REARRANGEMENTS OF SUBSTITUTED 1-PHENYLALLYL ALCOHOLS

R.G.SALIH and M.Y.SHANDALA

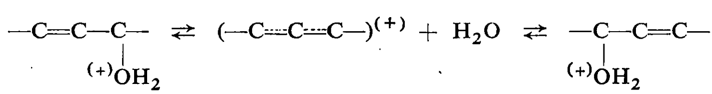
Department of Chemistry, College of Science,
University of Mosul, Iraq

Received April 25th, 1975

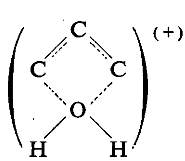
The rearrangement of X-substituted 1-phenylallyl alcohols ($X = H$, p-CH_3, o-CH_3, p-CH_3O, m-CH_3O, o-CH_3O, o-F, p-F, p-Cl, m-Cl, o-Cl, p-Br, and m-Br) to the corresponding 3-phenylallyl alcohols has been studied. The reactions are followed spectroscopically in aqueous dioxane and aqueous ethanol in the presence of hydrochloric acid as a catalyst at various acid concentrations and compositions of media. The correlations of rates with substituents are investigated.

The acid catalysed rearrangements of allylic alcohols have been studied in many systems[1-3]. The work of Burton and Ingold[4] on the rearrangements of 1-phenylallyl alcohols was of a qualitative character. Braude and coworkers[5-7] carried out a detailed kinetic investigation of acid catalysed rearrangements of allylic alcohols.

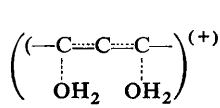
In connection with anionotropic rearrangements, three mechanisms (analogous to S_N1, S_N2, and S_Ni) were originally proposed. The carbonium ion mechanism was postulated[4]. Catchpole and Hughes[8] concluded that the rearrangement occurred by S_N1 mechanism. The intramolecular mechanism was put forward by Kenyon and his coworkers[9]. Braude reformulated[1] the three proposed mechanisms. He suggested that the entity undergoing rearrangement is not the neutral molecule but the oxonium ion formed by the reversible addition of a proton to the α-carbon atom as shown in *I*, *II* and *III*.



I



II



III

Braude[1] regarded mechanism *III* as predominant in non isomeric systems and intermolecular isomeric anionotropy while the rearrangements in dilute solutions in inert solvents take place by mechanism *II*. In aqueous solvents, the intermolecular and intramolecular reactions proceed side by side. Goering and coworkers[2,3] proposed that in aqueous solvents the carbonium ion process *I* and the S_N2 process are likely mechanisms for the rearrangements, and of these two the carbonium ion mechanism is more likely. Bunton and Poker[10] suggested that the rearrangements entirely occur *via* carbonium ion mechanism.

In order to gain more information about the mechanism of rearrangement of substituted 1-phenylallyl alcohols to the corresponding 3-phenylallyl alcohols, a detailed kinetic study has been performed in the present work. Hammett and Taft's equations are used to correlate the rates of reactions.

EXPERIMENTAL

Kinetics: The reactions were followed by observing the increase in the absorption intensity of the medium at λ_{max} of the resulting 3-phenylallyl alcohol using SP 800 spectrophotometer connected to an automatic SP 825 program controller. The temperature has been controlled by water cir-

