35. *The Kinetics of Anionotropic Rearrangement. Part III. Substituent Effects in the Oxotropic * Formation of the Vinylacetylene System.*

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Rate constants, energies of activation and solvent effects are reported for the acid-catalysed isomerisation of twenty carbinols of the type $CR_1R_2{:}CR_3{\cdot}CR_4(OH){\cdot}C{\vdots}CR_5$. The rate constants at one temperature vary over a range of 10^9, increasing with increasing alkyl substitution, and the isodielectric energies of activation, which are independent of solvent composition, vary from 20 to 32 kg.-cals. per mol. These results are explained by the mechanism proposed in Parts I and II (J., 1944, 436, 443) for the rearrangement of propenylethynylcarbinol ($R_1 = Me$; $R_2 = R_3 = R_4 = R_5 = H$), the establishment of the oxonium-ion equilibrium, $ROH \rightleftharpoons ROH_2^+$, being followed by the rate-determining isomerisation. A quantitative comparison is made of the general inductive and tautomeric effects of a number of alkyl and alkenyl groups.

In Parts I and II (*loc. cit.*) a detailed kinetic study of the acid-catalysed rearrangement of propenylethynylcarbinol (IV) to hex-3-en-5-yn-2-ol was reported, the course of the reaction being followed by measuring the

$$\text{(IV.)}\quad CH_3{\cdot}CH{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH \xrightarrow{\text{acid}} CH_3{\cdot}CH(OH){\cdot}CH{=}CH{\cdot}C{\equiv}CH$$

changing intensity of ultra-violet light absorption. The investigation has now been extended to 20 other carbinols of the same type, all of which have been prepared in the course of other studies carried out in these laboratories (Heilbron, Jones, *et al.*, J., 1942—1946) and a suitable opportunity has been provided for a quantitative comparison of the electronic effects of a number of alkyl and alkenyl groups in purely aliphatic systems.

As in the case of propenylethynylcarbinol (subsequently referred to as (IV)), the reaction was always found to be of the first order and the first-order rate constant was independent of the carbinol concentration. Rate

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* For the definition of Oxotropy, see Part I (J., 1944, 442).

constants, solvent effects, Arrhenius and isodielectric energies of activation are given in Table I. As far as possible, 0·002—1M-solutions of hydrochloric acid in 60 and 80% (by volume) alcohol were used as reaction media and, for convenience, a carbinol concentration of 0·700% w/v was employed throughout, except in the case of the sparingly soluble glycol (XX) where c_{ROH} was 0·14%. The 60 and 80% alcohol–water mixtures were chosen since most of the carbinols studied are insufficiently soluble when $c_{\mathrm{EtOH}} < 60\%$, and for $c_{\mathrm{EtOH}} > 80\%$ the relation between dielectric constant (*D*) of the medium and log *k* is no longer linear (Part II, *loc. cit.*) and

TABLE I.

c_{A} = Concentration of HCl (mols./l.); c_{EtOH} = vol.-% EtOH; k = first-order rate constant (in min.$^{-1}$); carbinol concentration c_{ROH} = 0·700% w/v throughout, except with (XX), where c_{ROH} = 0·140%; E_{60}, E_{80} = Arrhenius energy of activation (in kg.-cals.) 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.*); $E_{[\mathrm{D}]60}$, $E_{[\mathrm{D}]80}$ = isodielectric energies of activation (in kg.-cals.) for c_{EtOH} = 60, 80.

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

t.	c_{A}.	c_{EtOH}.	10^4k.*	
30°	4	20	*0·8*	E_{60} ~17 E_{80} ~20 m = 0·033 $E_{[\mathrm{D}]60}$ ~22 $E_{[\mathrm{D}]80}$ ~23
	4	40	*0·4*	
	4	60	*0·3*	
50	1	20	*0·9*	
	1	40	*0·4*	
60	1	20	*2*	
	1	40	*1*	

(II) $\mathrm{CH_2{=}CH{\cdot}CMe(OH){\cdot}C{\equiv}CH}$.

t.	c_{A}.	c_{EtOH}.	10^4k.*	
30	1	60	2	E_{60} ~25 E_{80} ~29 m = 0·045 $E_{[\mathrm{D}]60}$ ~31 $E_{[\mathrm{D}]80}$ ~33
	1	80	0·5	
40	1	60	6	
	1	80	2	
50	0·1	60	1	
	1	60	28	
	1	80	10	

(III) $\mathrm{CH_2{=}CMe{\cdot}CH(OH){\cdot}C{\equiv}CH}$.

