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STUDIES ON β-METHYL-1-AND 3-PHENYL ALLYL CHLORIDES

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Abstract—The hydrolysis of β-methyl-1- and 3-phenylallyl chlorides (**1a** and **1b**) have been investigated in aqueous dioxan and the proposed mechanism compared with those reported for the corresponding 1- and 3-phenylallyl chlorides (**2a** and **2b**). Hydrolysis of **1a** and **1b** proceeds via the same mechanism as **2a** and **2b**, respectively, with different behavior by the first intermediate. The first intermediate of **1a** rearranges to the corresponding conjugated compound through a transition state rather than an intermediate. Theoretical calculations on the carbonium ions of **1** and **2** using a semiempirical MINDO/3 molecular orbital method show that the charge densities on carbon atoms of **1** are nearly the same as those of **2**. The main difference is in the bond angle C^1–C^8–C^9.

Vernon[1] investigated kinetically the reaction of cinnamyl chloride in absolute and aqueous ethanol. He concluded that the solvolysis is unimolecular in the more ionizing aqueous solvent, but showed a tendency toward bimolecularity in absolute ethanol.

Waight *et al.*[2] re-examined the solvolysis of cinnamyl chloride, and suggested that an ion pair is formed in the rate determing step without assistance by the solvent. For the hydrolysis, they suggested an ion-pair is formed in the rate determining step, and that this can either react with the solvent to give rise to the corresponding cinnamyl alcohol, or can dissociate to the free carbonium ion which can give rise to the two isomeric alcohols. In the most highly aqueous media the counter ions are sufficiently well separated before reaction with solvent for the positive charge to be completely delocalized and the isomeric alcohol are thus obtained in about the same ratio as from the free carbonium ion.

In the present work, the influence of methyl group on the mechanism of the hydrolysis (rate and the composition product) were investigated, in order to suggest whether the rearrangement of the first intermediate of **1a** proceeds through a transition state or an intermediate by using experimental and theoretical data.

RESULTS AND DISCUSSION

The molecular geometries, electron densities and heats of formation of phenylallyl and β-methylallyl cations have been calculated by semiempirical MINDO/3 molecular orbital method.[3] These results for both cations are obtained after allowing the molecular parameters to vary until the energy is completely minimized using the Davidon–Fletcher–Powell method.[4] The results for the molecular geometries are tabulated in Table 1. It can be seen from this table, the difference in the bond angle C^1–C^8–C^9.

The calculated heats of formation of phenylallyl and β-methylphenylallyl cations are 222.733 kcal mol^{-1} and 222.283 kcal mol^{-1}, respectively. This result suggests that methyl group stabilizes allyl cations by 0.45 kcal mol^{-1}, which is in agreement with ab initio calculations.[5]

The calculated electron densities for the two cations are listed in Table 2. The electron densities on the carbon atoms for both cations are nearly the same. It can be seen from this table, that slight differences are observed in electron densities for carbon atoms α, β and γ.

In addition to theoretical calculations, the hydrolyses of 1- and 3-β-methylphenylallyl chlorides were investigated in aqueous dioxan mixture. The results

Table 1. MINDO/3 calculations for the molecular geometries of phenylallyl and methylphenyallyl cations