TABLE I

The Physical Constants for 1- and 3-Phenylallyl Alcohols

	1-Isomer[a]				3-Isomer			
Substituent	λ_{max} nm[b]	ε	b.p. °C/Torr	n_D^{25}	λ_{max} nm	m.p., C°	ε, kinetic	ε, preparative
H	252	550	105–107/9·5	1·5386	251	33	17,200	18,100
o-CH_3	252	750	120–122/10	1·5400	252	41–42	15,460	17,000
m-CH_3	256	510	115–117/11	1·5370	254·5	[c]	16,400	17,300
p-CH_3	257	800	120–122/10	1·5370	254·5	51–52	19,500	20,300
o-CH_3O	256	990	84–86/0·2	1·5153	251	72–73	17,300	19,000
m-CH_3O	259	750	115–118/8	1·5449	256	70–71	19,150	20,800
p-CH_3O	262	1 700	96–98/04	1·5470	261	80	21,400	22,250
o-F	251	650	82–84/3	1·5137	249	54·55	15,560	17,100
m-F	251	500	84–85/10	1·5165	250	52	15,580	17,300
p-F	252	700	100–102/5	1·5148	250	57	16,800	17,900
o-Cl	253	980	100–103/10	1·5609	250	[d]	16,650	18,100
m-Cl	255·5	900	110–112/5	1·5569	255	51–52	17,650	19,400
p-Cl	258	850	125–128/12	1·5518	256	57	19,800	22,000
m-Br	260	950	85–86/0·1	1·5795	254	60–61	17,650	19,650
p-Br	259	980	90–91/0·2	1·5712	258	67–68	21,600	24,000

[a] Contains about 3% of unidentified materials and some 3-phenylallyl alcohol; [b] in ethanol as [a] solvent; [c] liquid b.p. 96–97°C/0·2 Torr.; [d] liquid b.p. 94–95°C/0·3 Torr.

TABLE II

Rate Constants (min^{-1}) of Rearrangement of Substituted 1-Phenylallyl Alcohols in Aqueous Dioxane and Aqueous Ethanol in the Presence of 0·05M-HCl. (conc. of alcohol c. 9 . 10^{-5}M).

Substituent	°C	% Ethanol	10^3K_T[a]	% Dioxane	10^3K_T
H	50	50	4·06	50	5·25
	50	30	13·24	40	8·74
	50	20	27·30	30	14·95
o-CH_3	50	50	10·33	50	13·32
	50	40	19·53	40	21·88
	50	30	41·51	30	36·82
	40	30	15·67	40	7·18
	35	30	9·66	40	12·26[b]
m-CH_3	50	50	7·46	50	4·58
	50	40	14·88	50	6·84
	50	30	28·15	40	11·48
	45	30	16·60	40	7·73
	40	30	10·11	40	4·34
	50			30	18·88
p-CH_3	50	70	14·42	60	33·11
	50	60	21·32	50	52·00
	50	50	35·01	40	79·00
	50	30	102·00	40	46·38[b]
	40	30	43·60	40	28·82
	35	30	27·46	30	120·00[c]
o-CH_3O	50	60	58·70	60	104·8
	50	50	96·26	50	138·0
	50	40	158·5	40	195·5
	45	40	94·20	40	117·1
	40	40	62·67	40	73·2
	35	40	38·40	40	45·8[d]
	50	30	285·3	30	305·5
m-CH_3O	50	40	3·72	40	3·92
	50	30	6·92	30	7·22
	50	20	11·00	20	11·80
	50	20	22·81[e]	20	2·36[e]
	45	20	13·80[e]	20	12·19[e]
	40	20	7·41[e]	20	6·38[e]
p-CH_3O	50	80	41·93[f]	80	71·20[f]
	45	80	29·15[f]	80	44·80[f]
	40	80	19·50[f]	80	27·96[f]
	45	75	31·20[f]	75	46·15[f]
	45	70[f]	35·76[f]	70	51·08[f]
	50	30	1 867·9[g]	30	190·10[g]

TABLE II
(*Continued*)