t.	c_{A}.	c_{EtOH}.	10^4k.*	
30	4	60	*2*	E_{60} ~26 E_{80} ~28 m = 0·036 $E_{[\mathrm{D}]60}$ ~31 $E_{[\mathrm{D}]80}$ ~32
50	1	60	*0·3*	
	1	80	*0·15*	
60	1	60	*1*	
	1	80	*0·4*	

(IV) $\mathrm{CHMe{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH}$.

t.	c_{A}.	c_{EtOH}.	10^4k.*	
30	0·02	60	0·078	E_{60} 25·7 E_{80} 25·7 m = 0·044 $E_{[\mathrm{D}]60}$ 31·4 $E_{[\mathrm{D}]80}$ 30·7
	0·1	60	0·58	
	0·1	80	0·210	
	1M-AcOH	60	0·170	
40	0·02	60	0·366	
	0·1	60	2·22	
	0·1	80	0·85	
50	0·02	60	1·36	
	0·1	60	8·1	
	0·1	80	3·10	
60	0·02	60	3·98	
	0·1	60	28·1	
	0·1	80	10·0	

(V) $\mathrm{CHMe{=}CH{\cdot}CMe(OH){\cdot}C{\equiv}CH}$.

t.	c_{A}.	c_{EtOH}.	10^4k.*	
30	0·02	60	17·5	E_{60} 23·7 E_{80} 25·7 m = 0·040 $E_{[\mathrm{D}]60}$ 28·8 $E_{[\mathrm{D}]80}$ 29·7
	0·1	60	93	
	0·1	80	30·7	
40	0·02	60	56	
	0·1	60	290	
	0·1	80	95	
50	0·02	60	210	
	0·1	60	1070	
	0·1	80	431	

(VI) $\mathrm{CHPr^{\alpha}{=}CEt{\cdot}CH(OH){\cdot}C{\equiv}CH}$.

t.	c_{A}.	c_{EtOH}.	10^4k.*	
30	0·04	60	1·17	E_{60} 27·2 E_{80} 27·7 m = 0·031 $E_{[\mathrm{D}]60}$ 31·2 $E_{[\mathrm{D}]80}$ 30·8
	0·1	60	2·80	
	0·1	80	1·25	
40	0·04	60	4·84	
	0·1	60	13·5	
	0·1	80	6·0	
50	0·04	60	18·0	
	0·1	60	46·7	
	0·1	80	21·9	

(VII) $\mathrm{CMe_2{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH}$.

t.	c_{A}.	c_{EtOH}.	10^4k.*	
30°	0·02	60	27·3	E_{60} 21·7 E_{80} 23·2 m = 0·046 $E_{[\mathrm{D}]60}$ 27·6 $E_{[\mathrm{D}]80}$ 27·6
	0·02	80	6·9	
	0·1	60	133	
40	0·02	60	85	
	0·02	80	26·4	
50	0·02	60	256	
	0·02	80	81	

(VIII) $\mathrm{CMe_2{=}CH{\cdot}CMe(OH){\cdot}C{\equiv}CH}$.

t.	c_{A}.	c_{EtOH}.	10^4k.*	
30	0·002	60	70	E_{60} 21·4 E_{80} 21·6 m = 0·030 $E_{[\mathrm{D}]60}$ 25·2 $E_{[\mathrm{D}]80}$ 24·6
	0·02	60	820	
	0·02	80	337	
40	0·002	60	221	
	0·002	80	98	
	0·02	60	2530	
50	0·002	60	640	
	0·02	60	7000	
	0·02	80	3620	

(IX) $\mathrm{CH_2{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CBu}$ (*n*).

t.	c_{A}.	c_{EtOH}.	10^4k.*	
30	1	60	1·4	E_{60} ~18·5 E_{80} ~19·5 m = 0·038 $E_{[\mathrm{D}]60}$ ~23·5 $E_{[\mathrm{D}]80}$ ~23
	1	80	0·5	
40	1	60	4·7	
	1	80	1·8	
50	0·1	60	0·56	
	1	60	9·4	
	1	80	2·8	

(X) $\mathrm{CH_2{=}CH{\cdot}CMe(OH){\cdot}C{\equiv}CBu}$ (*n*).

t.	c_{A}.	c_{EtOH}.	10^4k.*	
30	0·02	60	2·90	E_{60} 26·0 E_{80} 27·6 m = 0·043 $E_{[\mathrm{D}]60}$ 31·5 $E_{[\mathrm{D}]80}$ 31·9
	0·1	60	16·4	
	0·1	80	5·0	
40	0·1	60	68	
	0·1	80	21·1	
50	0·1	60	244	
	0·1	80	86	

