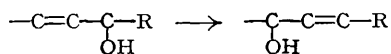


79. The Kinetics of Anionotropic Rearrangement. Part V. Oxotropic Formation of the Styrene System.

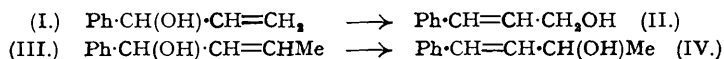
By ERNEST A. BRAUDE, E. R. H. JONES, and E. S. STERN.

In continuation of previous studies (Parts I, III, and IV, Braude and Jones, *J.*, 1944, 436; this vol., pp. 122, 128; Part II, Braude, *J.*, 1944, 443) a detailed kinetic investigation has been made of the acid-catalysed rearrangements of phenylvinyl- (I) and phenylpropenyl-carbinols (III) to cinnamyl alcohol and styrylmethylcarbinol, respectively. Both isomerisations proceed smoothly in aqueous alcohol and dioxan, hydrochloric or acetic acid being used as catalyst. In aqueous alcoholic media considerable proportions of the ethyl ethers of the rearranged carbinols are formed and reaction-product analysis shows that ether formation proceeds simultaneously with [and with (I) also before] rearrangement. The first-order rate law is accurately obeyed, except with (I) in alcoholic media, where the rate constants decrease as the reaction proceeds. The variations of the rate constants with medium composition and acid and carbinol concentrations have been studied in detail and closely resemble those previously observed in the oxotropic rearrangement of propenylethynylcarbinol (Parts I and II, *loc. cit.*). Arrhenius energies of activation for the temperature range 0–60° have been determined, and isodielectric energies of activation (Part II, *loc. cit.*) deduced; the latter are independent of solvent composition within the limits of experimental error. These results and the reaction mechanism are discussed with reference to earlier work in this series and that of other authors, and a comparison is made of the electronic properties of the phenyl, vinyl, and acetylenyl groups.

In Parts I–IV (*loc. cit.*), rearrangements of the type



where R = CH=CH₂ or C≡CR' were studied, the selective high-intensity light absorption in the near ultra-violet exhibited by the conjugated butadiene and vinylacetylene systems formed providing a ready means of measuring reaction velocities. The present investigation deals with the corresponding rearrangements leading to the styrene system (R = Ph), the isomerisations of phenylvinylcarbinol to cinnamyl alcohol, and of phenylpropenylcarbinol to styrylmethylcarbinol, being chosen as the two simplest examples:



The marked differences in the ultra-violet light absorption of the phenyl and the styryl systems (Figs. 1 and 2) again permitted the application of the convenient spectro-kinetic method.

Phenylvinylcarbinol has been known for many years (Klages and Klenk, *Ber.*, 1906, 39, 2552; Kohler, *Amer. Chem. J.*, 1908, 38, 511), and its isomerisation to cinnamyl alcohol by the action of dilute acids was first reported by Valeur and Luce (*Bull. Soc. chim.*, 1920, 27, 611). These authors also made the important observation that cyclohexylvinylcarbinol resisted all isomerisation attempts, indicating clearly that the formation of the conjugated (styrene) system in the former case was an essential feature of the reaction. Burton and Ingold (*J.*, 1928, 904) were unable to repeat the isomerisation of phenylvinylcarbinol, using both aqueous sulphuric and hydrochloric acids, and aqueous-alcoholic hydrochloric acid. It was shown by a number of other workers, however, that derivatives of cinnamyl alcohol could be obtained by replacement reactions of

phenylvinylcarbinol, under acidic reaction conditions. Meisenheimer and Schmidt (*Annalen*, 1929, **475**, 157) reported that the reaction of phenylvinylcarbinyl *p*-nitrobenzoate with hydrogen chloride gives both cinnamyl chloride and *p*-nitrobenzoate. Similarly, the treatment of phenylvinylcarbinol with phosphorus tribromide yields cinnamyl bromide (Moureu and Gallagher, *Bull. Soc. chim.*, 1921, **29**, 1009; Delaby, *Compt. rend.*, 1932, **194**, 1248) and treatment with phthalic anhydride yields some cinnamyl hydrogen phthalate (Kamai, *Chem. Zentr.*, 1932, I, 3047) unless the reaction is carried out in the presence of pyridine (Duveen, *Compt. rend.*, 1938, **206**, 1185). It is now shown that Burton and Ingold's findings (*loc. cit.*) are incorrect and that phenylvinylcarbinol itself rearranges in alcoholic acid media to give a mixture of cinnamyl alcohol and its ethyl ether. Rearrangement in aqueous dioxan results in almost quantitative conversion into the alcohol.

Phenylpropenylcarbinol was first prepared by Burton (*J.*, 1929, 455), who made a qualitative study of its isomerisation to styrylmethylcarbinyl acetate on boiling with acetic anhydride. Kenyon, Partridge, and Phillips (*J.*, 1937, 207) showed that optically active phenylpropenylcarbinol is isomerised to styrylmethylcarbinol by 0.5% acetic acid at room temperature in 40 hours with almost complete racemisation, and from variations in optical rotation they showed that the hydrogen phthalate of (–)phenylpropenylcarbinol isomerises

FIG. 1.