Substituent	°C	% Ethanol	$10^3 K_T$	% Dioxane	$10^3 K_T$
o-F	50	30	0·678	30	0·611
	50	25	0·765	25	0·868
	50	20	1·05	20	1·02
	55	15	2·69	15	2·18
	45	15	0·733	15	0·666
m-F	50	30	0·873	30	0·944
	50	25	1·09	25	1·18
	50	20	1·54	20	1·45
	50	15	2·05	15	1·77
	55	15	3·24	15	3·39
	45	15	1·06	15	1·12
	50	50	3·92	50	3·86
	50	40	7·36	40	7·15
	50	30	14·15	305	12·86
	50	15	39·31	1	33·20
	55	15	66·20	15	57·09
	45	15	23·20	15	19·28
	50	30	0·681	30	0·578
	50	25	0·872	20	0·989
	50	20	1·25	15	1·36
	50	15	1·74	15	2·3[h]
	55	15	2·96	15	0·692
	45	15	0·866	—	—
	50	30	0·568	30	0·485
	50	20	1·08	20	0·830
	50	15	1·38	15	1·11
	55	15	2·60	15	2·02
	45	15	0·755	15	0·582
p-Cl	50	30	4·44	30	3·92
	50	20	8·60	20	7·01
	50	15	11·88	15	9·28
	55	15	19·28	15	14·79
	45	15	7·24	15	5·50
m-Br	50	30	0·778	30	0·542
	50	25	0·910	25	0·742
	50	20	1·24	20	0·890
	50	15	1·46	15	1·18
	55	15	2·75	15	2·27
	45	15	0·822	15	0·668
p-Br	50	80	3·59	30	2·94

TABLE II
(*Continued*)

Substituent	°C	% Ethanol	10^3K_T	% Dioxane	10^3K_T
	50	20	6·99	20	5·46
	50	15	8·67	15	7·53
	55	15	15·03	15	13·34
	45	15	5·01	15	4·42

[a] Mean values of several runs; [b] at 45°C, in dioxane; [c] at 50°C in dioxane; [d] at 35°C in dioxane; [e] conc. of HCl 0·02M; [f] conc. of HCl 0·01M; [g] by extrapolation; [h] at 55°C in dioxane.

culating inside the cell compartment using U-10 Ultrathermostat. This method is similar to that adopted by Braude[11]. First order rate constants were calculated from

$$k = (2{\cdot}3/t) \log (E_\infty - E_0)/(E_\infty - E_t)\,, \qquad (1)$$

where E_t and E_∞ are the optical densities after t minutes and at the end of the reaction, respectively. The % of rearrangement was calculated from the ratio of the molecular extinction coefficient (ε) at λ_{max} obtained at the end of a kinetic run to that of the corresponding 3-phenylallyl alcohol.

Materials: Substituted 1-phenylallyl alcohols were prepared by Grignard condensation of the appropriate aryl halides with acrolein. Substituted 3-phenylallyl alcohols were prepared by rearrangements of the corresponding 1-phenylallyl alcohols in 60% aqueous acetone in the

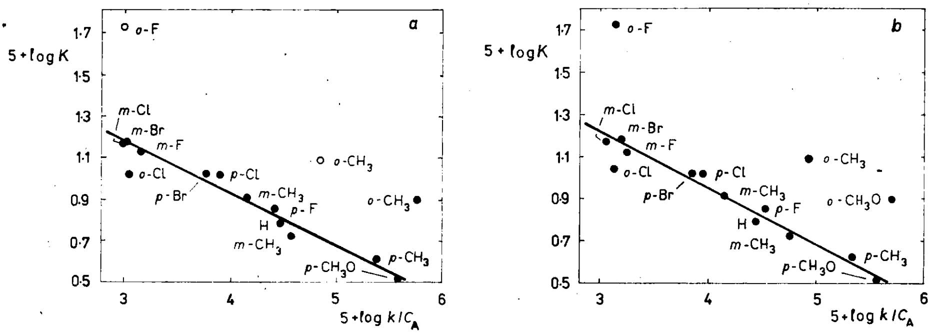


FIG. 1

Plot of log k/C_A for *meta* and *para* Substituted Alcohols in 30% Aqueous Dioxane (*a*) and 30 % Aqueous Ethanol (*b*) in the Presence of 0·05M-HCl *versus* log K

k, Rate constant of rearrangement of substituted 1-phenylallyl alcohol, *K*, dissociation constant of the corresponding benzoic acid in water at 25°C.

presence of 0·2M-HCl. The products were isolated by distillation or crystallization from benzene–light petroleum. The physical constants for the conjugated and nonconjugated alcohols are summarized in Table I.

