36. *The Kinetics of Anionotropic Rearrangement. Part IV. Substituent Effects in the Oxotropic Formation of the Butadiene System. A Comparison of the Electron-attracting Properties of the Ethylenic and Acetylenic Bonds.*

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First-order rate constants, energies of activation and solvent effects have been determined for the acid-catalysed isomerisation of four vinylcarbinols of the type $CR_1R_2{:}CR_3{\cdot}CR_4(OH){\cdot}CH{:}CH_2$. The results are discussed in relation to the data already reported in Part III (preceding paper) for the corresponding ethynylcarbinols. The reaction mechanism is the same in both series and the effect of methyl substituents is similar, but the vinylcarbinols have rate constants greater, by factors of 200 to 10,000, than those of the ethynylcarbinols, due to the smaller electron deficiency (negative inductive effect) of the ethylenic as compared with the acetylenic carbon atom adjacent to the carbinol group.

In Part III (*loc. cit.*) a detailed study was presented of substituent effects in the rearrangement of acetylenylcarbinols derived from αβ-unsaturated carbonyl compounds to the corresponding vinylacetylenic alcohols. The analogous oxotropic formation of the butadiene system by the rearrangement

$$CR_1R_2 = CR_3{\cdot}CR_4(OH){\cdot}CH = CH_2 \xrightarrow{\text{acids}} CR_1R_2(OH){\cdot}CR_3 = CR_4{\cdot}CH = CH_2$$

has now been examined, but the number of compounds studied has, for the time being, had to be restricted to four. Sufficient data have been accumulated, however, to show that the effect of methyl substituents is very similar in the two series and to obtain a measure of the relative magnitudes of the electron-attracting effects of the ethylenic and acetylenic bonds.

First-order rate constants, solvent effects, Arrhenius and isodielectric energies of activation (*i.e.*, energies of activation for media of temperature-invariant dielectric constant, calculated according to the method outlined in Part II, J., 1944, 443) are given in Table I. As in the case of the acetylenylcarbinols, the reaction is strictly of the first order and the first-order rate constants (k) are independent of the concentration of carbinol (c_{ROH}), nearly proportional to the acid concentration (c_A) below $c_A = 0{\cdot}1$, and decreased by factors of 2—4 on increasing the alcohol concentration from 60 to 80% by volume. Again, the ratio of the rate constants of (III) in 0·02M-

Table I.

c_A = Concentration of HCl (mols./l.); c_{EtOH} = vol.-% EtOH; k = first-order rate constant; carbinol concentration (c_{ROH}) = 0·700% w/v throughout for (I) and (III), 0·350% w/v throughout for (II) and (IV); E_{60}, E_{80} = Arrhenius energy of activation for c_{EtOH} = 60, 80; m = $(\log k_{60} - \log k_{80})/(D_{60} - D_{80})$, where D = dielectric constant (see Part II, *loc. cit.*); $E_{[D]60}$, $E_{[D]80}$ = isodielectric energies of activation for c_{EtOH} = 60, 80.

(I) $CH_2{=}CH{\cdot}CH(OH){\cdot}CH{=}CH_2$.

t.	c_A.	c_{EtOH}.	10^4k (min.$^{-1}$).	
30°	0·02	60	0·340	E_{60} 24·3 E_{80} 26·9 m = 0·043 $E_{[D]60}$ 29·6 $E_{[D]80}$ 31·2
	0·1	60	1·80	
	0·1	80	0·50	
	0·4	60	10·4	
	1·0	60	37·7	
40	0·02	60	1·12	
	0·1	60	5·7	
	0·1	80	2·05	
50	0·02	60	4·13	
	0·1	60	22·2	
	0·1	80	8·0	
60	0·02	60	14·3	

(II) $CH_2{=}CMe{\cdot}CH(OH){\cdot}CH{=}CH_2$

t.	c_A.	c_{EtOH}.	10^4k (min.$^{-1}$).	
30	0·02	60	0·54	E_{60} 21·7 E_{80} 26·6 m = 0·049 $E_{[D]60}$ 27·9 $E_{[D]80}$ 31·0
	0·1	60	3·28	
	0·1	80	0·74	
40	0·02	60	2·28	
	0·1	60	11·4	
	0·1	80	3·15	
50	0·02	60	6·9	
	0·1	60	34·1	
	0·1	80	10·6	

