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NATURE OF SOLVOLYSIS OF NEOPENTYL TOSYLATE IN AQUEOUS ALCOHOL IN THE PRESENCE OF BASE

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Nucleophilic substitutions on neopentyl carbon were found to be notoriously difficult although not impossible under forcible conditions; a few such examples have been reported.[1-3] However, the nucleophilic solvent assistance (Ks) on the neopentyl carbon is sterically hindered and thus, neopentyl systems are used frequently to study the effectiveness of neighboring group participation.[4]

It has been reported that the rates of the solvolysis of neopentyl halides in aqueous alcohol were independent of the concentration of hydroxide ion present.[5] The solvolysis gave quantitatively the WAGNER-MEERWEIN Rearrangement products, viz; t-amyl alcohol (1), ethyl t-amyl ether (2) and olefin (3). However, we have found, that when the concentration of NaOH was increased, the nucleophilic substitution products, neopentyl alcohol (4) and ethyl neopentyl ether (5) were produced and their yields were increased accordingly with the NaOH concentration (Fig. 1). The products were analyzed by gc and characterized by comparison with authentic samples. The results are summarized in Table 1.

These products were produced from the competitive reactions of the ionization and the nucleophilic substitution by bases. The products 1, 2, and 3 were derived from the same carbonium ion intermediate.[6] The amounts of 1 and 2 were decreased considerably by increasing the NaOH concentration. The decrease in 1 and 2 was due to the increased nucleophilic substitutions on the tosylate ion by bases. The olefins produced were derived from the carbonium ion intermediate and thus, the amount should also be decreased by increasing NaOH. However, the 3 obtained remained almost constant. This may be attributed to the elimination of proton from the carbonium ion, which is enhanced by the base; i.e., the olefin formation is increased by increasing NaOH concentration. Thus, the absence of the net effect of NaOH on the olefin production results from the fortuitous cancellation of these opposite effects of NaOH.

Table 1. Effect of NaOH Concentration on the Solvolysis of Neopentyl Tosylate in Aqueous Ethyl Alcohol[a)]

NaOH N	Ethyl neopentyl ether	Neopentyl alcohol	Ethyl t-amyl ether	t-Amyl alcohol	Olefin	1- and 2-Olefin, %	
						2-Methyl -1-butene	2-Methyl -2-butene
0.25[b)]	1.4	2.4	18.3	44.3	33.6[d)]	42	58
0.63	3.3	4.5	19.2	43.6	29.4	40	60
1.25	7.9	14.2	12.5	34.6	30.8	46	54
1.87	11.8	22.5	11.1	24.0	30.6	49	51
2.25	14.1	24.2	10.1	19.4	32.2	48	52
2.50[c)]	15.5	26.5	10.5	19.0	28.5	49	51

a) The reactions were performed in a Teflon vessel. Tosylate (0.004 mole) was solvolyzed in EtOH (13 ml) - H_2O (7 ml) in the presence of NaOH. The reactions were carried out at 100° for 20-22 hours. The yields, based on the product recovered were 70-80%.

b) 0.25 N corresponds to 0.005 mole

c) This solution was slightly heterogeneous at room temperature.

d) The olefin and t-amyl substitution products of the solvolysis of neopentyl bromide in 50% aqueous ethanol in the presence of NaOH (0.075N) at 125° were reported as 36 and 63%, respectively.[5]

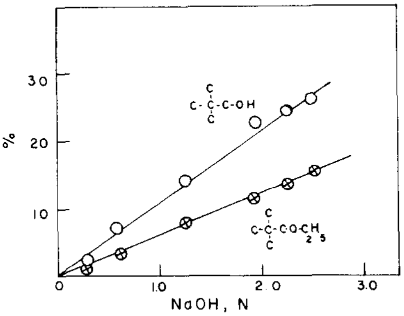

Fig. 1, Effects of NaOH Concentration on the Solvolysis of Neopentyl Tosylate

Comparable amount of 5 obtained should be derived from the nucleophilic substitution of the tosylate with ethoxide ion which would be formed by the equilibrium reaction (I).

$$C_2H_5OH + NaOH \rightleftarrows C_2H_5ONa + H_2O \quad --- \quad (I)$$

A number of investigations on the kinetic study of alkyl halides with hydroxide ion in aqueous-alcohol medium have been reported.[7] Generally, the ether formation from alkyl halide in aqueous alcohol in the presence of NaOH was derived from one of the nucleophilic substitutions by alcohol (Ks) or the reaction of the carbonium ion with alcohol or with alkoxide ion, or a combination of these reactions. They are usually indistinguishable. Neopentyl system presents an interesting case in which Ks is impossible and the ionization process gives only the WAGNER-MEERWEIN Rearrangement products. Therefore, the present results (formation of 5) show that the considerable amount of ethoxide ion exists under the conditions studied and the ethoxide ion directly attacks the tosylate to give ethyl neopentyl ether.

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   The solvolysis reactions were carried out in 70% aqueous ethyl alcohol at 95° in the presence of NaOH up to 0.200N.
6. The methyl-migrated t-amyl cation or bridged methyl cation ion.
7. E.g., C.K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd Ed., Cornell University Press, Ithaca, New York (1969), p. 685.