(XI) $\mathrm{CHMe{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CBu}$ (*n*).

t.	c_{A}.	c_{EtOH}.	10^4k.*	
0	0·1	60	1·49	E_{60} 22·2 E_{80} 23·7 m = 0·030 $E_{[\mathrm{D}]60}$ 26·0 $E_{[\mathrm{D}]80}$ 26·7
30	0·02	60	16·5	
	0·1	60	81	
	0·1	80	32·0	
	1	60	1760	
	1M-AcOH	60	0·84	
40	0·02	60	44·7	
	0·1	60	219	
	0·1	80	105	
50	0·02	60	162	
	0·1	60	800	
	0·1	80	395	

(XII) $\mathrm{CHMe{=}CH{\cdot}CMe(OH){\cdot}C{\equiv}CBu}$ (*n*)

t.	c_{A}.	c_{EtOH}.	10^4k.*	
30	0·0004	90	1·26	E_{60} 22·8 E_{80} 23·2 m = 0·042 $E_{[\mathrm{D}]60}$ 28·1 $E_{[\mathrm{D}]80}$ 27·4
	0·002	60	111	
	0·002	80	32·6	
	0·02	60	1040	
40	0·002	60	352	
	0·002	80	141	
50	0·0004	90	12·8	
	0·002	60	1160	
	0·002	80	363	

t.	c_A.	c_{EtOH}.	10^4k.*	
(XIII) $CMe_2{=}CH{\cdot}CMe(OH){\cdot}C{\equiv}CBu$ (*n*).				
30°	0·0004	90	98	E_{60} 20 ~25
	0·002	90	1700	
40	0·0004	90	206	
50	0·0004	90	820	
(XIV) $CHMe{=}CH{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}CH_2OMe$.				
30	0·1	60	2·30	E_{60} 27·5 m = 0·035 $E_{[D]60}$ 32·0
	0·1	80	0·90	
	0·2	60	5·8	
	1	60	90	
40	0·1	60	9·3	
50	0·1	60	39·4	
(XV) $CHMe{=}CH{\cdot}CMe(OH){\cdot}C{\equiv}C{\cdot}CH_2OMe$.				
30	0·02	60	63	E_{60} 26·1 m = 0·033 $E_{[D]60}$ 30·2
	0·02	80	25·5	
	0·1	60	355	
40	0·02	60	288	
50	0·02	60	*930*	
(XVI) $CMe_2{=}CH{\cdot}CMe(OH){\cdot}C{\equiv}C{\cdot}CH_2OMe$.				
30	0·002	60	201	E_{60} 19·2 m = 0·032 $E_{[D]60}$ 23·3
	0·002	80	84	
	0·02	60	2040	
40	0·002	60	560	
50	0·002	60	1470	
(XVII) $CHMe{=}CH{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}CH{=}CH_2$.				
30	0·02	60	5·9	E_{60} 22·4 E_{80} 24·1 m = 0·036 $E_{[D]60}$ 27·0 $E_{[D]80}$ 27·7
	0·1	60	34·8	
	0·1	80	12·4	
40	0·02	60	21·3	
	0·1	60	113	
	0·1	80	43·2	
50	0·02	60	68	
	0·1	60	352	
	0·1	80	150	

t.	c_A.	c_{EtOH}.	10^4k.*	
(XVIII) $CHMe{=}CH{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}CMe{=}CH_2$.				
30°	0·02	60	7·9	E_{60} 20·9 E_{80} 22·9 m = 0·034 $E_{[D]60}$ 25·2 $E_{[D]80}$ 26·3
	0·1	60	42·6	
	0·1	80	15·7	
40	0·02	60	22·1	
	0·1	60	123	
	0·1	80	51	
50	0·02	60	79	
	0·1	60	370	
	0·1	80	167	
(XIX) $CHMe{=}CH{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}CMe{=}CHMe$.				
30	0·04	60	47·8	E_{60} 22·5 m = 0·025 $E_{[D]60}$ 25·7
	0·1	60	116	
	0·1	80	65·0	
40	0·1	60	368	
50	0·1	60	1200	
(XX) $CHMe{=}CH{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}CH(OH){\cdot}CH{=}CHMe$.				
30	0·04	60	2·50	E_{60} 25·4 E_{80} 26·9 m = 0·032 $E_{[D]60}$ 29·5 $E_{[D]80}$ 30·1
	0·1	60	7·3	
	0·1	80	2·94	
40	0·04	60	9·2	
	0·1	60	29·2	
	0·1	80	11·4	
50	0·04	60	39·5	
	0·1	60	96	
	0·1	80	47·6	

* Values extrapolated to zero time in italics.

does not permit of the evaluation of isodielectric energies of activation. In three cases, however, other media had to be used. At room temperature, the rates of rearrangement of (I) and (III) are so slow and the extent of polymerisation and decomposition so great that 4M-hydrochloric acid had to be used as catalyst to attain measurable rates, although considerable chloro-compound formation takes place at such high acid concentrations. Solutions of carbinol (XIII) could only be obtained in 90% alcohol, a comparison of the relative rate constant being obtained by carrying out the rearrangement of (XII) in this medium also.