(III) $CHMe{=}CH{\cdot}CH(OH){\cdot}CH{=}CH_2$

t.	c_A.	c_{EtOH}.	10^4k (min.$^{-1}$).	
0°	0·005	60	2·36	E_{60} 20·1 E_{80} 21·7 m = 0·044 $E_{[D]60}$ 25·2 $E_{[D]80}$ 25·7
30	0·005	60	77	
	0·02	60	345	
	0·02	80	114	
40	0·005	60	235	
	0·02	60	1040	
	0·02	80	341	
50	0·005	60	690	
	0·02	60	2750	
	0·02	80	1080	

(IV) $CHMe{=}CH{\cdot}CMe(OH){\cdot}CH{=}CH_2$.

t.	c_A.	c_{EtOH}.	10^4k (min.$^{-1}$).	
30	0·002	60	444	E_{60} 19·8 E_{80} 21·4 m = 0·044 $E_{[D]60}$ 25·4 $E_{[D]80}$ 25·8
	0·002	80	129	
	0·01	60	2200	
40	0·002	60	1340	
	0·002	80	415	
50	0·002	60	3410	
	0·002	80	1180	

Table Ia.

Rearrangement of (III) in 1M-AcOH.

t.	c_{ROH}, % w/v.	c_{EtOH}, % vol.	10^4k (min.$^{-1}$).	
30°	0·700	40	100	E_{60} 19·0 m = 0·075 $E_{[D]60}$ 28·0
	0·700	60	14·7	
	0·700	80	1·38	
	3·50	80	1·41	
40°	0·700	60	38·6	E_{60} 19·0 m = 0·075 $E_{[D]60}$ 28·0
50	0·700	60	105	

hydrochloric and 1M-acetic acid is practically the same as those found for propenylethynyl- and propenylhexynylcarbinols (Part I, Braude and Jones, J., 1944, 436; Parts II and III, *loc. cit.*), the values of $k_{0\cdot02\text{M-HCl}}/k_{1\text{M-AcOH}}$ in 60% EtOH being 23, 20 and 20 respectively; also the solvent effect is much larger for the weak acid.

EXPERIMENTAL.

The preparation and properties of the carbinols studied have already been described (Heilbron, Jones, McCombie, and Weedon, J., 1945, 84; Cymerman, Heilbron, and Jones, J., 1945, 90), and the procedure employed in the kinetic measurements was identical with that described in Parts I and III (*loc. cit.*). The absorption intensities of the butadienylcarbinols are considerably higher than those of the vinylacetylenylcarbinols, with an average value of $\varepsilon_{\max.} = 25{,}000$ at $\lambda_{\max.} = 2230$ A. in the former as compared with $\varepsilon_{\max.} = 13{,}000$ in the latter series. End values (a), initial values (x_0) and the estimated accuracies of the rate constants are given in Table II ($\alpha \pm 2\%$, $\beta \pm 5\%$, $\gamma \pm 10\%$).

TABLE II.

Carbinol.	$\lambda_{\max.}$, A.	a, $E_{1\,\mathrm{cm.}}^{1\%}$ (max.), "kinetic."	"preparative."	x_0.	Accuracy of k's.
(I)	2240	3000 *	3000 [1]	<2	γ
(II)	2280	2300 *	2400 [1]	<2	γ
(III)	2240	2550	2800 [1]	<2	α
(IV)	2280	1800	2100 [2]	35	β

* Assumed. [1] Heilbron, Jones, McCombie, and Weedon, *loc. cit.* [2] Cymerman, Heilbron, and Jones, *loc. cit.*

Both (I) and (II) and their rearranged isomers are rather unstable in alcoholic acid solution probably owing to accompanying polymerisation and cyclisation reactions. The solutions discolour after $x = ca.\ 0\cdot5a$ and only the first 45% of the rearrangements were followed in the determination of k's. The end-values a were assumed in these two cases; the highest values of $E_{1\,\mathrm{cm.}}^{1\%}$ actually reached being about 1500—2000. No chloro-compound formation was ever observed in hydrochloric acid runs, but the rearrangement of (III) in 1·0M-acetic acid on a large scale gave a product which, from refractive index and active hydrogen determinations, contains some of the ethyl ether or di-ether of the isomer. The acid normality of the solution was unchanged, however, indicating that no acetate formation had occurred.

