

SHORT COMMUNICATION

INTERMEDIATE OBTAINED FROM PHOTOIONIZATION, SERVING AS PRECURSOR FOR THE SYNTHESIS OF SCHIFF'S BASE

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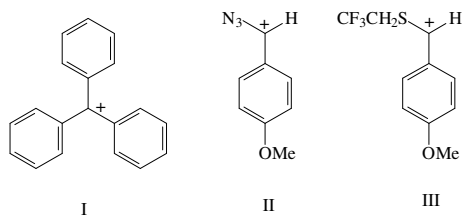
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ABSTRACT. In this article, we have introduced an intermediate benzyl carbocation (formed as a result of photoionization) which serves as precursor for the synthesis of Schiff's base. Lifetimes of many carbocations were determined from our laboratory. During the determination of the lifetimes, our endeavor was to obtain a carbocation with high selectivity, $s = k_{\text{nu}}/k_{\text{H}_2\text{O}}$. The selectivity is the ratio of the rate constant of the reaction of carbocation with an externally added nucleophile, (nu, aniline) to that of the rate constant of the water. Our intention was to obtain a carbocation with high selectivity, so that one can pave a path for the synthesis of Schiff's base by the reaction of the carbocation intermediate with aniline.

KEY WORDS: Carbocation, Selectivity, Intermediates, Solvolysis, Photoionization and Iminodiazonium ion

INTRODUCTION

Appreciable amount of work was done with regard to different carbocations from our laboratory [1]. All the while, our intent was to produce carbocations with high selectivity $s = k_{\text{nu}}/k_{\text{H}_2\text{O}}$. Large values of selectivities are obtained when the reaction with nucleophile, Nu, is hastened and comes within the reach of diffusion controlled limited type reaction and the reaction with water is slow and approaches activation controlled type [2-7]. For example, the selectivity, $s = k_{\text{nu}}/k_{\text{H}_2\text{O}}$ is about 10^5 M^{-1} for reactions of triphenylmethyl carbocation (I) [8], $8,600 \text{ M}^{-1}$ for α -azido-4-methoxybenzyl carbocation (II) [9] and $71,000 \text{ M}^{-1}$ for 4-methoxy- α -(2,2,2-trifluoro)-thioethyl benzylcarbocation (III) [10].



As the rate of the reaction of the carbocation with water increases, the selectivity decreases [2-6, 8], approaching a value of about 6-100. When the reaction of the nucleophile, Nu, and water, (both with the carbocation) are either slow and activation controlled, or both are fast and diffusion-controlled, the selectivity, s , would turn out to be approximately same for the reactions with different carbocations in spite of their different intrinsic reactivities.

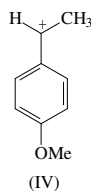
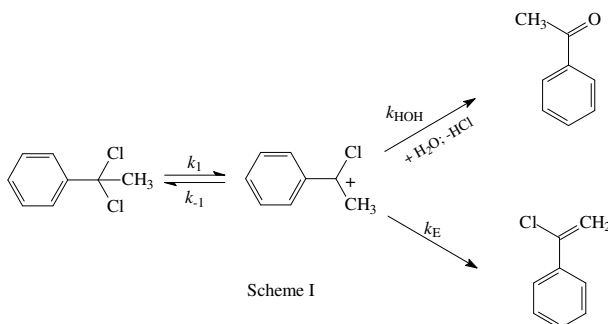
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Throughout our research, our main objective was to generate a carbocation with high selectivity. To realize this objective we strived to all possible means by virtue of which one could increase the selectivity of the intermediate benzyl-carbocation. After the realization of this aim, our final objective was to synthesize new compounds by the reaction of the selective carbocation with a nucleophile. In order to realize our main objective to generate a carbocation with high selectivity we employed two methods, i.e. incorporating different electron donating groups at *para* position or changing the solvent polarity.