The rate constants are roughly proportional to the acid concentration (c_A) up to c_A = 0·1M [for the rearrangement of (IV) in 20% alcohol (Part I, *loc. cit.*) this proportionality was strict]; in 60% and 80% alcohol the rate constants generally increase slightly more rapidly than c_A, but the increase in the " catalytic constant " (k/c_A) in no case exceeds 20% for a ten-fold increase in c_A. The degree of deviation from linearity of the k–c_A curve varies for different carbinols; it is definitely greater than the maximum experimental error in several cases and the differences are probably to be ascribed to solvation effects. If the deviations were solely due to the fact that the catalytic effect of the medium at high alcohol concentrations is no longer proportional to c_A even for c_A <0·1M, the differences should be the same for all carbinols. In 90% alcohol the proportionality between k and c_A is completely destroyed, as shown by the values of k for (XIII).

Above c_A = 0·1, k increases more rapidly than c_A as in the case of (IV), where k is proportional to Hammett's acidity function H_0 (Part I, *loc. cit.*). Again, the ratio of the rate constants of the rearrangement of (XI) in hydrochloric and acetic acid is nearly the same as in the case of (IV).

The solvent effect varies somewhat for different carbinols, the rate constants decreasing by factors ranging from 2 to 4 when c_{EtOH} is increased from 60 to 80%. Arrhenius energies of activation range from 19 to 27 kg.-cals./mol., and the values for 60 and 80% alcohol respectively show a maximum difference of ±1 kg.-cal. and an average difference of ±0·6 kg.-cal. Isodielectric energies of activation, calculated from the solvent-effect data by the method previously described (Part II, *loc. cit.*), are also given in Table I. They range from 18·5 to 31·5 kg.-cals./mol., but differences between the values for 60 and 80% alcohol are reduced to a maximum of ±0·5 kg.-cal. and an average of ±0·3 kg.-cal. The accuracy of the rate constants and hence of the energies of activation varies considerably for different carbinols (see Experimental), but since the average probable error in E is estimated at ±0·3 kg.-cal./mol., isodielectric energies of activation are therefore independent of medium composition within the limits of experimental error, as has already been observed in the case of propenylethynylcarbinol (IV) (Part II, *loc. cit.*).*

* The isodielectric energy of activation ($E_{[D]}$) is the energy of activation when D is constant *at different temperatures* for *one* solvent, *i.e.*, for a solvent of temperature-invariant dielectric constant, but different solvents of different dielectric constants may of course give rise to different values of $E_{[D]}$.

EXPERIMENTAL.

The technique of the kinetic measurements has been described in Part I, but owing to the fact that the more unstable carbinols studied often showed appreciable initial light absorption, a slightly different method of computation was employed. The first-order rate constant k was calculated from $k = (2{\cdot}3/z) \log[(a - x_0)/(a - x)]$ where z = time in minutes, x_0 = intensity of absorption at $z = 0$, x = intensity at z mins., a = intensity at $z = \infty$, intensities being expressed as $E^{1\%}_{1\,\text{cm.}}$ at the wave-length of the maximum. In order to reduce incidental errors to a minimum, x_0 was determined directly from the carbinol, not from the reaction mixture, and was repeatedly checked since it often increased slowly on standing during several weeks, even at 0°. The range of x_0 values is shown in Table II. Initial absorption is particularly marked in the tertiary carbinols, possibly owing to slow dehydration, and in the propargylcarbinols. No definite case of thermal isomerisation has been observed, and the initial absorption could usually be eliminated by refractionation, but in general it was impracticable to use freshly distilled samples for every run owing to lack of material.