Solvents: Dioxan was refluxed over sodium for 12 hours and fractionated. Ethanol (B.D.H.) was used after distillation. Distilled water was boiled over potassium permanganate and redistilled.

RESULTS AND DISCUSSION

In order to gain more information on the mechanism of rearrangement of 1-phenylallyl alcohol to the corresponding 3-phenylallyl alcohol, the rearrangements of substituted 1-phenylallyl alcohols were carried out in aqueous dioxane and aqueous

TABLE III

Entropy and Enthalpy of Activation of Rearrangement of Substituted 1-Phenylallyl Alcohols in the Presence of 0·05M-HCl in Aqueous Organic Solvents

Substituent	% Solvent	$\Delta S^{\ddagger}$, e.u.[a]	$\Delta H^{\ddagger}$, Kcal/mol[a]
	Ethanol		
o-CH_3	30	−2·80	19·70
m-CH_3[b]	30	−1·22	21·26
p-CH_3	30	−3·76	22·26
o-CH_3O	40	−3·48	19·90
m-CH_3O	20	+1·12	23·19
p-CH_3O[c]	80	−6·19	15·90
o-F	15	+1·53	27·20
m-F	15	+2·14	23·4
p-F	15	−2·61	22·06
o-Cl	15	+4·39	25·77
	Dioxane		
o-CH_3	40	−0·60	24·99
m-CH_3	40	−2·60	21·43
p-CH_3	40	−0·95	20·95
o-OCH_3	40	−1·22	19·78
m-OCH_3	20	+3·75	25·89
p-OCH_3	80	−1·88	19·51
o-F	15	+1·75	24·85
m-F	15	+1·52	23·36
p-F	15	−0·67	22·83
o-Cl	15	+4·32	25·20

[a] The average at three different temperatures; *b* 0·02M-HCl; [c] 0·01M-HCl.

ethanol in the presence of 0·05M-HCl as shown in Table II. From the data recorded it can be seen that in aqueous dioxane the rate of isomerization increases in the sequence m-Cl < m-Br < o-Cl < o-F < m-F < p-Br < p-Cl < m-CH_3O < p-F < H < < m-CH_3 < p-CH_3 < o-CH_3O < p-CH_3O, while the rate of rearrangement in aqueous ethanol increases in the sequence m-Cl < o-Cl < o-F < m-Br < m-F < < p-Br < p-Cl < m-CH_3O < H < p-F < m-CH_3 < o-CH_3 < o-CH_3O < p-CH_3O. It can be noticed that the sequence of increasing rates in both aqueous dioxane and aqueous ethanol is nearly the same. The rate constants (k_t) for each alcohol are proportional to the acid concentrations c_A. Values k/c_A are nearly constant for each alcohol in the same media and decrease with increasing organic solvent concentration up to 85%. The rate constants in media of different composition at the same concentration of HCl and constant temperature obey the equation $\log k = mD + n$, where D is dielectric constant of the organic mixture[12], m and n are constants. A fall in the first order rate constants is observed for the rearrangements of the alcohols in aqueous ethanol which may be due to the formation of substituted 1-phenylallyl ethers before and after rearrangement but the ether itself is less easily rearranged than the original alcohol. The rate constants at different temperatures accurately obey the Arrhenius equation. Values of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are listed in Table III. It is also observed from Table II that in the rearrangement of substituted 1-phenyl-