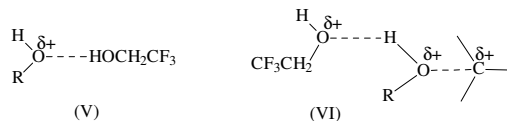
RESULTS AND DISCUSSION

The solvolyses of benzyl-*gem*-dichloride and different *para* substituted benzyl-*gem*-dichlorides, were carried out, in an attempt to obtain a stable and highly selective α -chloro (*para*) substituted benzyl carbocation. But all these carbocations showed similar reactivity towards the chloride ion (leaving group) and water. For instance, the solvolysis of benzyl-*gem*-dichloride was carried out in presence of aniline to trap the α -chlorobenzyl cation by aniline. Aniline which is more nucleophilic than water did not react with the carbocation to give the anticipated aniline reaction product, i.e. Schiff's base, apart from benzaldehyde. The reason for Schiff's base not being formed could be the following: (a) HCl which is produced as a by-product during the solvolysis of benzyl-*gem*-dichloride might be protonating the aniline, and render it un-reactive or (b) if at all the Schiff's base is formed, it is unstable in presence of accumulated HCl. In order to overcome this setback of accumulated HCl during the solvolyses, the solvolyses was carried out in presence of 0.1 M potassium carbonate, which would neutralize the accumulated HCl, so that the addition product Schiff's base would be formed. But even in presence of potassium carbonate, the anticipated product Schiff's base was not formed. The reason for this failure is sought from the time dependent spectrum of the solvolyses of benzyl-*gem*-dichloride (1×10^{-4} M) in presence of aniline (1×10^{-4} M) and 0.1 M potassium carbonate. This time dependent spectra did not show any presence of Schiff's base. This observation may be consistent with the conclusion that high barrier for the reaction of aniline with the carbocation in aqueous solution is composed primarily of water-aniline hydrogen bond [9]. Literature survey reflects that, apart from making the carbocations more selective by incorporating different electron-donating substituents (at *para* position) in benzyl carbocations [2-6, 8], the selectivity can also be enhanced by-changing the solvent polarity. Even less selective benzyl carbocations can be made more selective (by changing the polarity of the solvent) and can proceed in two different paths or to react with two different nucleophiles. As an example [10], in more polar solvent, i.e. with increase in percentage of water in dioxane-water mixture, the amount of elimination product decreases, and levels off at approximately 10-15%; and the sole reaction goes in a single path. Where as in less polar solvents, i.e. in dioxane-water with increase of dioxane content in the mixture, α -chloro- α -methyl benzyl cation did yield both, solvent-addition product (acetophenone) and elimination product (α -chloro-styrene) (Scheme I). This may be consistent with the fact that due to decrease in bulk nucleophilicity of water with increase in dioxane content, the cation is yielding two products.

The effects of changing solvent polarity on carbocation reactivity are complex, because these changes affect both the electrophilic reactivity of the carbocation and overall nucleophilic reactivity of the bulk solvent. There is a reduction in the reactivity of methanol, water and trifluoroethanol (TFE) and increase in the rate constant ratios $k_{\text{MeOH}}/k_{\text{TFE}}$ and $k_{\text{HOH}}/k_{\text{TFE}}$ of 1-(4-methoxyphenyl)ethyl carbocation (IV) [4] on changing from 20/80 (v/v) to 90/10 (v/v) trifluoroethanol/water.



These results have been attributed to the tendency of TFE, strong hydrogen bond donor and weak acceptor, to reduce the nucleophilic reactivity of hydroxylic solvent like water with developing carbocation by strengthening hydrogen bond to the lone pair of electrons at the nucleophile (V) and by weakening the solvation of the developing positive charge in the transition state through hydrogen bonding (VI) [4]. The increase in selectivity is consistent with dominant role for reducing the bulk nucleophilicity of solvents.



We had carried out the aqueous solvolyses of benzyl-*gem*-dichloride in presence of aniline, but aniline did not react with the α -chlorobenzyl cation. We attributed this failure to low selectivity of the cation and due to the presence of strong amine-water hydrogen bond between water and aniline. Because of this unsuccessful attempt we thought it was worthwhile to use a solvent for solvolyses which has low polarity in which the selectivity $s = k_{\text{nu}}/k_{\text{H}_2\text{O}}$, of α -chloro benzyl cation would increase and render the trapping of the α -chlorobenzyl cation by externally added aniline. This aniline might compete with water and chloride ion (the leaving group). In order to achieve this, acetonitrile was selected as an ideal solvent for the solvolyses. But the solvolyses of benzyl-*gem*-dichloride in acetonitrile, did not take place at all. Even increasing the percentage of water content in acetonitrile-water mixture was in vain, i.e. the added aniline did not react with the α -chlorobenzyl cation (even though the solvolyses did take place). Finally, to trap the aniline by the α -chlorobenzyl cation, photoionization of benzyl-*gem*-dichloride in pure acetonitrile (E-Merck commercial HPLC grade acetonitrile was used) containing 0.1% of water was carried out.