The end-values a were again averaged from all the end-values obtained in individual runs; the absorption intensities so obtained are in most cases close to those reported in the preparative work (Heilbron, Jones, *et al.*, *loc. cit.*) where the carbinols were rearranged heterogeneously and the pure products isolated (Table II). In some cases the kinetic end-values are slightly higher, suggesting that the heterogeneous rearrangements were not quite complete; in others they are somewhat lower, suggesting that side reactions occur in the homogeneous media leading to less strongly absorbing products. The third alternative, namely, that an equilibrium is set up between the unrearranged and the rearranged isomers, can be discounted because end-values were the same at different temperatures; if an equilibrium did occur, the equilibrium constant, and, therefore, the final absorption intensity would, of course, vary with temperature. The isomerisations of the four vinylcarbinols (I), (II), (III), and (IX) are so slow, and decomposition so rapid, that it is impossible to follow the reactions to completion. The highest extinction coefficients attained correspond to 10, 80, 10 and 90% rearrangement respectively. Except in the case of (II) the previous attempts to effect these rearrangements heterogeneously had failed completely. The rearranged isomer of (I) has, however, been prepared *via* the corresponding chloro-compound, and the intensity there obtained was used for a; end-values for (III) and (IX), the isomers of which have not been isolated, were deduced by assuming $\varepsilon_{\text{max.}}$ ($= E^{1\%}_{1\,\text{cm.}} \times M/10$) = 13000 for the fully rearranged carbinol, this being the average value in this series; but with (I) and (III), no conclusive evidence has been obtained as to whether *complete* rearrangement does in fact occur or not.

TABLE II.

Rearrangement of carbinol.	$\lambda_{\text{max.}}$, A.	$E^{1\%}_{1\,\text{cm.}}$ (max.), "kinetic."	"preparative."	x_0.	Accuracy of k's.
(I)	2230	1650 *	1650 [7]	< 2	δ
(II)	2235	1300 *	1300 [8]	20	γ
(III)	2230	1300 *	—	< 2	δ
(IV)	2235	1300	1300 [1]	< 2	α
(V)	2240	1130	1200 [8]	35	α
(VI)	2270	815	820 [1]	35—45	β
(VII)	2235	1140	1180 [1]	25	β
VIII)	2240	965	960 [8]	50	α
(IX)	2280	1000 *	—	65—140	γ
(X)	2280	870	920 [6]	80	β
(XI)	2280	1100	1060 [2]	< 2	α
(XII)	2280	920	870 [6]	20	α
(XIII)	2280	575	680 [6]	100	β
(XIV)	2280	940	910 [9]	180	α
(XV)	2280	800	770 [9]	70—80	β
(XVI)	2280	600	760 [9]	65—105	β
(XVII)	2585	1400	1450 [5]	10—20	α
(XVIII)	2590	1250	1260 [5]	10—20	α
(XIX)	2620	1100	1100 [3]	30—40	α
(XX)	2640	1290	1060 [4]	< 2	α

* Assumed.

[1] Jones and McCombie, J., 1943, 261. [2] Heilbron, Jones, and Raphael, J., 1943, 264. [3] Heilbron, Johnson, Jones, and Raphael, J., 1943, 265. [4] Heilbron, Jones, and Raphael, J., 1943, 268. [5] Heilbron, Jones, and Weedon, J., 1944, 140. [6] Cymerman, Heilbron, and Jones, J., 1944, 144. [7] Heilbron, Jones, Lacey, McCombie, and Raphael, J., 1945, 77. [8] Cymerman, Heilbron, and Jones, J., 1945, 90. [9] Heilbron, Jones, and Lacey, this vol., p. 27.

The instability of several of the carbinols studied has already been commented upon and severely limited the accuracy of the rate-constant determinations, the precaution of carrying out the rearrangements under nitrogen proving of little avail. Definite drifts in the rate constant were, however, only observed in isolated cases, and in these k was extrapolated to zero time, as indicated in Table I. The average maximum errors in the rate constants for each carbinol are indicated in Table II, where α denotes an accuracy in k of about ±2%, β of ±5% and γ of ±10%, whereas δ denotes that the maximum error is uncertain and may considerably exceed 10%. Some 30% of the rate constant determinations were carried out in duplicate. Four individual runs, exemplifying the four grades of accuracy attained, are reproduced below. The carbinol concentration was 0·7% w/v throughout.

Rearrangement of (V) in 0·1M-HCl, 80% by vol. EtOH, 30°.

Time (mins.).	$E^{1\%}_{1\,\text{cm.}}$ at 2240 A.	10^4k (min.$^{-1}$).	Time (mins.).	$E^{1\%}_{1\,\text{cm.}}$ at 2240 A.	10^4k (min.$^{-1}$).
0	36	—	367	785	30·6
163	465	30·5	∞	1130	—
272	658	30·9			Mean 30·7 (± <2%)

Rearrangement of (VII) in 0·02M-HCl, 60% by vol. EtOH, 50°.

