

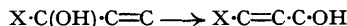
206. *The Kinetics of Anionotropic Rearrangement. Part VI. The Effects of Methyl, Methoxy-, and Halogen Substituents attached to a Phenyl Group.*

By ERNEST A. BRAUDE and E. S. STERN.

The kinetics of the acid-catalysed oxotropy of substituted phenylpropenylcarbinols to the corresponding styrylmethylcarbinols (p. 1097, I \longrightarrow II) have been studied. The effects of nuclear substituents in this molecular rearrangement are in accord with those observed in substitution reactions and in the dissociation constants of substituted benzoic acids. The reaction is facilitated by methyl and methoxyl substituents, and retarded by halogen substituents, first-order rate constants at one temperature varying in the order $p\text{-Br} < p\text{-Cl} < p\text{-F} < \text{H} < m\text{-Me} < o\text{-Me} < p\text{-Me} < p\text{-MeO}$. The differences in the rate constants are due to small

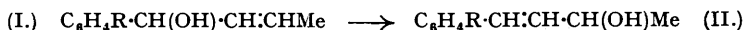
changes both in the isodielectric energy of activation and in the non-exponential factor of the Arrhenius equation. The results are discussed in terms of the electronic effects of the substituent groups and the unexpected sequence previously noted by other authors of tautomeric effects decreasing in the order $F > Cl > Br$, is confirmed.

In previous papers in this series, detailed investigations have been described of rearrangements of the type where X is an acetylenic, ethylenic, or phenyl group. A reaction mechanism has



been outlined which accounts for the kinetic features of the reaction and their dependence on medium composition. The effects of many aliphatic substituents have been examined and found to be those expected for a reaction requiring electron accession at the point of reaction. It appeared worth while to extend this work to a study of the effects of aromatic substituents, data for which have hitherto been largely derived from substitution reactions and dissociation constants.

It was shown in Part V (*J.*, 1946, 396) that the rearrangement of phenylpropenylcarbinol (I, R = H) to styrylmethylcarbinol (II, R = H) proceeds smoothly in aqueous dioxan in the presence of hydrochloric acid, that the reaction follows the first-order law, and that the rate constants are practically independent of the carbinol concentration, roughly proportional to the acid concentration (c_A) when $c_A \ll 0.1M$, and decreased by increasing dioxan concentration (c_s) when $c_s \ll 80\%$ v/v. The same characteristics apply to the rearrangements of substituted



phenylpropenylcarbinols (I) where R = *o*-Me, *m*-Me, *p*-Me, *p*-F, *p*-Cl, *p*-Br, and *p*-MeO (Tables I, II, and III). The rate constants determined at 10° intervals between 30° and 60° accurately obey the Arrhenius equation.

It was previously observed (Part V, *loc. cit.*) that in the rearrangements of phenylvinyl- and phenylpropenyl-carbinols, the highest extinction coefficients reached in kinetic runs were lower by some 3—8% than those of the pure styryl isomers isolated from the reaction mixture, and it was suggested that the formation of stereoisomers or the establishment of equilibria at 92—97% rearrangement was among the more likely explanations of the discrepancies. With

TABLE I.

The effect of carbinol concentration.

First-order rate constants (10^4k , min.⁻¹) for the rearrangement of $C_6H_4R \cdot CH(OH) \cdot CH : CHMe$ in 60% (by vol.) aqueous dioxan at 30.0°. c_{ROH} = carbinol concentration (% w/v); c_A = hydrochloric acid concentration (mols./l.).

R =	H.	<i>p</i> -Me.	<i>p</i> -Cl.	<i>p</i> -MeO.
c_{ROH} .	$c_A = 0.01M$.	$c_A = 0.001M$.	$c_A = 0.01M$.	$c_A = 0.0001M$.
0.020	185	154	40.0	179
0.10	184	161	40.8	185
0.500	180	157	36.2	177

TABLE II.

The effect of acid concentration.