Acetonitrile solution containing 1×10^{-4} M benzyl-*gem*-dichloride which did not photoionize for 2 years, did solvolyse within two and half hours when photolysed with a 200-W mercury lamp. Figure 1 shows the UV-Visible spectrum of benzyl-*gem*-dichloride photolysed at different time intervals. After two and half hours of photolysis, there was growth in the peaks at 250 nm and 280 nm, and remained constant on further photolysis. When compared, the

photolysed solution with that of the authentic benzaldehyde, it was observed that, 20% to 25% conversion did take place (Figure 1). This was consistent with the fact that the benzyl halides produced benzyl carbocations on photolysis [11, 12], in the same way as benzyl-*gem*-dichlorides produced α -chloro benzyl cation. The lifetime of benzyl carbocation in aqueous solution was estimated as $t = 0.5 \text{ ns}^{13}$ and the lifetime of the α -chlorobenzyl cation in aqueous solution was 0.15 ns^1 . Thus α -chlorine substituent makes the benzyl carbocation 3 times more reactive. There is an increase in the product benzaldehyde from 20-25% to 36% when water concentration was increased from 0.02 M (0.1%) to 0.32 M (Figure 2).

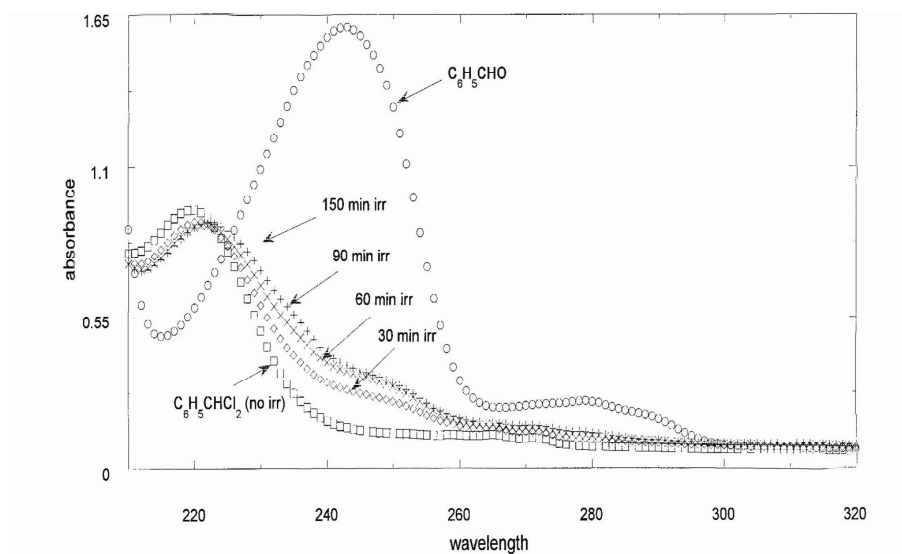


Figure 1. Time dependent spectrum of $\text{C}_6\text{H}_5\text{CHCl}_2$ in CH_3CN after irradiation at different time intervals.

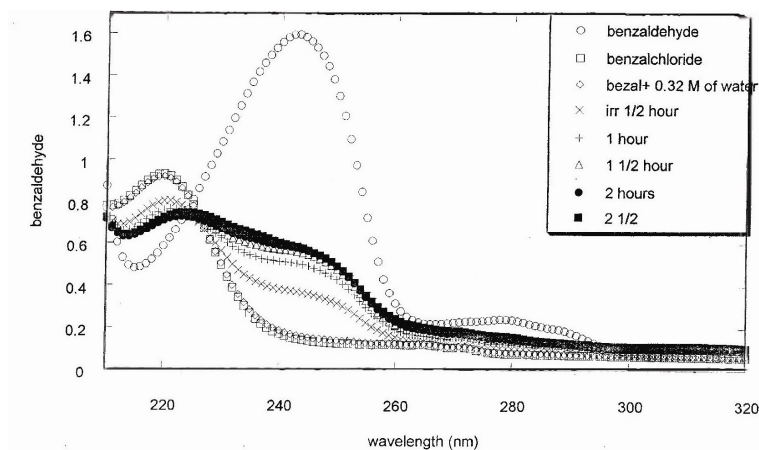


Figure 2. Time dependent spectrum of $\text{C}_6\text{H}_5\text{CHCl}_2$ in CH_3CN after irradiation at different time intervals in the presence of 0.32 M of water.