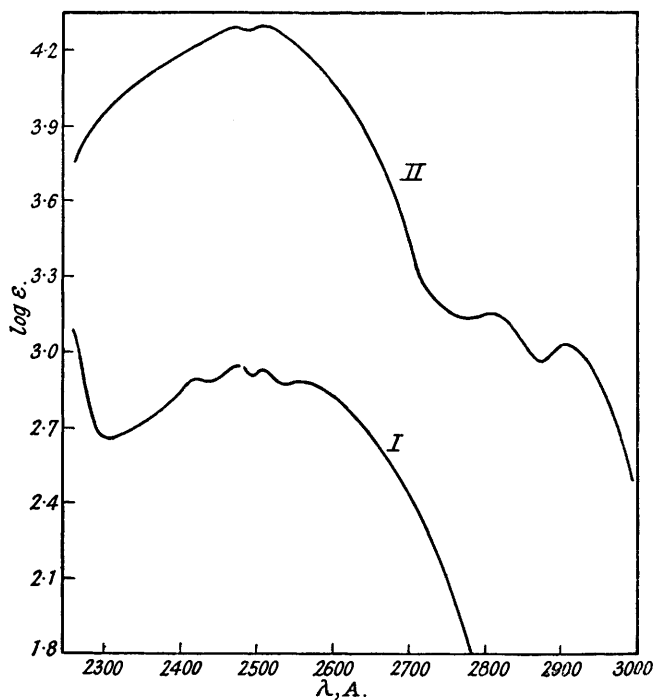
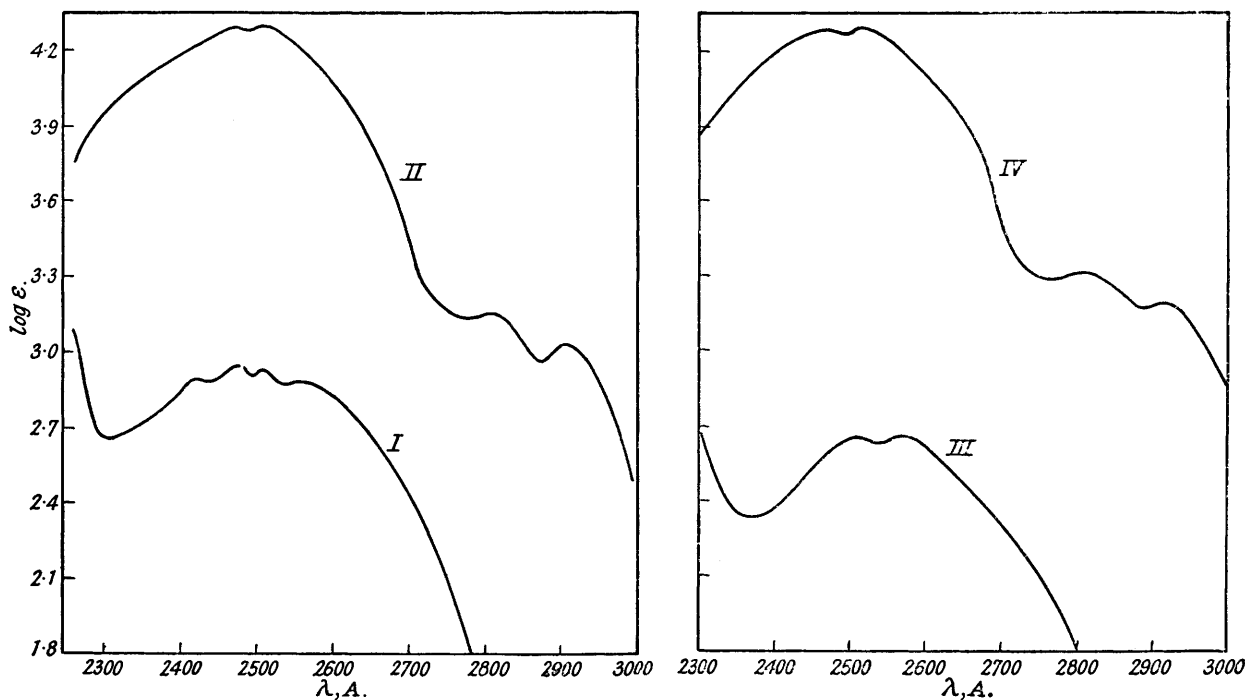


FIG. 2.



in benzene solution according to first-order kinetics with a rate constant $k = 0.575 \times 10^{-4}$ (min.⁻¹) at 37° and an Arrhenius energy of activation of 28.8 kg.-cals./mol. with partial retention, but inversion, of optical activity. Salts of the acid ester, on the other hand, do not undergo self-rearrangement, indicating that the presence of hydrogen ions is essential for the reaction to occur. Similarly, neutral esters are quite stable, in the absence of acids, but (+)phenylpropenylcarbinyl acetate is isomerised in 17 hours by acetic acid at room temperature with considerable racemisation.

Data for the rearrangement of the two carbinols in aqueous alcohol and dioxan over a wide range of conditions are collected in Tables I—VI. The following symbols are used throughout: t = temperature (°C.); c_{EtOH} and c_{diox} = concentration of organic solvent (% by vol.); c_{A} = acid concentration (mols./l.); c_{ROH} = carbinol concentration (% w/v); k = first-order constant; D = dielectric constant of solvent, taken or calculated from the data of Wyman (*J. Amer. Chem. Soc.*, 1931, **53**, 3292), Akerlöf and Short (*ibid.*, 1936, **58**, 1241) and Herz and Lorentz (*Z. physikal. Chem.*, 1929, **140**, A, 406); m is defined by $\log k = mD + n$ (Part II, *loc. cit.*), where m and n are constants; E_{Arr} = Arrhenius energy of activation; b is defined by $D = a - bt$; $E_{\text{(D)}}$ = isodielectric energy of activation calculated by $E_{\text{(D)}} = E_{\text{Arr}} + \Delta E_{\text{D}}$, where $\Delta E_{\text{D}} = 2.3RT_1T_2mb$ (Part II, *loc. cit.*). The first-order rate law is accurately obeyed, except with phenylvinylcarbinol in aqueous alcohol where the values of k decrease as the reaction proceeds (see Experimental). In this latter case, the rate constants given are extrapolated to zero time.

