, and mechanisms (III) and (IV) should be distinguishable by criteria similar to those now employed to distinguish between mechanisms (I) and (II). [In particular, in a reaction proceeding by mechanism (IV), not only the rate constants, but the energies of activation as well should be dependent on the dielectric constant of the medium; cf. Part II, *loc. cit.*] However, there is no definite evidence that such a reaction has ever been observed hitherto. It is clear that reactions by mechanism (III) or (IV) will take place very much less readily and have a much higher activation energy than by mechanism (I), since covalent or ionic fission of a bond is involved in the former, and only ion–dipole fission in the latter (Part I, *loc. cit.*), and that in the presence of hydrogen ion the catalytic mechanism (I) will therefore always take control. In the presence of hydrogen ion, since the reaction $A^- + H^+ \longrightarrow AH$ will be fast, the mechanism of aniontropy postulated by

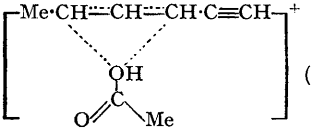
Burton and Ingold (IV, p. 801) becomes identical with that represented by (II) for A = OH (p. 800). Such a mechanism is inapplicable in the examples of A = OH and A = OAc so far studied kinetically, and, contrary to its requirements, the mobility of the hydroxyl and the acetoxyl group are very similar.

The Rearrangement of Propenylethynylcarbinyl Acetate.—Adopting a mechanism of type (I) for the rearrangement of propenylethynylcarbinyl acetate in dilute acid solution on the basis of the above discussion, this may be represented by

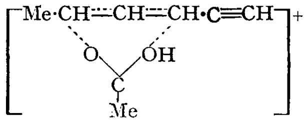
$$\mathrm{RA} + \mathrm{H}^+ \overset{\text{fast}}{\rightleftharpoons} \mathrm{RAH}^+ \xrightarrow{\text{slow}} \mathrm{R'AH}^+ \overset{\text{fast}}{\rightleftharpoons} \mathrm{R'A} + \mathrm{H}^+$$

where A = OAc. The point of attachment of the proton is bound to be the alkoxy-oxygen rather than the less basic carbonyl oxygen atom (cf. Day and Ingold, *Trans. Faraday Soc.*, **1941**, **37**, 686). The transition state will be represented by (*A*) or (*B*) depending on whether the reaction is intra- or inter-molecular :

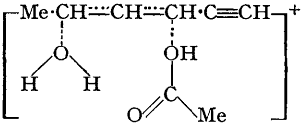
(*A*)



(*A'*)



(*B*)



(*A'*), in which the initially acyl instead of the alkoxy-oxygen atom becomes attached to the γ-carbon atom and which involves the transitory formation of a six- instead of a four-membered ring (cf. Kenyon, Partridge, and Phillips, *loc. cit.*), is a possible alternative to (*A*). Since the speed of rearrangement exceeds that of hydrolysis at temperatures above 80°, the intramolecular reaction must then take place to some extent, even though the rearranged acetate is also subsequently hydrolysed. As with the carbinol (see above), both modes of reaction probably take place side by side under suitable conditions.