First-order rate constants for the rearrangement of $C_6H_4R \cdot CH(OH) \cdot CH : CHMe$ in 60% (by vol.) aqueous dioxan at 30.0°. c_A = hydrochloric acid concentration (mols./l.).

c_A .	10^4k (min. ⁻¹).	k/c_A .	c_A .	10^4k (min. ⁻¹).	k/c_A .
R = H.			R = <i>p</i> -F.		
0.002	34.7	1.74	0.002	29.9	1.50
0.01	184	1.84	0.01	146	1.46
0.1	1760	1.76	0.1	1520	1.52
R = <i>p</i> -Me.			R = <i>p</i> -Cl.		
0.0001	15.0	15.0	0.001	4.34	0.434
0.001	161	16.1	0.01	40.8	0.410
0.01	1540	15.4	0.1	432	0.432
R = <i>p</i> -MeO.			R = <i>p</i> -Br.		
0.0001	185	185	0.001	3.40	0.340
0.001	1890	189	0.01	35.2	0.352
0.002	3660	183	0.1	365	0.365

TABLE III.

Temperature and solvent effects.

First-order rate constants (10^4k , min.⁻¹) for the rearrangement of $C_6H_4R\cdot CH(OH)\cdot CH:CH\cdot CH_3$. Carbinol concentration 0.1% (w/v) throughout. c_A = Hydrochloric acid concentration (mols./l.). c_S = Dioxan concentration (% v/v).

<i>t.</i>	R = H.		<i>o</i> -Me.	<i>m</i> -Me.	<i>p</i> -Me.	<i>p</i> -F.	<i>p</i> -Cl.	<i>p</i> -Br.	<i>p</i> -MeO.
	c_S	$c_A = 0.01$	0.001	0.001	0.001	0.01	0.01	0.01	0.001
0.0°	40	25.5	5.17	2.96	22.9	19.2	4.60	3.59	177
	60	5.40	1.18	0.56	3.98	3.62	0.83	0.75	31.5
	40	716	139	80.9	406	580	135	127	647
30.0	60	184	35.9	21.7	161	146	40.8	35.2	185
	40	1,890	382	163	1,300	1550	436	364	1340
40.0	60	545	127	62.7	414	401	99.8	94.5	521
	40	4,500	840	408	3,060	3900	1070	865	2960
50.0	60	1,510	281	195	1,080	1200	302	272	1290
	40	11,700	2350	1380	10,200	9390	2770	2350	5930
60.0	60	3,650	910	571	2,900	2902	908	778	2780

the substituted phenylpropenylcarbinols, the ratios of "kinetic" to "preparative" end-values vary from 0.87 to 0.97, and are again temperature-independent within the experimental error ($\pm 2\%$) (see Experimental). Now, since the type and number of bonds broken and formed in the reaction is otherwise equal and opposite, the heat of reaction should be of the same order as the additional resonance energy of the conjugated (styryl) system, *i.e.* *ca.* 5 kg.-cals./mol. (Pauling and Sherman, *J. Chem. Physics*, 1933, 1, 606; Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Amer. Chem. Soc.*, 1936, 58, 146). This corresponds to an approximately two-fold change in the equilibrium constant for a temperature change from 30° to 60°, and to a change in conversion from 95 to 90%, *i.e.*, only just more than the limit of experimental error. The present data are thus indecisive. If equilibrium formation does take place, the over-all rate constants k actually represent the sum ($k_1 + k_{-1}$) of the rate constants of the forward and backward reactions $ROH \xrightleftharpoons[k_{-1}]{k_1} R'OH$, but the values of k_1 will only be 3–13% lower than those of k , and the values of the Arrhenius parameters will hardly be affected.

It was pointed out in Part II (*J.*, 1944, 443) that two types of solvent effect may be distinguished in considering the dependence of the rate constants, energies of activation, etc., of a catalysed reaction on the reaction medium. Those directly affecting the reactants were termed primary solvent effects, while those resulting in the first place in a change in the catalytic properties, such as the proton-donating properties, of the medium were termed secondary solvent effects. Evidence was adduced for both types of effects in oxotropic rearrangements.

It was shown that in the rearrangement of propenylethynylcarbinol in aqueous ethanol the decrease in rate constant with increasing concentration of organic solvent (c_S) could be expressed in the form $\log k = mD + n$ where D is the dielectric constant, and m and n are constants and $c_S \ll 80\%$. This was interpreted mainly as a secondary solvent effect, the decrease in dielectric constant resulting in a decrease in the proton-donating properties of the medium. It was further shown that on this basis a correction could be applied to the Arrhenius energy of activation to allow for the change in dielectric constant of the medium with temperature, the *isodielectric energy of activation* being given by $E_{[D]} = E_{Arr.} + RT_1T_2mb$ where T_1 , T_2 are the limits of the temperature range investigated, and b is a constant defined by $D = a + bt$, t being the temperature in °C. Whereas $E_{Arr.}$ varied considerably with solvent composition, $E_{[D]}$ was independent of it within the limits of experimental error. Similar observations were made (Part V, *loc. cit.*) with the rearrangement of phenylpropenylcarbinol in aqueous ethanol and aqueous dioxan, though $E_{[D]}$ in the latter case was *ca.* 4 kg.-cals./mol. lower than in the former, the difference being ascribed to a primary solvent effect, namely, increased solvation of the carbinol group by the dioxan.

