Tetrahedron Letters No.14, pp. 919-921, 1971. Pergamon Press. Printed in Great Britain.

# EFFECTS OF PRESSURE AND SOLVENT ON THE SOLVOLYSIS OF 2,2,2-TRIPHENYLETHYL TOSYLATE IN ALCOHOL-DIOXANE SOLUTIONS

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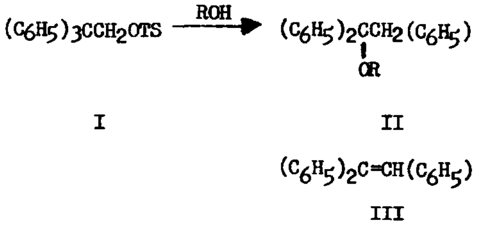
(Received in USA 26 February 1971; received in UK for publication 16 March 1971)

Mechanisms of the olefin formation in the solvolytic reactions of alkyl halides have been widely investigated[1]. Generally, increasing the size of the alkyl substituent on the carbon bearing the halide, increases the olefin yield and decreases the yield of substitution product (with solvent). This phenomenon was attributed to the operation of steric effects[2,3]. A similar trend may be observed if the bulkiness of solvent is increased; this possibility has never been explored. Substitution involves the reaction of one molecule of solvent with the carbonium ion and the volume of the system in the transition state may become smaller than that during the elimination reaction. Thus, the pressure on the system may have an influence on the proportion of the products[4].

2,2,2-Triphenylethyl tosylate (I) is a highly substituted compound and the solvolysis is accompanied with phenyl migration from $C_\beta$ to $C_\alpha$ [6]. Thus, in alcohol-dioxane solution, in the presence of either a slight excess of base or absence of a base, I is solvolyzed to form quantitatively the phenyl rearranged products, viz., 1,2,2-triphenylethyl ether (II) and triphenylethylene (III). This system presents an interesting case for the study of 1) effects of solvent and 2) effects of pressure in the solvolytic products, because the possibility of back side nucleophilic attack by solvent and the normal 1,2-elimination are both impossible. Therefore, the solvolyses of I were studied



$$(C_6H_5)_3CCH_2OTS \xrightarrow{ROH} (C_6H_5)_2\underset{\substack{|\\OR}}{C}CH_2(C_6H_5)$$

I II

$$(C_6H_5)_2C{=}CH(C_6H_5)$$

III

in dioxane solutions containing MeOH, EtOH or i-PrOH at 90° under 1 atm and under 5000 atm.[7] The reaction products were analyzed by nmr and uv measurements. The results are summarized in Table I.

Table I. Solvolysis Products of 2,2,2-Triphenylethyl Tosylate[a)]

| Solvent[b)] | Products (%) | | | |
|---|---|---|---|---|
| | 1 atm. | | 5000 atm[c)] | |
| | ether | olefin | ether | olefin |
| MeOH - dioxane | 55 | 45 | 92 | 8 |
| EtOH - dioxane | 49 | 51 | 77 | 23 |
| i-PrOH - dioxane | 9.5 | 90.5 | 45 | 55 |

a) The reaction was carried out in a Teflon vessel. Tysolate ($3.3 \times 10^{-4}$ mole) was solvolyzed in 3 ml of alcohol-dioxane solution in the presence of a slight excess of the corresponding sodium alcoholate, which was used to neutralize the acid produced. The reactions were carried out at 90° for 20-22 hrs. under 1 atm and for 10-12 hrs. under 5000 atm. The rates of the solvolysis of I in 30% (vol.) methanol-dioxane solution at 65° were 20.5 and 220 $sec^{-1}$ under 1 and 5000 atm, respectively.

b) Alcohols (0.16 mole) were used to make up a 20 ml solution of alcohol-dioxane solution.

c) The pressure was kept with ± 10% during the course of reaction.

Recently, much attention has been focussed on the large rate enhancement in the solvolytic reaction of I, which is 4000 times faster than that of neopentyl tosylate in acetic acid[6]. The relief of steric strain at the $C_\beta$ atom in the ionization stage is accounted for wholly or partly on the driving force for the enhancement and the phenyl bridge ion is proposed as the transition state[6,8]. The reaction of the ion with solvent in the second stage would involve steric compression in going to the substitution product. Thus, the substitution product sharply decreased by increasing the bulkiness of solvent, i.e., 55, 49, 9.5% in MeOH, EtOH and i-PrOH, respectively.

Brower and Chen[9] investigated the reaction of t-amyl chloride at pressures up to 1360 atm. They studied the reaction in aqueous alcohol in the presence or absence of a strong base; they found that the pressure had no effect on the composition of the products. However, we have found the effect is significant, i.e., olefin products are 8, 23 and 55% under 5000 atm vs. 45, 51 and 90.5% under 1 atm in MeOH, EtOH and i-PrOH, respectively. These results indicate that the formation of the substitution product is more favorable than the elimination reaction under high pressure, due to the decrease in the volume of the system. Generally, highly sterically hindered systems show more pronounced pressure effects on the reaction rate[10]. In the case of the solvolysis of t-amyl chloride, the carbonium ion is considerably less hindered compared to that of I and the pressure applied was much lower than that of the present study. Therefore, the effect of pressure on the products may have been too small to detect.

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