The relative values of the kinetic parameters for the rearrangements of the acetate and its parent carbinol must next be considered. The measured steps of mechanism (I) are of the general type $\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \xrightarrow{k_r} \mathrm{C}$, where k's represent first-order constants. For such a system, when $k_{-1} > k_1, k_r$ as postulated in the present case, the overall rate constant (k) is given by $k = Kk_r$, where $K = k_1/k_{-1}$. Since the overall rate constants are nearly the same for A = OH and A = OAc in the present case, either (*a*) the separate values of the K's and k_r's must be nearly the same or (*b*) the separate values of the K's and k_r's must be different but such that their products are the same. The first alternative means that the proton affinities (which the K's express) of the carbinol and acetate are the same. This is most unlikely on structural grounds alone, since in the acetate group the electron availability on the alkoxy-oxygen atom will be more strongly reduced by the adjacent carbonyl group than increased by the methyl group, and there is experimental evidence that the acetoxyl is less basic than the hydroxyl group (cf. Heston and Hall, *J. Amer. Chem. Soc.*, **1934**, **56**, 1462). Hence, the second alternative (*b*) must apply, and in order that the products Kk_r be nearly the same for A = OH and A = OAc, the k_r's must be in the inverse order to the K's, *i.e.*, k_r must be smaller for A = OH than for A = OAc. This is a very plausible result : since the *separation* of the positive carbonium ion and the water or acetic acid molecule will be conditioned by the same factors, but in the inverse ratio, as the attraction of a proton considered above, k_r would indeed be expected to be greater for the acetate which has the lower electron-density at the alkoxy-oxygen. The almost identical values of the isodielectric energies of activation and A factors for the carbinol and acetate will similarly arise through the operation of these opposite effects, both E and A separately involving terms related to both K and k_r. The rather larger solvent effects observed with the acetate as compared with the carbinol must be ascribed to primary solvent effects (cf. Part II, *loc. cit.*), the change in solvent composition from 60 to 80% aqueous dioxan resulting in larger solvation differences with the more highly solvated acetate than with the hydroxyl group.

The Hydrolysis of the Acetate.—The likely modes of acid hydrolysis of carboxylic esters have been clearly summarised by Day and Ingold (*loc. cit.*), who distinguish alkyl–oxygen and acyl–oxygen fission, each proceeding by either a uni- or a bi-molecular mechanism. In either case, the first step is the formation of the oxonium ion now postulated as intermediate in anionotropy, by fast reversible transfer of a proton from the medium to the alkoxy-oxygen of the ester. The second step is either the slow fission of the ion followed by a fast reaction with a water molecule, or else a slow reaction between the oxonium ion and a water molecule. The " normal " mode of acid hydrolysis is known to be bimolecular acyl–oxygen fission.

The only mode of hydrolysis rigidly excluded in the present case is unimolecular alkyl–oxygen fission, since it would involve the liberation of the free positive carbonium ion (cf. Ingold and Ingold, *J.*, 1932, 758). Rearrangement of the ion is likely to be very fast, and hence unimolecular alkyl–oxygen fission would require rearrangement to be consequent upon hydrolysis, whereas rearrangement is in fact kinetically independent of, and slower than, the latter below 60° under the conditions examined. Alkaline hydrolysis similarly does not result in any rearrangement.

The values of the kinetic parameters for hydrolysis as compared with those for rearrangement indicate a bimolecular mechanism for the former. The probability of the appropriate collision between the oxonium ion and a water molecule will be lower than that of the less restricted collisional or internal activation of the oxonium ion necessary for rearrangement, hence the non-exponential factor $A_{\text{Arr.}}$ (defined by $k = A_{\text{Arr.}}\mathrm{e}^{-E_{\text{Arr.}}/\boldsymbol{R}T}$) is lower in the former case. Expressed in terms of the transition state, the entropy of activation (defined by the equation $k = \boldsymbol{R}T/\boldsymbol{N}h \times \mathrm{e}^{-E_{\text{Arr.}}/\boldsymbol{R}T}\mathrm{e}^{\Delta S/\boldsymbol{R}}$) is positive for the rearrangement and negative for the hydrolysis, as expected for a uni- and a bi-molecular reaction of this type, respectively (cf. Glasstone, Laidler, and Eyring, " The Theory of Rate Processes," McGraw-Hill, 1941). Furthermore, in the hydrolysis, unlike in the rearrangement, the solvent effects are strongly temperature-dependent, and the isodielectric energies of activation are not independent of medium composition. This shows that a change in the water content of the medium does not affect the hydrolysis reaction through the change in dielectric constant and proton-availability alone and again indicates the participation of water molecules in the rate-determining step.