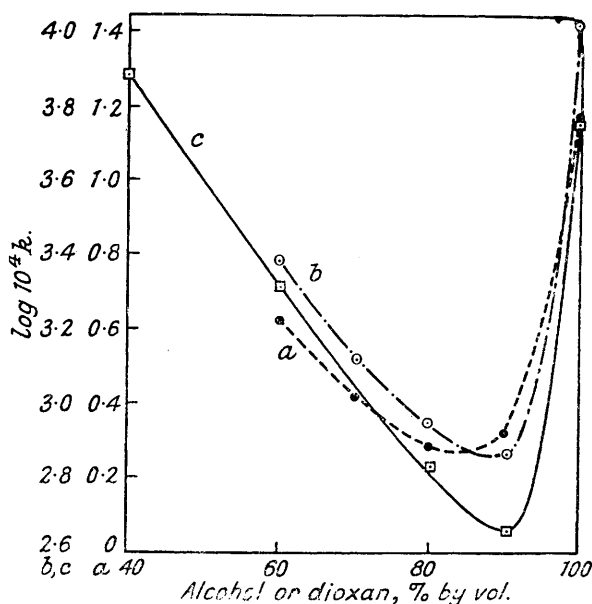
The rate constants are independent of c_{ROH} within the limits of experimental error (Table I), except with phenylvinylcarbinol in alcoholic media where they decrease slightly with increasing carbinol concentration, an effect possibly connected with the partial etherification referred to below.

TABLE I.
The effect of carbinol concentration ($t = 30.0^\circ$ throughout).

Carbinol.	c_A	10^4k , min. ⁻¹ .		c_A	10^4k , min. ⁻¹ .	
		c_{ROH} In 80% EtOH.			c_{ROH} In 60% dioxan.	
(I)	0.1M-HCl	0.028	2.06	0.1M-HCl	0.02	3.78
		0.14	1.95		0.1	3.80
		0.7	1.84		0.5	3.81
(II)	0.02M-HCl	0.028	158	0.01M-HCl	0.02	185
		0.14	155		0.1	184
		0.7	159		0.5	180

Increasing the proportions of both alcohol and dioxan first results in a decrease in k , the relation $\log k = mD + n$ being obeyed; when the concentration of organic solvent is increased beyond 90%, k again increases sharply (Table II and Fig. 3). Also, k increases with increasing acid concentration, the ratio k/c_A remaining nearly constant up to $c_A =$ about 0.1 and then rapidly increasing with c_A (Table III).

FIG. 3.



- (a) Rearrangement of phenylvinylcarbinol in aqueous alcohol.
 (b) Rearrangement of phenylpropenylcarbinol in aqueous alcohol.
 (c) Rearrangement of phenylpropenylcarbinol in aqueous dioxan.
 Acid concentration = 0.1M-HCl, temperature 30.0°, throughout.

TABLE II.
The effect of solvent composition ($t = 30.0^\circ$, $c_A = 0.1M-HCl$ throughout).

(I).				(II).				(III).			
c_{EtOH}	10^4k , min. ⁻¹ .	c_{EtOH}	10^4k , min. ⁻¹ .	c_{EtOH}	10^4k , min. ⁻¹ .	c_{EtOH}	10^4k , min. ⁻¹ .	$c_{diox.}$	10^4k , min. ⁻¹ .	$c_{diox.}$	10^4k , min. ⁻¹ .
60	4.26	90	2.04	60	2430	85	817	40	7530	90	620
70	2.71	100	14.2	70	1350	90	738	60	2110	100	5740
80	1.95			80	886	100	10,600	80	688		

TABLE III.
The effect of hydrochloric acid concentration ($t = 30.0^\circ$ throughout).

(I); $c_{EtOH} = 80$, $c_{ROH} = 0.14$.			(II); $c_{EtOH} = 80$, $c_{ROH} = 0.14$.			(II); $c_{diox.} = 60$, $c_{ROH} = 0.1$.		
c_A	10^4k , min. ⁻¹ .	k/c_A	c_A	10^4k , min. ⁻¹ .	k/c_A	c_A	10^4k , min. ⁻¹ .	k/c_A
0.01	0.138	13.8	0.002	14.8	7,400	0.002	34.7	17,400
0.02	0.266	13.3	0.01	84.9	8,500	0.01	184	18,400
0.1	1.95	19.5	0.02	155	7,800	0.1	2,110	21,100
0.4	7.45	18.6	0.1	886	8,900	0.4	9,900	24,800
1	70	70	0.4	3,950	9,900	1	28,500	28,500
2	448	224	1	24,000	24,000			

The relative catalytic effect of acetic and hydrochloric acids is practically the same for phenylpropenyl- as for propenylethynyl-carbinol; for phenylvinylcarbinol it is somewhat lower (Table IV).

TABLE IV.

The effect of acid catalyst ($t = 60.0^\circ$, $c_{\text{EtOH}} = 80$).

Carbinol.	10^4k , min. ⁻¹ .		$k_{0.01\text{M-HCl}}/k_{1\text{M-AcOH}}$.
	$c_A = 0.01\text{M-HCl}$.	$c_A = 1\text{M-HOAc}$.	
Phenylvinyl-	4.54	0.135	33.6
Phenylpropenyl-	2030	43.1	47.1
Propenylethynyl-	1.0 *	0.020 *	50.0

* Part I (*loc. cit.*).

TABLE V.

Temperature and Solvent Effects.