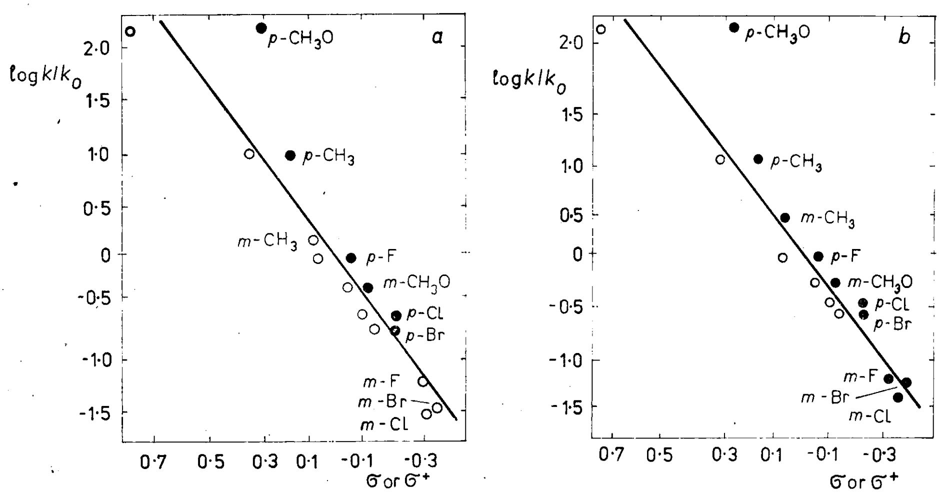


FIG. 2

Relative Rates of Rearrangements of 1-Phenylallyl Alcohols in 30% Aqueous Dioxane (a) and 30% Aqueous Ethanol (b) in the Presence of 0·05M-HCl *versus* σ(●) and σ^+(○)

k, Rate constant of rearrangement of *meta* and *para* substituted 1-phenylallyl alcohol, k_0, rate constant of rearrangement of 1-phenylallyl alcohol.

allyl alcohols the highest extinction coefficient, reached in kinetic runs, is lower by some 5–10% than that of the pure 3-phenylallyl alcohol; this may be attributed to: *a*) Substituted 1-phenylallyl alcohols contain about 3% impurities which resulted from the acrolein used; *b*) The maximum absorption decreases with time after the kinetic run is finshed, in accordance with Goering and Silversmith view[3]. On the other hand Braude[5] attributed this discrepancy to the formation of stereoisomers or the establishment of equilibrium at 92–97% rearrangement. According to the above observation, if equilibrium is established, it will be at a higher percentage of rearrangement.

The plot of log k/c_A for the *meta* and *para* substituted alcohols in aqueous dioxane and aqueous ethanol (Fig. 1*a* and 1*b*) *versus* log K does approximate to a straight line where K is the dissociation constant of substituted benzoic acid in water at 25°C. Hammett equation[13], $\log k/k_0 = \varrho\sigma$, was used to correlate the rates of *meta* and *para* substituted 1-phenylallyl alcohols. It can be seen from Fig. 2*a* and 2*b* that the relative rates of rearrangement deviate from the usual Hammett equation. A better correlation is obtained when σ^+ is used. When the modified Hammett equation of Yukawa and Tsuno[14] is used, the correlation approximates to a straight line as shown in Fig. 3*a* and 3*b*:

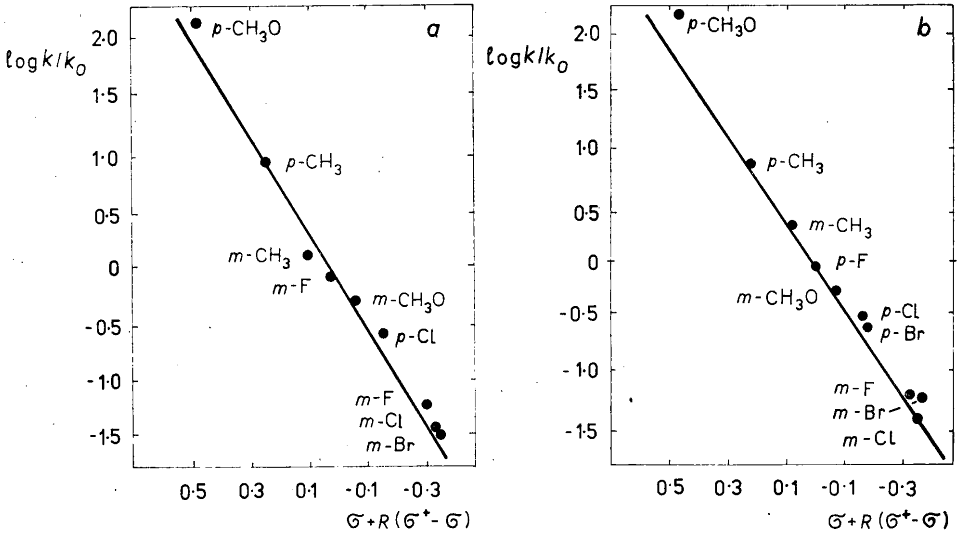


FIG. 3

Relative Rates of Rearrangements of 1-Phenylallyl Alcohol in 30% Aqueous Dioxane (*a*) and 30% Aqueous Ethanol (*b*) *versus* $\sigma + R(\sigma^+ - \sigma)$

k/k_0, Ratio of the rate constant of rearrangement of substituted 1-phenylallyl to the rate constant of 1-phenylallyl alcohol, R 0·396.

$$\log k/k_0 = \varrho\sigma + R(\sigma^+ - \sigma), \quad (2)$$

where R is proportionality constant giving the contribution of the enhanced resonance effect of electron releasing substituents. The value of $\varrho = 3{\cdot}7$ is neither so high in both aqueous dioxane and aqueous ethanol to suggest that the reaction proceeds *via* carbonium ion nor so low to suggest that the rearrangement proceeds *via* intermolecular mechanism. The value of ϱ is in good agreement with the suggestion of Braude[1] that "in aqueous solvents the intra and intermolecular mechanism possibly proceed side by side", however the carbonium ion mechanism is more predominant.

The data obtained for the *ortho* substituted alcohols gives a reasonable fit in Taft's equation[14-16] $\log k/k_0 = \varrho\sigma_{ortho}$, which implies that the steric effect does not cause differences in rates within the series. No correlation could be obtained when a plot of $\log k/k_0$ against E_s was attempted; *i.e.* no correlation could be found with the equation[17] $\log k/k_0 = \varrho E_s$.

REFERENCES

1. Braude E. A.: Quart. Rev. Chem. Soc. *4*, 404 (1950).
2. Goering H. L., Dilgren R. E.: J. Amer. Chem. Soc. *81*, 2556 (1959).
3. Goering H. L., Silversmith E. F.: J. Amer. Chem. Soc. *79*, 348 (1957).
4. Burton H., Ingold C. K.: J. Chem. Soc. *1928*, 904.
5. Braude E. A., Jones E. R. H., Stern E. S.: J. Chem. Soc. *1946*, 396.
6. Braude E. A., Jones E. R. H., Stern E. S.: J. Chem. Soc. *1947*, 1087.
7. Braude E. A., Stern E. S.: J. Chem. Soc. *1947*, 1096.
8. Catchpole A. G., Hughes E. O.: J. Chem. Soc. *1948*, 41.
9. Kenyon J., Partridge S. M., Phillips H.: J. Chem. Soc. *1941*, 721.
10. Bunton C. A., Poker Y.: Chem. Ind. (London) *1958*, 1516.
11. Braude E. A., Gore P. H.: J. Chem. Soc. *1951*, 41.
12. Timmermans J.: *Physico-Chemical Constants of Binary Systems*, Vol. 4. Interscience, New York 1960.
13. Hammett L. P.: *Physical Organic Chemistry*, p. 355. McGraw Hill, New York 1970.
14. Yukawa Y., Tsuno Y.: Bull. Chem. Soc. Jap. *32*, 965 (1959).
15. Jaffe H. H.: Chem. Rev. *53*, 191 (1951).
16. Taft R. W.: J. Amer. Chem. Soc. *75*, 4231 (1953).
17. Taft R. W.: J. Amer. Chem. Soc. *74*, 3120 (1952).