The independence of $E_{[D]}$ of medium composition thus applies only as long as there is no appreciable change in solvating properties. Independent evidence for the occurrence of primary solvent effects was provided by the small but definite variations in the slope of the $\log k - c_A$, and $\log k - c_S$ plots with different substituted ethylenic and acetylenic carbinols (Parts III and IV, *J.*, 1946, 122, 128). These variations are presumably due to small differences in the extent of solvation of the carbinols by the solvent. If secondary solvent effects alone came into play, these slopes should be the same for different compounds undergoing the same reaction by

identical mechanisms. The data now obtained for substituted phenylpropenylcarbinols also indicate the occurrence of both primary and secondary solvent effects.

Specific * and relative rate constants, dielectric constant effects (expressed as m , the slope of the rate constant-dielectric constant plot), Arrhenius and isodielectric energies of activation, and reaction constants A (defined by $k/c_A = Ae^{-E_{(D)}/RT}$) † are given in Table IV; m varies somewhat for different carbinols, being lower when R = Me or MeO, and higher when R = Halogen, as compared with R = H (see I). But whereas values of $E_{Arr.}$ for any one carbinol are higher by 2–3 kg.-cals./mol. for 60% as compared with 40% aqueous dioxan, the corresponding values of $E_{(D)}$ differ by not more than 0.4 kg.-cal./mol. in seven cases, and by 0.9 kg.-cal./mol. when R = *p*-MeO. Within the range examined, the energy of activation is thus again independent, or nearly so, of the composition and hence of the dielectric constant of the medium, when allowance is made for the different temperature coefficients of the dielectric constants of different media.

TABLE IV.

Specific and relative rate constants, Arrhenius parameters, and isodielectric energies of activation for the rearrangement of $C_6H_4R \cdot CH(OH) \cdot CH:CHMe$ in aqueous dioxan (percentage of dioxan given in parentheses). r = Rate constant relative to phenylpropenylcarbinol (R = H).

R.	k/c_A for 0.001M-HCl, (60%), 30.0°.	m .	$E_{Arr.}$ (40%).	$E_{Arr.}$ (60%).	$E_{(D)}$ (40%).	$E_{(D)}$ (60%).	$\log A$ (60%).	r .	$10^5 K^*$
H	1.79	0.033	18.2	19.5	20.7	20.6	13.3	1	6.3
<i>o</i> -Me	3.59	0.032	18.2	19.5	20.7	20.6	13.6	2.0	12.3
<i>m</i> -Me	2.17	0.028	18.8	20.4	21.0	21.4	14.0	1.2	5.4
<i>p</i> -Me	16.1	0.033	18.1	19.6	20.7	20.7	14.4	9.0	4.2
<i>p</i> -F	1.50	0.036	17.7	19.4	20.5	20.7	13.4	0.84	7.2
<i>p</i> -Cl	0.434	0.036	19.6	20.3	22.2	21.6	13.4	0.24	10.6
<i>p</i> -Br	0.340	0.034	19.3	20.4	21.9	21.6	13.3	0.19	10.7
<i>p</i> -MeO	189	0.029	15.7	17.9	18.0	18.9	14.1	105	3.4

* Dissociation constants of $C_6H_4R \cdot CO_2H$ in water at 25° (Dippy, *Chem. Reviews*, 1939, **25**, 206).

Regarding the correlation of rate constants, energies of activation, and reaction constants with substituents, this may be summarised as follows: (i) The rate constants are increased by methyl substituents in the order $H < m\text{-Me} < o\text{-Me} < p\text{-Me}$, strongly increased by a *p*-MeO group, and decreased by *p*-halogen substituents in the order $H > p\text{-F} > p\text{-Cl} > p\text{-Br}$. (ii) Isodielectric energies of activation are constant at 20.6 (± 0.1) kg.-cals./mol. when R = H, *o*-Me, *p*-Me or *p*-F, slightly increased (by 0.3–1.5 kg.-cals./mol.) when R = *m*-Me, *p*-Cl or *p*-Br and decreased (by 2 kg.-cals./mol.) when R = *p*-MeO. (iii) Reaction constants (A) are constant at $13.4 (\pm 0.1) \text{ sec.}^{-1}$ when R = H or Halogen, and slightly increased by R = Me in the order $o\text{-Me} < m\text{-Me} < p\text{-Me}$, and by R = MeO.