t .	c_s *	D .	c_A .	10^4k , min. ⁻¹ .	m .	t .	c_s *	D .	c_A .	10^4k , min. ⁻¹ .	m .
Rearrangement of phenylvinylcarbinol in aqueous alcohol.											
30.0°	60	46.3	0.1M-HCl	4.26	0.036	50.0°	60	41.4	0.1M-HCl	50.0	0.039
	70	40.5	0.1 "	2.71			70	36.1	0.1 "	30.1	
	80	34.6	0.1 "	1.95			80	31.0	0.1 "	19.9	
	80	34.6	0.01 "	0.138			80	31.0	0.01 "	1.58	
40.0	60	43.9	0.1 "	13.4	0.043	60.0	60	39.6	0.1 "	171	0.040
	70	38.3	0.1 "	6.9			70	34.3	0.1 "	95.6	
	80	32.6	0.1 "	4.4			80	29.3	0.1 "	62.8	
	80	32.6	0.01 "	0.43			80	29.3	0.01 "	4.54	
Rearrangement of phenylvinylcarbinol in aqueous dioxan.											
30.0	40	40.9	0.1M-HCl	14.3	0.033	50.0	40	36.8	0.1M-HCl	153	0.033
	60	23.6	0.1 "	3.80			60	21.5	0.1 "	48.7	
	60	23.6	0.02 "	0.69			60.0	40	35.2	0.1 "	
40.0	40	38.8	0.1 "	47.5	0.031	60	60	21.0	0.1 "	180	0.032
	60	22.6	0.1 "	15.0							
Rearrangement of phenylpropenylcarbinol in aqueous alcohol.											
0.0	60	55.3	0.01M-HCl	6.85	0.039	40.0	60	43.9	0.01M-HCl	622	0.037
	70	48.5	0.01 "	4.14			70	38.3	0.01 "	377	
	80	41.6	0.01 "	1.90			80	32.6	0.01 "	237	
	80	41.6	0.002 "	0.369			80	32.6	0.002 "	46.0	
30.0	60	46.3	0.01 "	221	0.034	50.0	60	41.4	0.01 "	1840	0.039
	70	40.5	0.01 "	145			70	36.1	0.01 "	1190	
	80	34.6	0.01 "	84.9			80	31.0	0.01 "	745	
	80	34.6	0.002 "	14.8			80	31.0	0.002 "	134	
Rearrangement of phenylpropenylcarbinol in aqueous dioxan.											
0.0	40	47.2	0.01M-HCl	25.5	0.033	50.0	40	36.8	0.01M-HCl	4,500	0.031
	60	26.8	"	5.40			60	21.5	"	1,510	
30.0	40	40.9	"	716	0.032	60.0	40	35.2	"	11,700	0.036
	60	23.6	"	184			60	21.0	"	3,650	
40.0	40	38.8	"	1890	0.033						
	60	22.6	"	545							

* c_s refers to the solvent specified for the particular rearrangement.

Measurements at different temperatures (Table V) show that the solvent effects (m) remain fairly constant between 0° and 60° . The rate constants at different temperatures accurately obey the Arrhenius equation (Fig. 4). Arrhenius and isodielectric energies of activation are given in Table VI.

Isolation of the reaction products yields mixtures of the rearranged carbinols and their ethyl ethers from alcoholic media, and solely the rearranged carbinols from dioxan media. Estimations of the proportions of carbinol and (deduced by difference) ethyl ether produced in the former case were carried out by measuring the volume of methane evolved with an ethereal solution of methylmagnesium iodide, analysis by means of refractive index and extinction coefficient determinations proving unsuitable (see Experimental). The product of the rearrangement of phenylpropenylcarbinol in 60% alcohol at 50° contains 47% of the ethyl ether of styrylmethylcarbinol; in 80% alcohol the product contains 60% of the ether. If the reaction in 60% alcohol is stopped at half-rearrangement, the product contains 23% of ether, *i.e.*, half as much as after complete

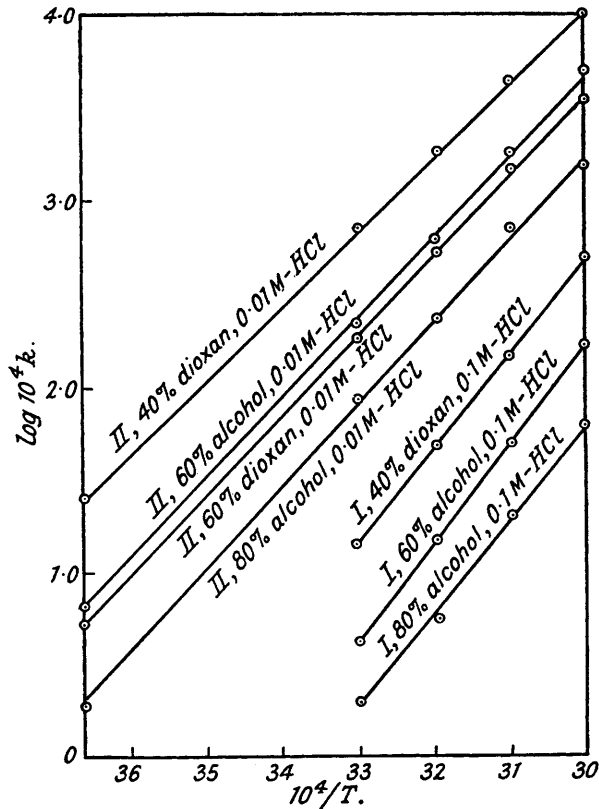
TABLE VI.

Arrhenius and isodielectric energies of activation.

Conditions.	$E_{\text{Arr.}}$	$m_{\text{Av.}}$	$b.$	$\Delta E_{\text{D.}}$	$E_{(\text{D})}$
Phenylvinylcarbinol.					
0.1M-HCl, 60% EtOH	24.3	0.038	0.286	5.0	29.3
" 70 "	23.3		4.5	27.8	
" 80 "	23.0		4.0	27.0	
0.01M-HCl, 80 "	23.5		0.225	4.0	27.5
0.1M-HCl, 40% Dioxan	23.5	0.032	0.187	2.8	26.3
" 60 "	25.7		0.084	1.2	26.9
Phenylpropenylcarbinol.					
0.01M-HCl, 60% EtOH	19.6	0.037	0.286	4.4	24.0
" 70 "	19.7		3.9	23.6	
" 80 "	20.5		3.4	23.9	
0.002M-HCl, 80 "	20.7		0.225	3.4	24.1
0.01M-HCl, 40% Dioxan	18.2	0.033	0.187	2.5	20.7
" 60 "	19.5		0.084	1.1	20.6

rearrangement. The half-times, and therefore the rates of rearrangement and etherification, thus appear to be the same. With phenylvinylcarbinol rearrangement in 60% and 80% alcohol results in products containing 52% and 64% of cinnamyl ethyl ether respectively. Half-rearrangement in 60% alcohol results in 48% etherification, *i.e.*, almost as much as complete rearrangement. Cinnamyl alcohol under the same conditions undergoes no etherification, nor does phenylvinylcarbinol in the absence of acid. These results clearly indicate that in acid solution phenylvinylcarbinol is etherified before as well as during rearrangement. The fall in first-order rate constants observed in this case is obviously due to the fact that the unrearranged ether is formed at a rate comparable to that of the rearrangement of the carbinol, but is itself less easily rearranged than the carbinol.