Two representative runs are reproduced below: c_{ROH} = carbinol concentration (% w/v), c_{A} = acid concentration (mol./l.), c_{EtOH} = alcohol concentration (% by vol.).

Rearrangement of (III), $c_{\mathrm{ROH}} = 0\cdot7$, $c_{\mathrm{A}} = 0\cdot02$M-HCl, $c_{\mathrm{EtOH}} = 60$, $t = 40°$.

Time (mins.).	$E_{1\,\mathrm{cm.}}^{1\%}$ at 2240 A.	10^4k (min.$^{-1}$).	Time (mins.).	$E_{1\,\mathrm{cm.}}^{1\%}$ at 2240 A.	10^4k (min.$^{-1}$).
4	843	1020	12	1830	1050
8	1400	1030	∞	2550	—
					Mean·1035

Rearrangement of (III), $c_{\mathrm{ROH}} = 3\cdot5$, $c_{\mathrm{A}} = 1$M-AcOH, $c_{\mathrm{EtOH}} = 80$, $t = 30°$

1480	407	1·40	6945	1360	1·39
4060	970	1·44	∞	2550 *	—
					Mean 1·41

* Assumed.

The dissociation constant of n-butylpropiolic acid was determined by electrometric titration of 5 ml. of 0·01 M-aqueous solution of the acid with 1 ml. of 0·1 M-potassium hydroxide, a glass electrode being used. The pH value at half-neutralisation was 2·85, hence $K = 0\cdot0014$.

DISCUSSION.

The characteristics of the reaction, such as reaction order, dependence of k on c_{ROH}, c_{A}, c_{EtOH}, etc., being the same as those found for the corresponding acetylenyl carbinols, the mechanism is clearly analogous to that deduced for the previous series (see p. 126), the terminal $\cdot C{:}CR_5$ group being replaced by $\cdot CH{:}CH_2$. A reversible oxonium-ion formation is followed by the rate-determining isomerisation, the driving force of the reaction being made up mainly of the tendency of the two ethylenic bonds to enter into conjugation.

Probability factors and relative rate constants are given in Table III, together with the data for the corresponding ethynylcarbinols (Part III, preceding paper). It is evident that there is no obvious correlation between

TABLE III.

r = Observed rate constant at 30° in 60% EtOH relative to (III) and (VII), respectively.

		10^4k in 0·1M-HCl, 60% EtOH, 30°.*	$E_{[\mathrm{D}}$ in 60% EtOH.	log A.	r.	log r.
	Vinylcarbinols this paper).					
(I)	$CH_2{=}CH{\cdot}CH(OH){\cdot}CH{=}CH_2$	1·80	29·6	15·9	0·0010	−3·0
(II)	$CH_2{=}CMe{\cdot}CH(OH){\cdot}CH{=}CH_2$	3·28	27·9	14·8	0·0019	−2·8
(III)	$CHMe{=}CH{\cdot}CH(OH){\cdot}CH{=}CH_2$	*1,730*	25·2	15·7	1	0
(IV)	$CHMe{=}CH{\cdot}CMe(OH){\cdot}CH{=}CH_2$	*22,000*	25·4	16·9	13	1·1
	Ethynylcarbinols (Part III).					
(V)	$CH_2{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH$	*0·00015*	~22	~6	0·0003	−3·5
(VI)	$CH_2{=}CMe{\cdot}CH(OH){\cdot}C{\equiv}CH$	*0·0011*	~31	~13	0·002	−2·7
(VII)	$CHMe{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH$	0·54	31·4	16·6	1	0
(VIII)	$CHMe{=}CH{\cdot}CMe(OH){\cdot}C{\equiv}CH$	93	28·8	17·0	160	2·2

* Extrapolated values in italics.