Time (mins.).	$E^{1\%}_{1\,\text{cm.}}$ at 2235 A.	10^4k (min.$^{-1}$).	Time (mins.).	$E^{1\%}_{1\,\text{cm.}}$ at 2235 A.	10^4k (min.$^{-1}$).
0	25	—	36	704	260
12	328	262	∞	1140	—
22	493	248			Mean 256 (± <5%)
29	610	255			

Rearrangement of (IX) in 1M-HCl, 60% by vol. EtOH, 30°.

Time (mins.).	$E^{1\%}_{1\,\mathrm{cm.}}$ at 2280 A.	10^4k (min.$^{-1}$).	Time (mins.).	$E^{1\%}_{1\,\mathrm{cm.}}$ at 2280 A.	10^4k (min.$^{-1}$).
0	65	—	7595	680	1·41
1410	243	1·50	∞	1000 *	—
2590	336	1·32			Mean 1·40 ($\pm < 10\%$)
4610	500	1·35			

Rearrangement of (I) in 4M-HCl, 60% by vol. EtOH, 30°.

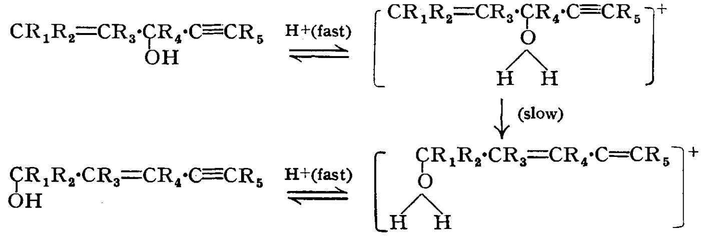
Time (mins.).	$E^{1\%}_{1\,\mathrm{cm.}}$ at 2230 A.	10^4k (min.$^{-1}$).	Time (mins.).	$E^{1\%}_{1\,\mathrm{cm.}}$ at 2230 A.	10^4k (min.$^{-1}$).
0	0	0·30 †	8,550	324	0·256
1540	72	0·292	11,200	395	0·230
2860	127	0·281	∞	1650 *	—
5800	256	0·290			

* Assumed. † Extrapolated.

Arrhenius energies of activation were calculated algebraically from $E = 2{\cdot}3\,\boldsymbol{R}\log(k_2/k_1) \times T_1T_2/(T_2 - T_1)$. The deviation from the mean of individual values of E varied from $\pm 0{\cdot}1$ to ± 2 kg.-cal./mol., the magnitude of the deviations being roughly proportional to the estimated probable errors in the rate-constant determinations. Isodielectric energies of activation were calculated by $E_{[D]} = E_{\mathrm{Arr.}} + 2{\cdot}3\boldsymbol{R}T_1T_2mb$, where $b = 0{\cdot}286$ and $0{\cdot}225$ respectively for $c_{\mathrm{EtOH}} = 60\%$ and $c_{\mathrm{EtOH}} = 80\%$ (see Part II, *loc. cit.*). Values of m are averaged over the temperature range employed.

DISCUSSION.

Since such characteristics of the isomerisation as reaction order, dependence of rate constants on carbinol, acid and alcohol concentrations, etc., are identical in every case with those found for the rearrangement of propenylethynylcarbinol (IV), it would appear that the mechanism throughout the series is that previously proposed for the isomerisation of the latter compound, *viz.*,



according to which a reversible oxonium-ion formation is followed by the rate-determining isomerisation, the driving force of which must consist essentially of the tendency of the double to become conjugated with the acetylenic linkage. Both steps of the reaction should be facilitated by an increased electron availability at the oxygen atom. Inspection of the rate constants of the rearrangement for the various carbinols under identical conditions (Table III) shows that this is indeed the case, the rate constants increasing rapidly with increasing substitution by (electron-repelling) alkyl groups, over a range of 10^9. An alkyl substituent on carbon atom 2 in the system $\overset{1}{C}{=}\overset{2}{C}{-}\overset{3}{C}(OH){-}\overset{4}{C}{\equiv}\overset{5}{C}$ has a much smaller effect, however, than a similar substituent

TABLE III.

r = Observed rate constant at 30° in 60% EtOH relative to that of carbinol (IV). $r_{\mathrm{calc.}}$ = Relative rate constant calculated by (1).