FIG. 4.



EXPERIMENTAL.

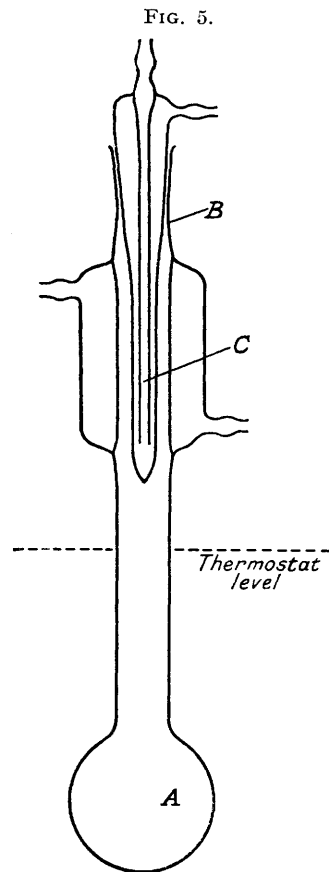
Materials.—*Phenylvinylcarbinol* (I). A solution of acraldehyde (28 g.) in ether (60 c.c.) was added to phenylmagnesium bromide (from Mg, 12 g.) in ether (300 c.c.) during one hour at 0°, the solution was stirred for 2 hours and then treated with a cold saturated solution of ammonium chloride. After isolation of the product in the usual manner, phenylvinylcarbinol (40 g.) was obtained with b. p. 53–54°/0.15 mm., $n_D^{14.5}$ 1.5464 (Burton and Ingold, *J.*, 1928, 904, give b. p. 106–107°/15 mm.; Delaby, *Compt. rend.*, 1932, 194, 1248, gives b. p. 77°/2 mm., n_D^{16} 1.5456). *Light absorption in alcohol* (see Fig. 1; ϵ = molecular extinction coefficient): Maxima, 2480 and 2510 Å.; ϵ = 830 and 820, respectively. Inflexions, 2420 and 2565 Å.; ϵ = 760 and 750, respectively. (Hillmer and Schorning, *Z. physikal. Chem.*, 1934, 168, A, 81, give maximum at 2470 Å.; ϵ = 1320, this higher intensity value probably indicating the presence of some rearranged material.)

Cinnamyl alcohol (II). This had b. p. 139°/16 mm., n_D^{20} 1.5805, m. p. 33° (Bruhl, *Annalen*, 1886, 235, 1, gives n_D^{20} 1.5819 for the *trans*-, and Gredy, *Bull. Soc. chim.*, 1936, 3, 1093, gives n_D^{20} 1.5710 for the liquid *cis*-isomer). *Light absorption in alcohol* (Fig. 1): Maxima, 2480, 2510, 2810, and 2910 Å.; ϵ = 19,000, 19,500, 1350, and 1050, respectively. (Hillmer and Schorning, *loc. cit.*, give maxima, 2493, 2830, and 2926 Å.; ϵ = 17,000, 1175, and 890, respectively.)

Phenylpropenylcarbinol (III). Freshly distilled crotonaldehyde (17.5 g.) in ether (70 c.c.) was added to phenylmagnesium bromide (from Mg, 12 g.) in ether (300 c.c.) during one hour at 0°, the solution was stirred for one hour and then treated with saturated ammonium chloride solution. Isolation of the product with ether, drying with anhydrous potassium carbonate, and distillation yielded phenylpropenylcarbinol (35 g.), b. p. 76–77°/0.4 mm., n_D^{18} 1.5389. *Active hydrogen* (Zerewitinoff), 1.0. [Values of n_D given in the literature vary (see p. 403): Burton, *J.*, 1929, 455, gives b. p. 121.5–123.5°/14 mm.; Ingold and Wilson, *J.*, 1933, 1493, give b. p. 88–90°/1 mm., n_D^{20} 1.5412; Kenyon, Partridge, and Phillips, *J.*, 1937, 207, give b. p. 126°/20 mm., n_D^{20} 1.5525.] *Light absorption in alcohol* (Fig. 2): Maxima, 2510 and 2580 Å.; ϵ = 450 and 450.

Styrylmethylcarbinol (IV). Freshly distilled cinnamaldehyde (122 g.) in ether (200 c.c.) was added to methylmagnesium bromide (from Mg, 24 g.) in ether (200 c.c.) during 2 hours at 0°, the solution was stirred for 15 hours, and then treated with cold saturated ammonium chloride solution. Isolation in the usual manner gave phenylbutadiene (about 15 g.) and styrylmethylcarbinol (75 g.), b. p. 104°/1 mm., n_D^{21} 1.5665, which partly solidified on standing at 0° and after two crystallisations from pentane had m. p. 30–32° [Muskat and Herrman, *J. Amer. Chem. Soc.*, 1931, 53, 252, give b. p. 117°/4 mm., n_D^{31} 1.5536 (*cis* ?) and n_D^{31} 1.5550 (*trans* ?); Wright, *J. Org. Chem.*, 1936, 1, 457, gives b. p. 109°/3.5 mm., m. p. 31°, n_D^{31} 1.5700; Kenyon, Partridge, and Phillips, *J.*, 1936, 85, give b. p. 129–131°/11 mm., n_D^{30} 1.5741, m. p. 33°]. *Light absorption in alcohol* (Fig. 2): Maxima, 2480, 2510, 2810, and 2920 Å.; ϵ = 19,000, 19,500, 2,000, and 1,550, respectively.