But conversion of benzyl-*gem*-dichloride to benzaldehyde was not the aim of photolysis. This conversion could have, as well carried out by aqueous solvolyses. Hence photoionization of benzyl-*gem*-dichloride was carried in pure acetonitrile containing 0.1% water in presence of aniline. In pure acetonitrile as anticipated [9] there was increase in selectivity, $s = k_{\text{nu}}/k_{\text{H}_2\text{O}}$, of α -chloro benzyl cation, and the absence of water-amine hydrogen bonding in acetonitrile rendered it possible to trap the α -chlorobenzyl cation by aniline to give corresponding Schiff-base (Figure 3 and Scheme 2). Figure 3 shows the UV-Visible spectrum of the two and half hour photolysed solution of benzyl-*gem*-dichloride (1×10^{-4} M) in presence of aniline (1×10^{-4} M) and the spectra of authentic Schiff's base in acetonitrile synthesized from benzaldehyde and aniline. The similar spectrum of the two samples is evidence that α -chlorobenzyl cation is certainly trapped by aniline in acetonitrile medium to form the Schiff's base (Scheme 2).

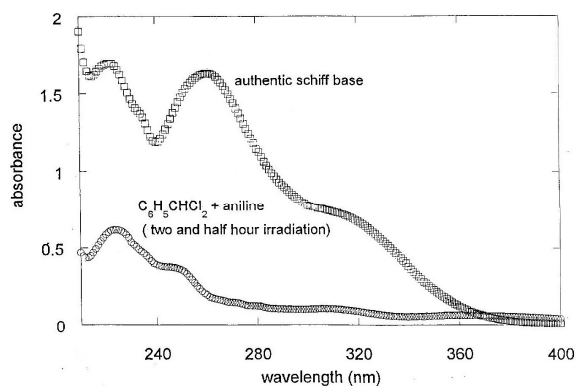
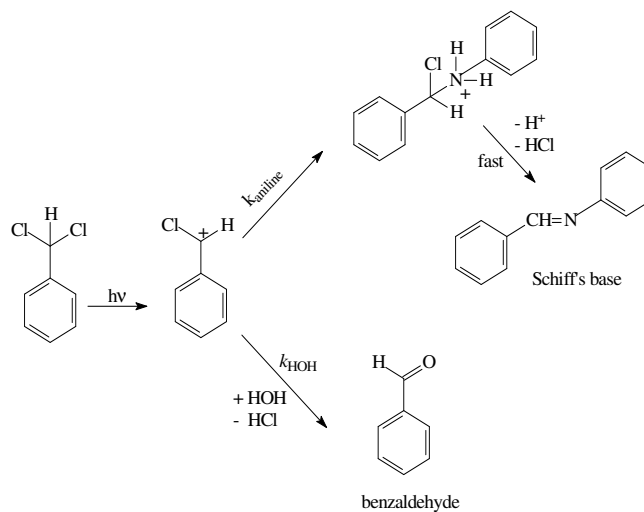


Figure 3. UV-VIS spectrum of authentic Schiff base and 2 and half hours irradiated solution of benzal chloride and aniline.



Scheme 2

CONCLUSION

Therefore it was concluded that the carbocations with less selectivity, $s = k_{\text{nr}}/k_{\text{H}_2\text{O}}$, can be made more selective either by appending strong electron-donating substituents at *para* position to the carbocation or by decreasing the solvent polarity. The increase in selectivity of carbocations can be exploited in the synthesis on new compounds. For instance more selective α -azido-methoxybenzyl carbocation [6] were used as an organic intermediate to synthesize mixed acetals and thioacetals [8]. In this work, the increase in the selectivity of α -chlorobenzyl cation (produced by photolysis of benzyl-*gem*-dichloride) in less polar solvent was exploited to trap aniline, and finally give the product Schiff's base (Scheme 2). Determination of individual rate constants, quantum yields of products etc can be further carried out to make the study complete.

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