Since alkyl–oxygen fission is involved in the ready anionotropic rearrangement of the acetate proceeding under conditions identical with those in the hydrolysis, it might be thought that the later reaction depends on the same mode of fission and that the mechanism involved is bimolecular alkyl–oxygen fission. Structural considerations, however, render such a conclusion unlikely. Alkyl–oxygen fission requires electron-release at the alkyl–oxygen link (Day and Ingold, *loc. cit.*). It has been shown to occur in the hydrolysis of the phthalates and benzoates of certain alkenylcarbinols where the reaction is accompanied by racemisation or inversion at the alkoxy-carbon atom (Balfe, Kenyon, *et al.*, *J.*, 1942, 556, 605; 1946, 797, 803, 807). Optical activity is not readily applicable as a criterion of hydrolytic mechanism in the present case, since the simultaneously occurring rearrangement is itself accompanied by racemisation (Part I, *loc. cit.*). The derivatives with least electron-release found to give rise to hydrolysis with alkyl–oxygen fission are those of methylpropenylcarbinol (αγ-dimethylallyl alcohol). In propenylethynylcarbinol, the somewhat electron-repelling methyl group is replaced by an ethynyl group, which is strongly electron-attracting (cf. Part IV, *loc. cit.*). The total electron-availability at the alkoxy-carbon atom will therefore be very much smaller than that due to the propenyl group alone, in fact not appreciably greater and possibly smaller than in a saturated secondary carbinol, and therefore probably too small to result in alkyl–oxygen fission in the hydrolysis of the acetate. Hence bimolecular acyl–oxygen fission, the " normal " mode of acid hydrolysis, is most probably involved.

Confirmatory evidence for this conclusion is provided by the fact that in aqueous ethanol the hydrolysis and ethanolysis of the ester occur simultaneously. The substance of the argument may be stated as follows. If the ester (in the form of its oxonium ion) is attacked by water molecules only, then the products of hydrolysis resulting from either alkyl–oxygen or acyl–oxygen fission will be the carbinol and acetic acid. If, however, the attack is by water and ethanol molecules simultaneously, then, since the only likely mode of reaction of the ethanol molecule under these conditions is ethoxy–hydrogen fission (as shown below), alkyl–oxygen fission in the ester will give the ethyl ether of the carbinol and acetic acid, whereas acyl–oxygen fission in the ester will give the carbinol and ethyl acetate as products of ethanolysis :

$$\text{Alkyl–oxygen fission * } \mathrm{R}\vdots\mathrm{-O-Ac} + \mathrm{Et-O-}\vdots\mathrm{H} \longrightarrow \mathrm{R{\cdot}OEt} + \mathrm{Ac{\cdot}OH} \underset{\mathrm{H_2O}}{\overset{\mathrm{EtOH}}{\rightleftharpoons}} \mathrm{R{\cdot}OEt} + \mathrm{Ac{\cdot}OEt}$$

$$\text{Acyl–oxygen fission * } \mathrm{R-O-}\vdots\mathrm{Ac} + \mathrm{Et-O-}\vdots\mathrm{H} \longrightarrow \mathrm{R{\cdot}OH} + \mathrm{Ac{\cdot}OEt}$$

In the former case, or if the attack is by water molecules only, the acetic acid liberated will be *subsequently* esterified by the ethanol in the solvent. In the latter case, ethyl acetate will be formed *simultaneously* with any acetic acid produced by hydrolysis. Since it has been shown that the formation of ethyl acetate takes place simultaneously with, and not subsequently to,

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* For the sake of clarity, the schemes have been written for the neutral ester molecule instead of the oxonium ion $\mathrm{R{\cdot}OHAc^+}$ which is the reacting entity.

hydrolysis, this constitutes conclusive evidence for acyl–oxygen fission in the ester during ethanolysis.* Since ethanolysis and hydrolysis are likely to involve the same mode of fission (the difference in basicity between the water and ethanol molecules being comparatively small) it also constitutes strong evidence for acyl–oxygen fission during hydrolysis. The rearrangement and hydrolysis of propenylethynylcarbinyl acetate thus provide an interesting example of two simultaneous reactions proceeding under identical conditions *via* the same intermediate (the oxonium ion), yet involving different subsequent bond fissions.

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