Kinetic Measurements.—These were carried out by the method already described (Parts I and III, *loc. cit.*). An improved type of reaction vessel (Fig. 5) was employed, allowing deep immersion of the bulb A in the bath and avoiding ground-glass joints in the vicinity of the solution. To start a run, a short tube containing the carbinol dissolved in 0.2 c.c. of alcohol or dioxan is added to the reaction medium (made up with a corresponding deficiency of 0.2 c.c. of the organic solvent) contained in A, the cold finger C is replaced, and the flask vigorously shaken. Samples are taken by means of a long, narrow-stem, 1-c.c. pipette introduced through the neck B after temporary removal of C. In very fast runs, the carbinol was injected into the reaction medium by means of a syringe, but the pipette with which successive samples were taken was merely drained after each withdrawal. First-order rate constants (k) were averaged, runs where deviations exceeded $\pm 5\%$ being rejected. The estimated maximum error in averaged values of k is $\pm 2\%$. In the rearrangement of phenylvinylcarbinol in alcoholic media, there is a marked decrease of the first-order rate constant as the reaction proceeds, owing to some etherification of the carbinol before rearrangement (see below). Measurements in the latter case were generally made during the first half of the reaction, the rate constant being extrapolated to zero time. Five typical runs are reproduced below:



Time, mins.	$E_{1\text{cm.}}^{1\%}$ at 2510 Å.	10^4k , min. ⁻¹ .	Time, mins.	$E_{1\text{cm.}}^{1\%}$ at 2510 Å.	10^4k , min. ⁻¹ .	Time, mins.	$E_{1\text{cm.}}^{1\%}$ at 2510 Å.	10^4k , min. ⁻¹ .
Rearrangement of phenylvinylcarbinol in 0.1M-HCl, 80% (by vol.) alcohol, 50.0°. Carbinol concentration 0.14% w/v.								
0	60	20.5 *	240	470	17.1	360	560	14.6
120	300	18.6	270	505	16.8	390	580	14.2
152	345	17.7	300	520	15.7	420	605	13.9
180	390	17.6	331	540	15.0	7500	1300	—

* Extrapolated.

Time, mins.	$E_{1\text{cm.}}^{1\%}$ at 2510 Å.	10^4k , min. ⁻¹ .	Time, mins.	$E_{1\text{cm.}}^{1\%}$ at 2510 Å.	10^4k , min. ⁻¹ .	Time, mins.	$E_{1\text{cm.}}^{1\%}$ at 2510 Å.	10^4k , min. ⁻¹ .
Rearrangement of phenylvinylcarbinol in 0.1M-HCl, 80% (by vol.) dioxan, 50.0°. Carbinol concentration 0.1% w/v.								
0	60	—	254	730	31.3	391	960	32.9
120	460	32.0	282	780	30.6	436	1000	32.4
150	540	32.3	315	840	31.3	2400	1300	—
182	620	32.7	360	900	31.3			(Mean) 31.9

Rearrangement of phenylpropenylcarbinol in 0.01M-HCl 80% (by vol.) alcohol, 40.0°. Carbinol concentration 0.14% w/v.

0	60	—	24	575	250	39	780	255
12	360	254	27	625	253	42	795	246
15	410	245	33	695	245	275	1200	—
18	475	251	36	735	249			(Mean) 250

Rearrangement of phenylpropenylcarbinol in 0.01M-HCl, 80% (by vol.) dioxan, 40.0°. Carbinol concentration 0.1% w/v.

0	60	—	24	540	190	44	800	199
9	305	208	29	615	193	49	845	198
14	395	201	34	675	192	54	925	215
19	500	212	39	750	200	350	1260	—
								(Mean) 201

Rearrangement of phenylpropenylcarbinol in 1M-HCl, 80% (by vol.) alcohol, 30.0°. Carbinol concentration 0.14% w/v.

0	60	—	0.50	845	23,200	10	1200	—
0.33	685	23,900	0.67	970	24,100			(Mean) 23,900

It will be noticed that the "kinetic" end values are somewhat lower (3—8%) than the absorption intensities of the pure rearranged carbinols prepared by an alternative route, or isolated from the reaction mixture (see below). For instance, the average end value obtained with phenylvinylcarbinol is $E_{1\text{cm}}^{1\%}$ (max.) = 1300, whereas pure cinnamyl alcohol has $E_{1\text{cm}}^{1\%}$ (max.) = 1400. With phenylpropenylcarbinol, the average end values are 1200 in aqueous alcohol and 1260 in aqueous dioxan, whereas pure styrylmethylcarbinol has $E_{1\text{cm}}^{1\%}$ 1300. Individual end values obtained in different runs in one type of medium agreed within ± 20 (*i.e.*, $\pm 2\%$) and the differences between "kinetic" and "preparative" end values are thus well outside the experimental error. Similar discrepancies have previously been noted in the oxotropic formation of vinylacetylenylcarbinols (Part III, *loc. cit.*). These discrepancies cannot be due to calibration or sampling errors; *e.g.*, pure cinnamyl alcohol ($E_{1\text{cm}}^{1\%} = 1400$), dissolved in 50 c.c. of solvent and sampled as in a kinetic run, gave identical values of $E_{1\text{cm}}^{1\%} = 1400, 1420, \text{ and } 1400$. Nor, in the case of rearrangements in alcoholic media, can the differences be due to the partial etherification of the carbinol during rearrangement, since the carbinols and their ethyl ethers have almost identical molecular extinction coefficients (see below). Amongst the more probable remaining explanations, are the following: (i) The reactions do not go quite to completion, but reach an equilibrium at *ca.* 95% rearrangement. (ii) In solution, the *cis*-isomers of the rearranged carbinols are predominantly formed and have slightly lower extinction coefficients than the *trans*-isomers. The latter explanation appears to be supported by the variable refractivity data, and the existence of the *cis*-isomer has also been demonstrated by Raman-spectra evidence (Gredy, *loc. cit.*), but no definite conclusion can at present be reached.

TABLE VII.

Composition of reaction product, %.

Carbinol.	Conditions.*			Composition of reaction product, %.			
	Catalyst.	Time.	Rearrange-ment.	Before distillation.		After distillation.	
				Carbinol.	Ether (by diff.).	Carbinol.	Ether (by diff.).
Phenylvinylcarbinol	No acid	30 hrs.	None	99	1	Not distilled	
"	0.1M-HCl	30 hrs.	Complete	48	52	52	48
"	"	3 hrs.	Half	52	48	Not distilled	
"	"	90 hrs.	Complete	36	64	32	68
Cinnamyl alcohol	"	30 hrs.	—	98	2	100	0
Phenylpropenylcarbinol ...	0.01M-HCl	1 hr.	Complete	53	47	51	49
"	"	4 mins.	Half	77	23	Not distilled	
"	"	3 hrs.	Complete	40	60	34	66

* All data relate to experiments at 50°, and all relate to 60% EtOH except the fourth and the last, which were in 80% EtOH.