In aqueous-ethanolic media, the first-order law is obeyed when R = H, *p*-Me, *p*-F, or *p*-MeO, but with the *p*-Cl and *p*-Br substituted carbinols the first-order rate constants fall as the reaction proceeds (see Experimental) in a manner reminiscent of that previously observed with phenylvinylcarbinol (Part V, *loc. cit.*) and shown there to be due to etherification occurring before, as well as simultaneously with, rearrangement.

EXPERIMENTAL.

Materials.—The preparation and properties of the phenylpropenylcarbinols and of their styryl isomers are described in the preceding paper. Dioxan was purified by the method of Hesse and Frahm (*Ber.*, 1938, **71**, 2629).

Kinetic Measurements.—The technique was the same as described in Part V (*loc. cit.*) and preceding papers. Initial and end values are given as $E_{1\%}^{100}$. [$= \log (I_0/I)/cl$, where I_0 = intensity of incident light, I = intensity of transmitted light, c = concentration in % w/v, l = cell length in cm.] (Table V).

Typical runs for each carbinol, in aqueous dioxan and ethanol media, are reproduced below. The first-order rate constants (k) are calculated by $k = (2.3/z) \log [(a - x_0)/(a - x)]$, where z = time in

* Since k is not directly proportional to c_A when $c_A > 0.1M$ in the present reaction, the specific rate constants (k/c_A) are not equal to k when $c_A = 1M$. Nevertheless for purposes of comparison of different series, specific rate constants are obviously preferable to k 's at an arbitrary acid concentration. The values given in Parts III and IV (J., 1946, **122**, 128, Tables III, cols. 1) for the rearrangement of acetylenyl- and vinyl-carbinols should be divided by 10^3 to convert them into k/c_A . Although these measurements refer to 60% aqueous ethanol media, the specific constants are then comparable to the present ones, since rate constants in 60% dioxan and ethanol are not appreciably different (see below and Part V, *loc. cit.*).

† In a catalysed reaction, A depends on the catalyst concentration, and the choice of the latter is arbitrary. For purposes of standardisation it appears preferable to base A on the specific rate constant k/c_A . The values given in Parts III and IV (*loc. cit.*, cols. 3) should accordingly be increased by 1.0.

TABLE V.

R.	$\lambda_{\max.}, \text{A.}$	Initial $E_{1\text{cm.}}^{1\%}$	Final $E_{1\text{cm.}}^{1\%}$		Ratio (col. 4/col. 5).
			"kinetic."	"preparative."	
H	2510	20	1260	1300	0.97
<i>o</i> -Me	2550	35	900	990	0.91
<i>m</i> -Me	2550	250	1030	1080	0.95
<i>p</i> -Me	2550	20	1300	1340	0.97
<i>p</i> -F	2480	90	1170	1260	0.93
<i>p</i> -Cl	2560	130	1100	1270	0.87
<i>p</i> -Br	2580	60	990	1120	0.87
<i>p</i> -MeO	2610	120	1300	1400	0.93

minutes, x_0 = absorption intensity at $x = 0$, x = absorption intensity at x mins., and a = final absorption intensity, intensities being expressed as $E_{1\text{cm.}}^{1\%}$ at the wave-length of the maximum chosen. In the rearrangement of *p*-chloro- and *p*-bromo-phenylpropenylcarbinol in 80% aqueous ethanol, the rate constants clearly fall as the reaction proceeds, and are extrapolated to zero time. In all other runs, the maximum deviation allowed in individual k 's was $\pm 5\%$. The maximum error in averaged k 's should not exceed $\pm 2\%$.

Rearrangements of C₆H₄R-CH(OH)-CH:CHMe in 60% (by vol.) aqueous dioxan, hydrochloric acid at 30.0°. [c_{ROH} = carbinol concentration (% w/v), c_A = acid concentration (mol./l.).]

(i) R = *o*-Me. $c_{\text{ROH}} = 0.1$, $c_A = 0.001$.