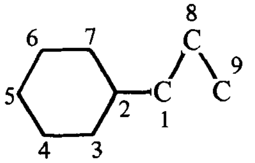
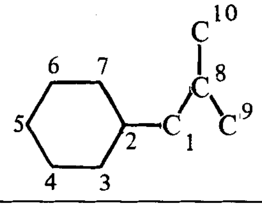
Compound	Molecular geometries, bond lengths in A°, and bond angles in degrees
	C^1C^2, 1.414; C^2C^3, 1.457; C^3C^4, 1.393; C^4C^5, 1.413; C^5C^6, 1.413; C^6C^7, 1.392; C^7C^2, 1.456; C^1C^8, 1.433; C^8C^9, 1.346; CH, 1.105; $C^8C^1C^2$, 134.7; $C^3C^2C^7$, 114.8; $C^2C^3C^4$, 122.7; $C^3C^4C^5$, 119.4; $C^4C^5C^6$, 120.7; $C^5C^6C^7$, 119.7; $C^2C^7C^6$, 122.7; $C^1C^8C^9$, 128.4;
	C^1C^2, 1.417; C^2C^3, 1.459; C^3C^4, 1.393; C^4C^5, 1.412; C^5C^6, 1.413; C^6C^7, 1.392; C^1C^8, 1.454; C^8C^9, 1.365; C^8C^{10}, 1.501; CH, 1.105; $C^8C^1C^2$, 139.9; $C^3C^2C^7$, 114.3; $C^2C^3C^4$, 123.0; $C^3C^4C^5$, 119.5; $C^4C^5C^6$, 120.4; $C^5C^6C^7$, 119.8; $C^2C^7C^6$, 122.9; $C^1C^8C^9$, 116.3; $C^{10}C^8C^9$, 123.0.

Table 2. Calculated electron densities for phenylallyl and methylphenylallyl cations

	Electron density	
Atom No	Phenylallyl cation	Methylphenylallyl cation
1	3.657(α)	3.676(α)
2	4.116	4.113
3	3.854	3.855
4	4.053	4.052
5	3.818	3.822
6	4.057	4.050
7	3.856	3.859
8	4.108(β)	4.069(β)
9	3.799(γ)	3.830(γ)
10	—	3.928

are presented in Table 3. It can be seen that the rates of hydrolysis of both 1- and 3-β-methylphenylallyl chlorides hydrolyses at slower rate than that of the corresponding 1- and 3-phenylallyl chlorides under the same experimental conditions, i.e. the methyl group at the β-position causes a retardation in the rate of hydrolysis.

Plotting log K_T for both **1a** and **1b** against the Grunwald–Winstein's Y-values[6] gives a straight line with slope $m = 1.03$ and 1.20 respectively. This is typical of unimolecular reactions, and is in quite good agreement with the values obtained for **2a** and **2b**.

The product ratio of the concentration of the conjugated and the unconjugated solvolysis product (C_c and C_p respectively) for each **1a** and **1b** is given by

$$r = \frac{C_p}{C_c} = \frac{\epsilon_c C_0 - E}{E - \epsilon_p C_0}$$

where P and C are respectively, the molecular extension coefficient (at λ max) of pure unconjugated and conjugated solvolysis products and C_0 is the initial molar concentration. Whilst for **1a** and **2a** the molar concentration of the three solvolysis products are given by

$$C_c = \frac{[E_\infty + T(\epsilon_{ccl} - \epsilon_p) - \epsilon_{ccl} C_0]}{\epsilon_c - \epsilon_p}$$

$$C_p = T - C_c$$

$$C_{ccl} = C_0 - C'_{ccl} - (C_p + C_c)$$

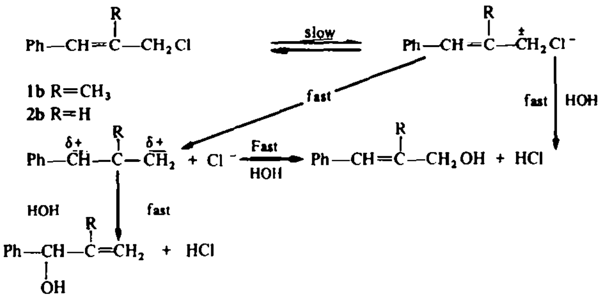
Where T is the molar concentration of librated acid referred to the initial concentration of the corresponding 1-phenylallyl chloride used C_0 in the spectrometric run. ϵ_{ccl} is the molar extension coefficient of the corresponding conjugated chloride used and C'_{ccl} the concentration of conjugated chloride originally present. The total hydrolysable chloride ($C'_{ccl} + C_{pcl}$) was determined by keeping a sample (*ca.* 0.05 g) in 50% aqueous dioxan for a few hours at 30.0°, the acid formed titrated with standard aqueous sodium hydroxide. The value obtained was used to correct the amount of chloride weighed out to give the initial concentration of the unconjugated chloride (C_0), the non hydrolysable material was assumed to have $\epsilon = 200$.