Analysis of Reaction Products.—Rearrangements were carried out with 2 g. of carbinol in 50 c.c. of medium. After dilution with 300 c.c. of water, the products were isolated with ether and fractionated in a micro-distillation apparatus (Shrader and Ritzer, *Ind. Eng. Chem. Anal.*, 1939, **11**, 54).

Rearrangement of phenylvinylcarbinol in 60% alcohol. Treatment with 0.1M-hydrochloric acid at 50° for 25 hours afforded: (i) Cinnamyl ethyl ether (0.5 g.), b. p. 48—51°/0.0025 mm., n_D^{20} 1.5420, light absorption maxima at 2475 and 2505 Å., $E_{1\text{cm}}^{1\%} = 1000$ (Bert, *Compt. rend.*, 1925, **180**, 1504, gives b. p. 127—128°/22 mm., n_D^{15} 1.547; Darmon, *Bull. Soc. chim.*, 1941, **8**, 414, gives b. p. 140—142°/30 mm., n_D^{35} 1.536). (ii) Cinnamyl alcohol (0.35 g.), b. p. 63—65°/0.0025 mm., n_D^{20} 1.5744, m. p. 32°, light absorption maximum at 2510 Å.; $E_{1\text{cm}}^{1\%} = 1300$. (iii) Mixed middle fractions (0.8 g.).

Rearrangement of phenylvinylcarbinol in 60% dioxan. Treatment with 0.1M-hydrochloric acid at 50° for 20 hours gave cinnamyl alcohol (1.7 g.), b. p. 62—65°/0.001 mm., n_D^{24} 1.5800, m. p. 33°, light absorption maximum at 2510 Å.; $E_{1\text{cm}}^{1\%} = 1380$.

Rearrangement of phenylpropenylcarbinol in 60% alcohol. Treatment with 0.01M-hydrochloric acid at 40° for one hour afforded: (i) Styrylmethylcarbinyl ethyl ether (0.85 g.), b. p. 77—79°/0.6 mm., $n_D^{14.5}$ 1.5324, light absorption maxima at 2470 and 2510 Å.; $E_{1\text{cm}}^{1\%} = 1050$ (Found: C, 81.75; H, 9.05. Calc. for $C_{12}H_{16}O$: C, 81.75; H, 9.15%) (Kenyon, Partridge, and Phillips, *J.*, 1937, 207, give b. p. 114°/11 mm., n_D^{17} 1.5262). (ii) Styrylmethylcarbinol (0.1 g.), b. p. 86—88°/0.6 mm., $n_D^{14.5}$ 1.5631, light absorption maximum at 2510 Å.; $E_{1\text{cm}}^{1\%} = 1300$. (iii) Mixed middle fractions (0.75 g.).

Rearrangement of phenylpropenylcarbinol in 60% dioxan. Treatment with 0.01M-hydrochloric acid at 40° for one hour gave styrylmethylcarbinol (1.8 g.), b. p. 66–69°/0.001 mm., n_D^{24} 1.5654, m. p. 30–32°, light absorption maximum at 2510 Å.; $E_{1\text{cm}}^{1\%} = 1300$.

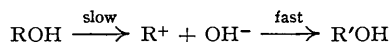
The procedure described above was not suitable for the accurate determination of the proportions of carbinol and corresponding ethyl ether formed in alcoholic media, for the following reasons: (i) The differences in refractive indices and extinction coefficients of the carbinols and their ethyl ethers are small, and the experimental error may amount to ca. 5% of the difference. (ii) The refractive indices, as recorded by different workers, as well as our own, vary over a considerable range, probably owing to the existence of geometrical isomers (Gredy; Muskat and Herrman; Wright; *loc. cit.*). (iii) Styrylmethylcarbinol is readily dehydrated to phenylbutadiene, and although this can be avoided by suitable precautions, e.g., distillation in small bulk at very low pressures from a trace of potassium carbonate, this tendency is enhanced by prolonged heating and fractionation.

The proportion of carbinol in the reaction product mixture could be accurately determined, however, by estimation of active hydrogen content, using the modified Zerewitinoff method described by Braude and Stern (following paper). Rearrangements were carried out using 1 g. of carbinol in 50 c.c. of medium, and the isolated products (< 0.8 g.) were examined, after thorough drying. The material was then distilled at 0.001–0.005 mm., and the active hydrogen content redetermined. The results are collected in Table VII. The percentage carbinol content tends to decrease slightly on distillation, but remains practically within the experimental error ($\pm 2\%$).

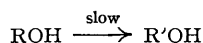
DISCUSSION.

The Reaction Mechanism.—The salient features of the reaction may be summarised as follows: In solution, the presence of hydrogen ions is necessary for rearrangement to occur. In the case of phenylpropenylcarbinol the reaction is of the first order and the rate constant is independent of the carbinol concentration. The variations of the rate constant with acid concentration and solvent composition closely resemble those found in the rearrangement of propenylethynylcarbinol (Parts I and II, *loc. cit.*), and the rate constant is directly proportional to the proton-donating properties of the medium as measured by the acidity functions, which will be reported in a subsequent paper. The energy of activation is practically independent of medium composition, if corrected for the temperature-dependence of the dielectric constant, but the isodielectric energy of activation is lower by ca. 3 kg.-cals./mol. for aqueous dioxan than for aqueous alcoholic media. In the latter the ethyl ether of the rearranged carbinol is formed in amounts roughly dependent upon the molecular proportion of alcohol in the medium, ether formation proceeding simultaneously with rearrangement. In the case of phenylvinylcarbinol the characteristics of the reaction in dioxan media closely resemble those found for the propenylcarbinol. In alcoholic media, however, some etherification also occurs before rearrangement, and the ethyl ether appears to rearrange less readily than the carbinol. The rate constants fall as the reaction proceeds and anomalies are observed in the energies of activation.