Time (mins.)	0	60	105	159	1440	
$E_{1\text{cm.}}^{1\%}$ (2550 A.)	35	205	305	410	900	
10^4k (min. ⁻¹)	—	36.5	35.6	35.7	—	(Mean) 35.9

(ii) R = *m*-Me. $c_{\text{ROH}} = 0.1$, $c_A = 0.001$.

Time (mins.)	0	90	150	210	1440	
$E_{1\text{cm.}}^{1\%}$ (2550 A.)	250	390	470	530	1030	
10^4k (min. ⁻¹)	—	22.0	22.0	21.1	—	(Mean) 21.7

(iii) R = *p*-Me. $c_{\text{ROH}} = 0.1$, $c_A = 0.001$.

Time (mins.)	0	30	50	70	90	600
$E_{1\text{cm.}}^{1\%}$ (2550 A.) ...	20	500	740	880	1000	1300
10^4k (min. ⁻¹)	—	157	165	159	162	—

(iv) R = *p*-F. $c_{\text{ROH}} = 0.1$, $c_A = 0.01$.

Time (mins.)	0	20	40	60	79	600
$E_{1\text{cm.}}^{1\%}$ (2480 A.) ...	90	370	570	710	830	1170
10^4k (min. ⁻¹)	—	150	147	142	145	—

(v) R = *p*-Cl. $c_{\text{ROH}} = 0.1$, $c_A = 0.01$.

Time (mins.)	0	60	120	180	240	1440
$E_{1\text{cm.}}^{1\%}$ (2560 A.) ...	130	340	500	630	750	1100
10^4k (min. ⁻¹)	—	40.6	40.8	40.3	41.4	—

(vi) R = *p*-Br. $c_{\text{ROH}} = 0.1$, $c_A = 0.01$.

Time (mins.)	0	58	98	142	201	1440
$E_{1\text{cm.}}^{1\%}$ (2580 A.) ...	60	190	275	360	470	990
10^4k (min. ⁻¹)	—	27.7	27.9	28.1	29.4	—

(vii) R = *p*-MeO. $c_{\text{ROH}} = 0.1$, $c_A = 0.001$.

Time (mins.)	0	2	3.5	5	6.5	30
$E_{1\text{cm.}}^{1\%}$ (2610 A.) ...	120	480	680	860	960	1300
10^4k (min. ⁻¹)	—	1820	1840	1970	1910	—

Rearrangements of C₆H₄R-CH(OH)-CH:CHMe in 80% (by vol.) aqueous ethanol, hydrochloric acid at 50.0°, except (v). [c_{ROH} and c_A as above.]

(i) R = *p*-Me. $c_{\text{ROH}} = 0.1$, $c_A = 0.002$.

Time (mins.)	0	4	8	12	16	360
$E_{1\text{cm.}}^{1\%}$ (2550 A.) ...	20	450	720	920	1040	1300
10^4k (min. ⁻¹)	—	1030	990	1010	1000	—

(ii) R = *p*-F. $c_{\text{ROH}} = 0.2$, $c_A = 0.02$.

Time (mins.)	0	1	2	3	4	5	120
$E_{1\text{cm.}}^{1\%}$ (2480 A.)	90	195	290	390	470	525	1200
10^4k (min. ⁻¹)	—	1020	1020	1080	1080	1030	—

(iii) R = *p*-Cl. $c_{\text{ROH}} = 0.1$, $c_A = 0.02$.

Time (mins.)	0	6	12	15	18	21	24	27	600
$E_{\text{act}}^{\ddagger}$ (2560 A.)	130	340	470	530	570	600	625	655	1100
$10^4 k$ (min. ⁻¹)	450 *	406	359	354	335	308	297	288	—

(iv) R = *p*-Br. $c_{\text{ROH}} = 0.2$, $c_A = 0.02$.

Time (mins.)	0	5	10	15	20	25	30	1440
$E_{\text{act}}^{\ddagger}$ (2580 A.)	80	220	350	450	525	590	630	990
$10^4 k$ (min. ⁻¹)	420 *	400	385	357	376	340	320	—

(v) R = *p*-MeO. $c_{\text{ROH}} = 0.2$, $c_A = 0.001$, $t = 30.0^\circ$

Time (mins.)	0	2	3	4	5	6	7	8	120
$E_{\text{act}}^{\ddagger}$ (2610 A.)	120	360	475	550	630	700	780	840	1300
$10^4 k$ (min. ⁻¹)	—	1140	1180	1130	1120	1130	1170	1180	— (Mean) 1150

* Extrapolated.