Table 3 shows that the product ratio (r) for (**1a**) is less than that of (**2b**) under the same experimental

Table 3. Hydrolysis of 1- and 3-β-methylphenyallyl chlorides in aqueous dioxan, 30°C

Compound	%dioxan	$10^3K_T(\text{min})^{-1}$	%ROH	(r)	%Solvolysis
1b	30	298.2	51.5	1.06	
	40	59.1	46.0	0.85	
	50	11.9	37.0	0.59	
2b*	30	703.0	59.0	1.44	
	40	165.0	56.0	1.27	
	50	31.6	54.0	1.17	
	60	5.72	52.0	1.08	
1a	65	99.35	69.2	2.24	29.3
	70	66.53	83.1	4.92	24.1
	80	5.51	95.2	19.83	21.3
2a*	80	169.0	70.0	2.33	43.4
	85	51.0	71.0	2.45	41.5
	90	9.7	67	2.03	36.1

*Results reported by Waight (Ref. 2).



Scheme 1.

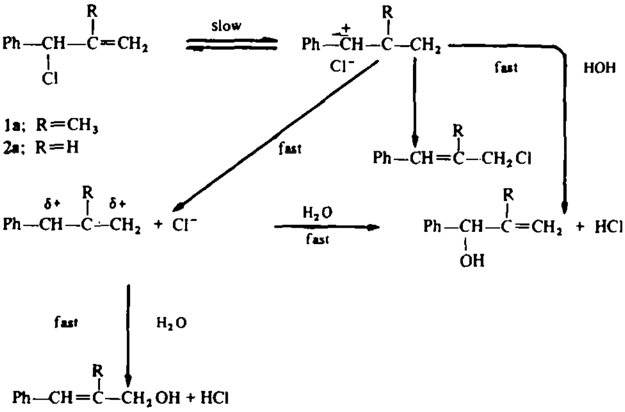
conditions, i.e. the percentage of alcohols produced from the former is higher than that for the latter.

According to the results obtained, it can be suggested that the hydrolysis of (**1b**) proceeds through the same mechanism as that for (**2b**), i.e. two intermediates are involved, the first, which is formed in the rate determining step gives either the cinnamyl alcohol or gives rise to the second intermediate from which both allylic alcohols are obtained (Scheme 1).

The theoretical calculations show that the differential reactivity of 1- and 3-positions of both phenylallyl and β-methyl-phenylallyl carbonium ions are nearly the same. Accordingly the amounts of both allylic alcohols produced from both carbonium ions are the same. But the proportion of the conjugated alcohol produced from the hydrolysis of I_b is higher than that produced from **2b**. This may be due either to a bimolecular reaction in **1b** which is rejected from the value of m, or that the first intermediate of I_b gives more conjugated alcohols. This indicates that the first intermediates for the two chlorides have different behaviours. In (**1b**), the ion-pair predominates due to the presence of the methyl group at the β-position (i.e. relatively the localization of the positive charge at the 3-carbon atom for that of **1b** is more pronounced than that for **2b** or the delocalization of the positive charge for the ion pair of **2b** is more pronounced than that for **1b**). This in turn causes an increase in the amount of conjugated product from the first intermediate of **1b** with respect to that of **2b**.

Table 3 also shows the mean values of the overall first order rate constants and the composition products of β-methyl-1-phenylallyl and 1-phenylallyl chlorides (**1a** and **2a** respectively) in a series of mixtures of dioxan.