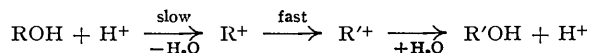
It is clear that these facts are not accounted for by mechanisms of the type proposed by Burton and Ingold (*loc. cit.*), namely,



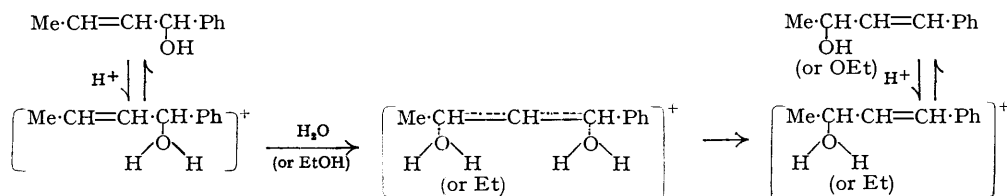
and Kenyon, Partridge, and Phillips (*J.*, 1937, 207), namely,



since, *inter alia*, they do not explicitly require the presence of hydrogen ions, or by a bimolecular mechanism of the type



since, *inter alia*, this should give rise to a reaction of the first order with respect to the carbinol and to hydrogen ions, whereas the rate constants are, in fact, independent of the carbinol concentration. All the facts can be explained, however, by a mechanism of the type elaborated in detail in Parts I and II (*loc. cit.*), except that the rearrangement is clearly not intramolecular in the present case.



A reversible oxonium-ion formation is followed by the rate-determining rearrangement, which involves the simultaneous detachment of a water molecule, migration of the electron-pair, and attachment of another water (or alcohol) molecule at the 3-carbon atom. The driving force of the reaction is the tendency of the phenyl

group and the ethylenic bond to enter into conjugation. It is noteworthy that both the hydrolysis and the etherification of cinnamyl halides lead to mixtures of cinnamyl alcohol and phenylvinylcarbinol derivatives (Charon, *Bull. Soc. chim.*, 1910, **7**, 86; Dupont and Labaume, *Chem. Zentr.*, 1910, II, 734; Meisenheimer and Link, *Annalen*, 1930, **479**, 211), and a reversal of the conjugating process is thus possible in a bimolecular substitution reaction requiring electron accession at the point of reaction.

The marked lowering of the energy of activation in aqueous dioxan as compared with aqueous-alcoholic media is not unexpected. Infra-red light absorption as well as other evidence (Gordy, *J. Chem. Physics*, 1936, **4**, 769) indicates that hydroxylic compounds are solvated by dioxan, and it has been shown theoretically as well as experimentally that an increase in solvation will result in a lowering of the energy of activation (Bell, *J.*, 1943, 629). In the present case, solvation of the carbinol will decrease the energy of separation of the carbonium ion and the dipolar water molecule in the transition state.

The lower mobility of the anionotropic system of the ethyl ether as compared with that of the carbinol, indicated by the falling rate constant in the rearrangement of phenylvinylcarbinol in alcoholic media, is paralleled by a much lower rate of rearrangement of ethers of propenylethynylcarbinol than of the carbinol itself (unpublished observation). It is to be ascribed to the smaller equilibrium constant of $\text{ROEt} + \text{H}^+ \xrightleftharpoons{K} \text{ROHET}^+$ as compared with $\text{ROH} + \text{H}^+ \xrightleftharpoons{K} \text{ROH}_2^+$, the overall rate constant being given by $k = Kk_r$, where K is the equilibrium constant of the proton-transfer reaction, and k_r the rate constant of the rate-determining step.

The Effect of Substituents on Mobility.—The enhanced mobility of phenylpropenyl- over phenylvinylcarbinol may be compared with the corresponding results in the oxotropic formation of the vinylacetylene and butadiene systems (Table VIII). Both steps of the reaction are facilitated by electron accession at the hydroxyl group, and the accelerating effect of the methyl group is to be ascribed to its positive inductive and tautomeric effects (cf. Part III, *loc. cit.*), (see inset).

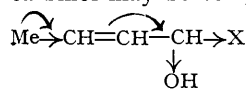


TABLE VIII.

K = Dissociation constant of $\text{X}\cdot\text{CO}_2\text{H}$, in water, 25°. k = Rate constant in 60% alcohol, 0.1M-HCl, 30°.

X.	$10^5 K$.	$10^4 k_{\text{CH}_2\text{OH}\cdot\text{CHX}\cdot\text{OH}}$.	$\log K + \log k$.	$10^4 k_{\text{CHMe}\cdot\text{CH}\cdot\text{CHX}\cdot\text{OH}}$.	$\log K + \log k$.
$\text{C}\equiv\text{CH}$	1400 ¹	0.00015	-1.32	0.538	2.88
$-\text{C}\equiv\text{CBu}(n)$	140 ²	0.0535	0.87	80.7	4.05
$-\text{CH}=\text{CH}_2$	5.5 ³	1.80	1.00	1725	3.98
-Ph	6.27 ³	4.26	0.70	2300	4.16

¹ Wilson and Wenzke, *J. Amer. Chem. Soc.*, 1935, **57**, 1265. ² Part IV, *loc. cit.* ³ Dippy, *Chem. Rev.*, 1939, **25**, 151.

Table VIII also shows the inverse relationship between the relative rate constants of the carbinols and the dissociation constants of the corresponding acids $\text{X}\cdot\text{CO}_2\text{H}$, the Hammett equation (*Chem. Rev.*, 1935, **17**, 125) $\log k + \log K = \text{const.}$ being obeyed except when $\text{X} = \text{C}\equiv\text{CH}$. The negative inductive effect of the group X, due to its intrinsic electron deficiency, is counteracted in the hexynyl group by the butyl substituent, and in the phenyl group by the increased electronic mobility of its conjugated system. The sequence of decreasing electron attraction, $\text{C}\equiv\text{CH} > \text{C}\equiv\text{CBu}(n) > \text{CH}=\text{CH}_2 > \text{Ph}$, indicated by the relative rate constants, is thus the expected one.

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