DISCUSSION.

With regard to the reaction mechanism, this is clearly the same throughout the series, since such characteristics as reaction order, dependence of the rate constants on carbinol, acid, and solvent concentrations, and the independence of the isodielectric energies of activation of solvent composition are the same in each case. The interpretation of substituent effects can therefore be based on the mechanism already outlined and discussed for the rearrangement of the parent compound, phenylpropenylcarbinol (Part V, *loc. cit.*)*

Table IV shows that the differences in the rate constants are due to variations in both the energy of activation and the non-exponential factor A of the Arrhenius equation. Except with the *p*-methoxy-compound, however, where $E_{\text{act}}^{\ddagger}$ is distinctly lower, while A is only slightly higher than for phenylpropenylcarbinol, these variations are only small and mostly entail differences of the same order of magnitude as the experimental error. In view of this fact, only tentative conclusions can be based on such regularities as can be discerned, and it will be preferable at this stage of the investigation to limit the discussion mainly to a consideration of the changes in the relative rate constants brought about by substituents.

Ingold's classification (*J.*, 1933, 1120; *Chem. Reviews*, 1934, 15, 233; see also Baker, "Tautomerism," Routledge, London, 1934; Remick, "Electronic Interpretation of Organic Chemistry," Wiley, New York, 1943) of substituent effects, which is now generally accepted, recognises two principal types: (i) the general inductive (I) and (ii) the tautomeric effect (T). The former depends on the capacity of the atom or group to attract or repel electrons and is mainly electrostatic in origin, I being negative with respect to hydrogen (electron-attraction) when the electronegativity of the substituent is greater than that of hydrogen, *i.e.*, when $x_{\text{R}} > x_{\text{H}}$, and positive (electron-repulsion) when $x_{\text{R}} < x_{\text{H}}$. The tautomeric effect, on the other hand, depends on the capacity of a substituent to share an additional electron pair, *i.e.*, on its capacity for covalency increase or decrease, and on its capacity to favour resonance forms of the type $\text{R}^+ = \text{A} - \text{B}^-$ or $\text{R}^- = \text{A} - \text{B}^+$ in systems classically represented by $\text{R} - \text{A} = \text{B}$. In the case of alkyl groups, the central atom carries no unshared electron-pair and their tautomeric effect must be ascribed to no-bond resonance in the C—H links, *i.e.*, contributions from $\text{H}^+ \text{C} = \text{C} - \text{C}^-$ to systems classically represented by $\text{H} - \text{C} - \text{C} = \text{C}$ (Baker, *J.*, 1939, 1150).

In the mechanism proposed for the present reaction, both steps require electron accession at the point of reaction and k should therefore be increased by $+I$ and $+T$ effects and retarded by $-I$ effects. This has been shown to be the case for alkyl and alkenyl substituents attached to the aliphatic part of the molecule (Parts III, IV, and V, *loc. cit.*). Similarly, the present data for the three tolylpropenylcarbinols are in accordance with expectations, the accelerating effect of the methyl substituent being least in the *m*-position ($+I$ effect only) and larger in the *o*- and *p*-positions ($+I$ and $+T$ effects). The fact that the increase in k due to an *o*-methyl group is less than that of a *p*-methyl group, although the $+I$ and probably the $+T$ effect should be greater for the former, provides yet another example of the well-known "ortho"-effect: the decrease in planarity due to the ortho-substituent inhibits the transmission of the T effect. However, even the "true" $+T$ effect is unlikely to be much larger in the *ortho*-

* The kinetic criterion given in Part V (*loc. cit.*, p. 403, lines 42 and 43) is erroneous. A valid criterion for the distinction between $\text{ROH} + \text{H}^+ \xrightarrow{\text{slow}} \text{ROH}_2^+ \xrightarrow{\text{fast}} \text{R}'\text{OH}_2^+$, and $\text{ROH} + \text{H}^+ \xrightarrow{\text{fast}} \text{ROH}_2^+ \xrightarrow{\text{slow}} \text{R}'\text{OH}_2^+$ was correctly stated in Part II (*J.*, 1944, 443) and depends on the linear relation between $\log k$ and the acidity function H_0 , rather than between $\log k$ and c_A .

than in the *para*-position, and the roughly tenfold increase in k due to a methyl substituent in the phenyl ring may be compared with its much larger effect when attached to the ethylenic double bond. Thus phenylpropenylcarbinol rearranges about 500 times faster than phenylvinylcarbinol under identical conditions (Part V, *loc. cit.*). This large difference is to be ascribed to the fact that the double-bond electron-pair moves towards the (electron-repelling) methyl substituent in one case, and away from it in the other, as well as possibly to a greater polarisability (allowing a readier transmission of the $+T$ effect) of the ethylenic double bond as compared with the aromatic system.