Carbinol.	10^4k (min.$^{-1}$) in 0·1M-HCl, 60% EtOH, 30°.*	$E_{[D]}$ in 60% EtOH.	log A.	r.	log r.	log $r_{\mathrm{calc.}}$.	log $r_{\mathrm{calc.}}$ − log r.
(I) $CH_2{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH$	*0·00015*	~22	~6	0·0003	−3·5	−3·5	0·0
(II) $CH_2{=}CH{\cdot}C\mathit{Me}(OH){\cdot}C{\equiv}CH$	*0·09*	~31	~15	0·15	−0·8	−1·1	−0·3
(III) $CH_2{=}C\mathit{Me}{\cdot}CH(OH){\cdot}C{\equiv}CH$	*0·0011*	~31	~13	0·002	−2·7	−2·7	0·0
(IV) $CH\mathit{Me}{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH$	0·58	31·4	16·6	1	0	0·0	0·0
(V) $CH\mathit{Me}{=}CH{\cdot}C\mathit{Me}(OH){\cdot}C{\equiv}CH$	93	28·8	17·0	160	2·2	2·4	+0·2
(VI) $CH\mathit{Pr}^{a}{=}C\mathit{Et}{\cdot}CH(OH){\cdot}C{\equiv}CH$	2·80	31·2	17·2	5	0·7	0·8	+0·1
(VII) $C\mathit{Me}_2{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH$	133	27·6	16·2	250	2·4	1·9	−0·5
(VIII) $C\mathit{Me}_2{=}CH{\cdot}C\mathit{Me}(OH){\cdot}C{\equiv}CH$	*4,550*	25·2	16·1	9,000	4·0	4·3	+0·3
(IX) $CH_2{=}CH{\cdot}CH(OH){\cdot}C{\equiv}C\mathit{Bu}(n)$	*0·054*	~23·5	~10	0·1	−1·0	−1·4	−0·4
(X) $CH_2{=}CH{\cdot}C\mathit{Me}(OH){\cdot}C{\equiv}C\mathit{Bu}(n)$	16·4	31·5	18·1	30	1·5	1·0	−0·5
(XI) $CH\mathit{Me}{=}CH{\cdot}CH(OH){\cdot}C{\equiv}C\mathit{Bu}(n)$	81	26·0	14·9	150	2·2	2·1	−0·1
(XII) $CH\mathit{Me}{=}CH{\cdot}C\mathit{Me}(OH){\cdot}C{\equiv}C\mathit{Bu}(n)$	*5,600*	28·2	18·3	11,000	4·0	4·5	+0·5
(XIII) $C\mathit{Me}_2{=}CH{\cdot}C\mathit{Me}(OH){\cdot}C{\equiv}C\mathit{Bu}(n)$	*354,000*	~25	~18	700,000	5·9	6·4	+0·5
(XIV) $CH\mathit{Me}{=}CH{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}\mathit{CH_2OMe}$	2·30	32·0	17·7	4	0·6	0·5	−0·1
(XV) $CH\mathit{Me}{=}CH{\cdot}C\mathit{Me}(OH){\cdot}C{\equiv}C{\cdot}\mathit{CH_2OMe}$	355	30·2	18·6	600	2·8	2·	−0·2
(XVI) $C\mathit{Me}_2{=}CH{\cdot}C\mathit{Me}(OH){\cdot}C{\equiv}C{\cdot}\mathit{CH_2OMe}$	*10,200*	23·3	15·1	2,000	4·3	4·5	+0·2
(XVII) $CH\mathit{Me}{=}CH{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}\mathit{CH{=}CH_2}$	34·8	27·0	15·2	60	1·8	1·8	0·0
(XVIII) $CH\mathit{Me}{=}CH{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}\mathit{CMe{=}CH_2}$	42·6	25·2	14·0	25	1·9	1·9	0·0
(XIX) $CH\mathit{Me}{=}CH{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}\mathit{CMe{=}CHMe}$	116	25·7	15·3	200	2·3	2·3	0·0
(XX) $CH\mathit{Me}{=}CH{\cdot}CH(OH){\cdot}C{\equiv}C{\cdot}CH(OH){\cdot}CH{=}CH\mathit{Me}$	7·3	29·5	16·4		1·1	—	—

* Extrapolated values in italics.

on carbon atoms 1, 3, or 5. An alkenyl group on carbon atom 5 has an effect similar in magnitude to that of an alkyl group, while an alkoxymethyl group has a smaller influence on the rate constant.