It can be seen that on the hydrolysis of β-methyl-1-phenylallyl chloride the fraction of conjugated chloride increases (i.e. a decrease in the % of solvolysis) as the concentration of water decreases



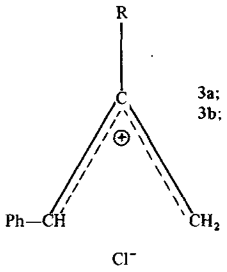
Scheme 2.

and the amount of conjugated alcohols produced are increased and this is more pronounced than that for 1-phenylallyl chloride itself. On the basis of the result obtained, it could be suggested that the hydrolysis of **1a** proceeds through the same mechanism as that for **2a**, as suggested by Waight *et al.*[2,7] but with different behaviour of the primary intermediate (Scheme 2).

It can be suggested that the primary intermediate can give rise to either the corresponding conjugated chloride or unconjugated alcohol, also that can ionise to give the free carbonium ion which can react with water to give nearly the same amounts of each of the two alcohols. The difference in the composition products for **1a** and **2a** indicates that the primary intermediates have different properties.

Comparing the primary intermediates and the composition products of **1a** and **2a**, it can be suggested that the primary intermediate of **1a** is more predominant than that for **2a**, i.e. the former isomerized to the conjugated chloride much more readily than to react with water or dissociate further to give the free carbonium ion with respect to that of the latter.

Weinstock[7] suggests that the first intermediate for **2a** isomerizes to the conjugate chloride through a transition state or intermediate (structure **3**).



3a; R=CH_3
3b; R=H

For the solvolysis of **1a** it is more likely that structure **3a** behave as a transition state rather than an intermediate. This may be attributed to the difference in the bond angle c^1 c^8 c^9 of **3a** and **3b**; the bond angle of **3a** is smaller than **3b**. This will cause that the chloride ion will be closer to the α and γ carbon atoms in structure **3a**, i.e. in structure **3a** it is more likely that the attack of the chloride ion to carbon atoms α or γ is more probable than to be attacked by solvent molecule, which will cause an increase in the percentage of rearranged chloride and a decrease in the percentage of solvolysis.

On the other hand, comparing the product ratio (r) of **1a** with **1b**, and **2a** with **2b** at nearly the same experimental condition, gives further support for ion-pair formation, the higher values of (r) for **1a** and **2a** with respect to **1b** and **2b** indicating that more unconjugated alcohol is formed from **1a** and **1b**, whilst more conjugated alcohol is formed from **2a** and **2b**.

EXPERIMENTAL

Kinetics

The reactions were followed by Braude and Gor's method[8] which was also used by Waight *et al.*[2] by observing the decrease in the absorption intensity at 250 nm of the corresponding chloride using a SP 800 spectrophotometer connected with automatic SP 825 programme controller. The temperature was controlled inside the cell by circulating water inside the cell compartment using U10 Ultrathermostat.

First order rate constants (in min^{-1}) and product ratio (r) were calculated by methods used by Waight *et al.*[2]

Materials

β-Methyl cinnamyl alcohol, commercial sample was recrystallized from pet-ether(b.p.40–60). It had λ_{max} 245 nm (ϵ 12923), m.p. 24–25°.[9] It was also prepared from the reduction of α-methyl-cinnamaldehyde or β-methylcinnamic acid.

β-Methyl-1-phenylallyl alchol

This was prepared from the reaction of phenyl magnesium bromide and α-methyl acrolein in dry ether. It had b.p. 55–56/2 mm, λ_{max} 250 nm (ϵ 500) in dioxan.

β-Methyl-1- and 3-phenylallylchlorides

These were prepared by the action of thionyl chloride on β-methyl-1-phenylallylalcohol or β-methyl-cinnamyl alcohol.[11] The reaction afforded a mixture of 1- and 3-β-methylphenylallyl chlorides. Several fractionations of the crude product gave β-methyl-1-phenylallyl chloride b.p. 60–61/2 mm, λ_{max} 250 nm (ϵ 1200) and β-methylcinnamyl chloride b.p. 63–64/2 mm, λ_{max} 251 nm (ϵ 14500).

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