A *p*-MeO group also has the expected accelerating influence owing to its large $+T$ effect, but with the halogeno-carbinols the results are not entirely those to be anticipated from *a priori* considerations. The $-I$ effect should lead to reduction in the rate constant and to the sequence $F < Cl < Br < H$, since the electronegativity differences are in this order (F 4.0, Cl 3.0, Br 2.8, H 2.1; Pauling, "Nature of the Chemical Bond," Cornell, 1940). The $+T$ effect should counteract this diminution, but since it should be largest for Br and least for F and since it is smaller than the $-I$ effect, the actual sequence $F < Cl < Br < H$ should remain unaltered. The observed sequence is the reverse, *i.e.*, $Br < Cl < F < H$, which means that the $+T$ effects vary in the order $F > Cl > Br$ and not $F < Cl < Br$. This is unexpected, since the control of the nucleus over the valency electrons should decrease, and the capacity for covalency increase on ascending a group of the periodic table. Similar results indicating a reversed sequence of the tautomeric effects in the halogens have been observed in several other cases (Shopee, *J.*, 1933, 696; Baddeley, Bennett, *et al.*, *J.*, 1933, 261, 1112; 1935, 1827). It must be emphasised, however, that this interpretation is based on the tacit assumption that the rate constants as such, rather than the energies of activation and reaction constants separately, represent an adequate and additive measure of I and T effects.

It is noteworthy that the *p*-methoxyl substituent, which is the only one producing a large (*i.e.*, over 100-fold) change in rate, results in pronounced lowering of the energy of activation ($\Delta E_{[D]} = ca. 2$ kg.-cals.), just as the 500-fold increase in rate due to the β -methyl group in phenylpropenyl- as compared with phenylvinyl-carbinol is accompanied by a large decrease in $E_{[D]}$ of *ca.* 5 kg.-cals./mol. (Part V, *loc. cit.*). The data for the rearrangements of acetylenyl- and vinyl-carbinols (Parts III and IV, *loc. cit.*) also bear out that, on the whole, an increase in rate is accompanied by a decrease in the energy of activation,* and that large changes in rate depend on large changes in the energy of activation rather than $\log A$. This is readily interpreted as indicating that although the effect of substituents is exerted to a small extent by changes in the equilibrium constant of the preceding proton-transfer equilibrium, $ROH + H^+ \rightleftharpoons ROH_2^+$, their main effect lies in altering the energy requirements of the rate-determining isomerisation $ROH_2^+ \rightarrow R'OH_2^+$. An electron-repelling substituent increases the electron-density at the point of reaction, through increased contribution from resonance forms such as (IV), thereby partly neutralises the positive charge at the reaction centre, and decreases the energy of separation of the carbonium ion and the dipolar water molecule. The existence of extended conjugation in the resonance form of the oxonium ions of phenylpropenylcarbinols may also explain why substituents exerting $+T$ effects enhance the tendency for equilibrium formation: rearrangement to the styryl isomer results in increased conjugation, and hence, lowering in potential energy, only in the "ordinary" form (III), but not in the resonance form (IV).