the values of $E_{[D]}$ and log A in the two series, but the gradation of rate constants is clearly very similar. Methyl substituents facilitate the rearrangement, and, as in the previous series, a substituent in the system $\overset{1}{C}R_1R_2{=}\overset{2}{C}R_3{-}\overset{3}{C}R_4(OH){-}CH{=}CH_2$, has the largest effect when attached to carbon atom 1, a smaller effect when attached to carbon atom 3, and a still smaller effect when attached to carbon atom 2 :

Substituent.	R_1 = Me.	R_3 = Me.	R_4 = Me.
Δ log r	3·0	0·2	1·1

The substituent effects in the two series are thus essentially the same, and this lends additional support to the identity of the reaction mechanisms.

Turning from the similarities to the differences between the two series, some of the latter are tabulated below. The ratio of the rate constants of the two reference compounds (R_1 = Me ; R_2 = R_3 = R_4 = H) under identical conditions at 30° is 3200. This ratio is almost unaltered when the single methyl substituent is in a different position (R_3 = Me), but it is much larger when no methyl substituents are present and much smaller when there are two. There is thus a very marked decrease of the ratio $k_{\text{vinylcarbinol}}/k_{\text{acetylenylcarbinol}}$ as the number of methyl substituents increases, but the number of compounds so far studied is insufficient to warrant any decision as to the generality of this relationship.

Substituents.	—	R_3 = Me.	R_1 = Me.	R_1 = R_4 = Me.
$k_{\text{vinylcarbinol}}/k_{\text{acetylenylcarbinol}}$	12,000	3000	3200	240

The large differences in rate constants between corresponding compounds [*e.g.*, $CHMe{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH$ and $CHMe{=}CH{\cdot}CH(OH){\cdot}CH{=}CH_2$] of the two series must be considered. These are in no way connected with the presence or otherwise of the acetylenic hydrogen atom, since its replacement (by, *e.g.*, an *n*-Bu group) does not alter the characteristics of the rearrangement (Part III, *loc. cit.*), and since any possible ionisation of the acetylenic hydrogen atom would in any case be suppressed in acid solution. The large increase in the rate constant brought about by the replacement of the acetylenyl by the vinyl group is easily accounted for, however, by the much smaller electron-attracting nature of the vinyl as compared with the acetylenyl carbon atom adjacent to the carbinol group. This electron-attraction arises from the co-ordinative unsaturation of atoms forming multiple linkages and represents a negative inductive effect (cf. Dippy, *Chem. Rev.*, **1939**, **25**, 151). The higher the multiplicity of the linkage, *i.e.*, the greater the number of electron pairs shared, the greater is the electron deficiency on the constituent atoms and thus the negative-inductive effect of the acetylenic group would be expected to be much greater than that of the ethylenic group. Both steps involved in the mechanism of the present reaction require electron accession at the reacting centre and are therefore facilitated by the replacement of an acetylenic by an ethylenic group. The reverse is true of the ionisation of a carboxylic acid. The differences in the dissociation constants of propiolic, butylpropiolic, and acrylic acids may be compared with the differences in the rate constants of the rearrangements of propenylethynyl-, propenylhexynyl-, and propenylvinyl-carbinols.

	10^4k (min.$^{-1}$) in 0·02M-HCl, 60% EtOH at 30°
$CHMe{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH$	0·11
$CHMe{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CBu(n)$	16·5
$CHMe{=}CH{\cdot}CH(OH){\cdot}CH{=}CH_2$	345

	10^5K in water, 25°.
$CH{\equiv}C{\cdot}CO_2H$	1400 [1]
$CBu{\equiv}C{\cdot}CO_2H$	140
$CH_2{=}CH{\cdot}CO_2H$	5·5 [2]

[1] Wilson and Wenzke, *J. Amer. Chem. Soc.*, 1935, **57**, 1265.

[2] Dippy, *loc. cit.*

Qualitative evidence for the greater electron-attraction of the acetylenic as compared with the ethylenic group has also been adduced by Baker, Cooper, and Ingold (J., 1928, 426) from a study of the nitration of cinnamic and phenylpropiolic acids.

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