In Table III columns from left to right represent (i) the carbinol, (ii) the rate constant in, or extrapolated to, 0·1M-hydrochloric acid in 60% (by vol.) alcohol at 30° (extrapolated values in italics), (iii) the isodielectric energy of activation ($E_{[D]}$) in 60% (by vol.) alcohol [estimated in the cases of (I) and (XIII) where the media actually employed were 20% and 90% alcohol respectively, and also in the cases of (II), (III), and (IX) where the logarithms of the rate constants do not vary linearly with $1/T$, probably because the rate of decomposition is greatly increased at higher temperatures], (iv) log A, where $k = Ae^{-E_{[D]}/RT}$, (v) r, the relative rate constant with respect to (IV) which was chosen as reference compound rather than (I), because it has been most thoroughly investigated and its data are the most accurate available, (vi) log r, (vii) log r calculated by equation (1) (see below).

The relative rate constants (r) vary over a range of 10^9, while $E_{[D]}$ varies from 18·5 to 31·5 kg.-cals./mol. and log A from 6·3 to 18·3. Variations in r are therefore due to simultaneous variations in both $E_{[D]}$ and A. There is no obvious correlation between the degree of substitution and either $E_{[D]}$ or log A separately, but the effect of a substituent on log r is reasonably constant, and the relative rate constants at one temperature can be expressed by the equation

$$\log r = \log r_0 + \Sigma\Delta \log r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where r_0 refers to the unsubstituted compound (I) and Δ log r represents the effect of each substituent present. The following values of Δ log r lead to the smallest average difference (±0·2) between log $r_{\text{calc.}}$ and log $r_{\text{obs.}}$ (log $r_0 = -3{\cdot}5$) :

Substituent effects in the rearrangement of $\overset{1}{C}R_1R_2{=}\overset{2}{C}R_3{\cdot}\overset{3}{C}R_4(OH){\cdot}\overset{4}{C}{\equiv}\overset{5}{C}R_5$.

Substituent.	Δ log r.	Substituent.	Δ log r.	Substituent.	Δ log r.
R_1 = Me or *n*-Pr	3·5	R_4 = Me	2·4	R_5 = CH=CH$_2$	1·8
R_2 = Me (when R_1 = Me)	1·9	R_5 = *n*-Bu	2·1	R_5 = CMe=CH$_2$	1·9
R_3 = Me or Et	0·8	R_5 = CH$_2$·OMe	0·5	R_5 = CMe=CHMe	2·3

These results demonstrate very forcibly the operation of two types of substituent effect, one (general inductive) decreasing rapidly with distance between the substituent and the reacting centre, and the other (tautomeric) effective only when an unsaturated, highly polarisable group, *e.g.*, an ethylenic bond, is interposed between the substituent and the reacting centre (Ingold, J., 1933, 1120). In the present instance, the inductive effect would be expected to be fully exerted by a substituent on carbon atom 3. Introduction of a methyl group in this position (R_4 = Me) increases the rate constant by an average factor of 250. When a methyl group is attached to carbon atom 2 (R_3 = Me), further away from the hydroxyl group, the rate constant only increases by a factor of about 5. A methyl substituent on carbon atom 1, however, again has a very large effect (a factor of *ca.* 2500), in spite of the fact that the distance between the substituent and the reacting centre has been increased still further. The effect of the methyl group in this position must be ascribed almost entirely to its tautomeric effect. A second methyl substituent on carbon atom 1 has a less powerful action than the first, presumably because the polarisability of the ethylenic bond decreases with its increasing polarisation. It may be noted that an alkyl substituent on carbon atom 2 (R_3 = Me or Et) exerts only its positive inductive effect, and not, as might be expected, a simultaneous negative tautomeric effect by causing a displacement of the double bond electrons away from the reacting centre. The tautomeric properties of the alkyl groups in the present reaction must therefore be mainly time-variable polarisability (electromeric) effects, coming into play only if they facilitate the reaction and at the demand of the attacking hydrogen ion (cf. Shoppee, J., 1930, 968).

A *n*-butyl group attached to carbon atom 5 increases the rate constant by an average factor of 100, *i.e.*, very much less than a methyl group on carbon atom 1. This may be due both to a smaller polarisability of the acetylenic as compared with the ethylenic bond, and to a smaller tautomeric effect of the *n*-butyl as compared with the methyl group (cf. Baker and Nathan, J., 1935, 184; Baker, J., 1939, 1150). The tautomeric effect of the methoxymethyl group (R_5 = CH$_2$·OMe) is much smaller than that of an alkyl group, as would be expected. A *conjugated* vinyl group (R_5 = CH=CH$_2$) has quite a large electron-donating tautomeric effect, although the ethylenic double bond is normally an electron acceptor, because, when in conjugation, the mobility of all the unsaturation electrons in the conjugated system is increased. This effect is further enhanced by methyl substituents (R_5 = CMe=CH$_2$ and CMe=CHMe).

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