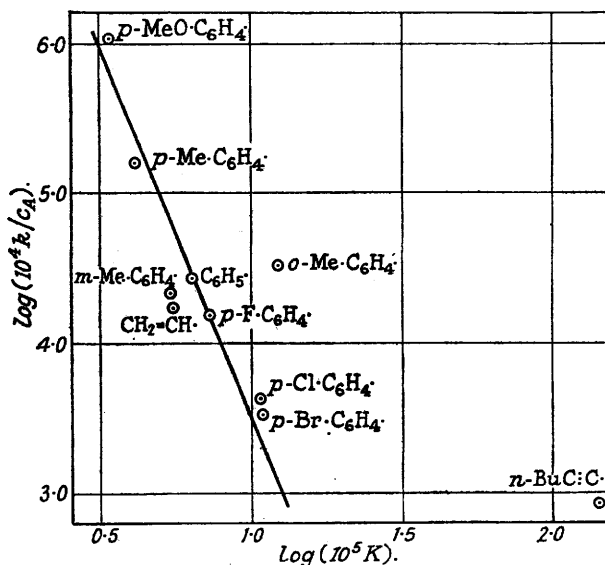


From a qualitative study of the rearrangement-acetylation of *p*-methylstyrylphenyl- and *p*-chlorostyrylphenyl-carbinols, and of *p*-tolyl- and *p*-chlorophenyl-vinylcarbinols, Burton and Ingold (*J.*, 1928, 904) and Burton (*J.*, 1928, 1650) concluded that the reaction is facilitated in the order $p\text{-Cl}\cdot\text{C}_6\text{H}_4 > p\text{-Me}\cdot\text{C}_6\text{H}_4 > \text{Ph}$, and that this was the expected order of reactivity. However, since the mechanism postulated by these authors, though different from the one adopted here, also requires electron-accession at the point of reaction, and since the overall electron-attracting effect of the halogens ($-I > +T$) is well known from aromatic substitution and other reactivity

* This conclusion was not drawn in the two papers referred to and only holds if the uncertain values of E (marked ~) for a few of the carbinols are disregarded. It now appears probable that the possibility, already envisaged in Part III, of equilibria being set up in these cases does apply, and that the E values derived from the temperature coefficients of the over-all rate constants do not represent real energies of activation in these cases.

data, this expectation is clearly incorrect, and the expected sequence should be $\text{Me}\cdot\text{C}_6\text{H}_4 > \text{Ph} > \text{Cl}\cdot\text{C}_6\text{H}_4$, as confirmed by the present data. Moreover, inspection of the experimental results of Burton and Ingold also appears to indicate this sequence of reactivity and not the one deduced by their authors. Thus phenylvinyl- and *m*- and *p*-tolylvinyl-carbinols are stated to be converted completely into the corresponding styrylcarbinyl acetates by treatment with boiling acetic anhydride for six hours, while identical treatment of *p*-chlorophenylcarbinol is stated to lead to a mixture containing only *ca.* 70% of the rearranged acetate. It may well be that the probable equilibrium formation in the rearrangements of *p*-chloro- and *p*-bromo-phenylpropenylcarbinols (see above) is enhanced in the less reactive phenylvinyl homologues.

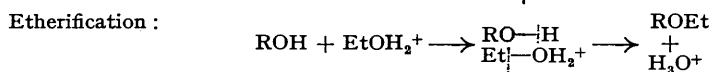
The electron-attracting effect of the chloro- and bromo-substituents is also well illustrated by the fact that they appear to facilitate ether formation in ethanolic acid solution sufficiently for it to occur before rearrangement; with a fluoro-substituent the effect is not sufficiently great to lead to a falling first-order constant. Unlike the rearrangement reaction, which depends on the fission of the carbon-oxygen bond and electron accession at the point of reaction,



k = Rate constant of $\text{R}\cdot\text{CH}(\text{OH})\cdot\text{CH}:\text{CHMe}$.

K = Dissociation constant of $\text{R}\cdot\text{CO}_2\text{H}$ (see Table IV).

ether formation probably depends on the bimolecular fission of the hydrogen-oxygen bond, *i.e.*, on electron recession at the point of reaction.



The ease of etherification of phenylvinylcarbinol (Part V, *loc. cit.*) is similarly to be ascribed to the strong electron-attraction ($-I$ effect) of the free vinyl group; in phenylpropenylcarbinol this is counteracted by the electron-repelling ($+I$, $+T$) effects of the β -methyl group and no etherification occurs prior to rearrangement.

Some correlation might again be expected between the specific rate constants of the carbinols and the dissociation constants (K) of the corresponding benzoic acids (cf. Parts IV and V, *loc. cit.*). The plot of $\log k/c_A$ against $\log K$ does in fact approximate to a straight line (Table IV; Fig.), except when $\text{R} = o\text{-Me}$. This is another instance of the "ortho"-effect (cf. Hammett, "Physical Organic Chemistry," McGraw Hill, New York, 1941). The point for vinylpropenylcarbinol (Part IV, *loc. cit.*) also falls on the straight line, but the points for ethynylpropenyl- and hexynylpropenyl-carbinols do not, and thus both the acetylenic groups and not the ethynyl group only, as previously thought, behave differently in this respect from the other groups so far examined.

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