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The E1 Reaction of Menthyl and Neomenthyl Tosylates in Aprotic Solvents

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The E1 reaction has been studied, especially in protic solvents, in relation to the S_N1 reaction.[1] In contrast to the insistence of Ingold[2] that the intermediates of the S_N1 and E1 reactions were the same, and that there was no solvent effect upon the ratio of the afforded olefin and the replaced product, Winstein[3] established that an elimination from the intimate ion pair occurred in the solvent with a low ionizing power:

$$\begin{tikzcd}
RX \arrow[r, shift left] & R^{\oplus}X^{\ominus} \arrow[l, shift left] \arrow[r, shift left] \arrow[d, "\text{intimate ion pair}"] & R^{\oplus}//X^{\ominus} \arrow[l, shift left] \arrow[r, shift left, "Y^{\oplus}"] \arrow[d, "\text{solvent separated ion pair}"] & RY + X^{\ominus} \arrow[l, shift left] \\
 & \text{olefin} & \text{olefin} &
\end{tikzcd}$$

Chart 1

We examined the E1 reactions of menthyl and neomenthyl tosylates in dimethylsulfoxide (DMSO), dimethylformamide (DMF), acetonitrile, methylene chloride, and 1,2-dichloroethane respectively in hopes of clarifying the effects of the aprotic solvents upon the rates and to obtain insight into the mechanism of this reaction.

The first-roder rate constants are tabulated in Table 1, along with the derived values of the thermodynamic quantities, the enthalpy and entropy of activation, ΔH^{*} and ΔS^{*}. Although no linearity between the rates and the dielectric constants of the solvents was observed, the rate increased as the dielectric constants of the solvent increased. These results may be explained as follows: the use of solvents with high dielectric constants is advantageous for the ionization and dissociation of the substrate.[4]

The rate ratios between neomenthyl and menthyl tosylates in various solvents are summarized in Table 2. It has been suggested that the hydrogen participation in the ionization step of neomenthyl tosylate contributes to the large acetolysis rate ratio between neomenthy

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[1] C.K. Ingold, "Structure and Mechanism in Organic Chemistry," Second Edition, Cornell University Press (1969), p. 649.

[2] K. A. Cooper, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, **1937**., 1280; E. D. Hughes and B. J. MacNulty, *ibid*,. **1937**; 1283 K. A. Cooper, E. D. Hughes, C. K. Ingold, and B. J. MacNulty, *ibid.*, **1948**, 2038.

[3] M. Cocivera and S. Winstein, *J. Amer. Chem. Soc.*, **85**, 1702 (1963).

[4] K. B. Wiberg, "Physical Organic Chemistry, " John Wiley & Sons, New York (1966), pp. 267, 381.

TABLE 1. SUMMARY OF RATE CONSTANTS

Compound	Solvent	Temp. °C	k, sec^{-1}	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$ e.u.
Menthyl OTs	DMSO	90	1.09×10^{-4}		
	DMSO	75	2.00×10^{-5}	28.7	2.1
	DMSO	60	2.78×10^{-6}		
	DMF	95	2.62×10^{-5}		
	DMF	85	6.56×10^{-6}		
	DMF	75	2.10×10^{-6}	31.1	4.3
	DMF a)	60	2.46×10^{-7}		
	CH_3CN	95	$2.6\ \times10^{-5}$		
	CH_3CN	85	7.63×10^{-6}		
	CH_3CN	75	2.06×10^{-6}	31.6	5.8
	CH_3CN a)	60	2.38×10^{-7}		
	CH_2Cl_2	95	4.39×10^{-6}		
	CH_2Cl_2	85	1.38×10^{-6}		
	CH_2Cl_2	75	3.48×10^{-7}	31.6	2.4
	CH_2Cl_2 a)	60	4.32×10^{-8}		
	CH_2ClCH_2Cl	95	4.12×10^{-6}		
	CH_2ClCH_2Cl	85	1.13×10^{-6}		
	CH_2ClCH_2Cl	75	3.09×10^{-7}	32.3	4.1
	CH_2ClCH_2Cl a)	60	3.54×10^{-8}		
Neomenthyl OTs	DMF	60	3.73×10^{-5}		
	DMF	45	6.93×10^{-6}	23.4	−8.8
	DMF	30	1.03×10^{-6}		
	CH_2Cl_2	60	9.71×10^{-7}		

a) Calculated from data at other temperatures.

TABLE 2. THE RATE RATIOS BETWEEN NEOMENTHYL AND MENTHYL TOSYLATE IN THE VARIOUS SOLVENTS

Solvent	Rate ratio (II/I)
DMF	150
Methylene chloride	22
EtOH	99
AcOH	59

and menthyl tosylates.5) The rate ratio in the reaction in DMF was 150, while in methylene chloride it was 22. These results suggest that the hydrogen paticipation does not play an important role, at least in the reaction in methylene chloride.

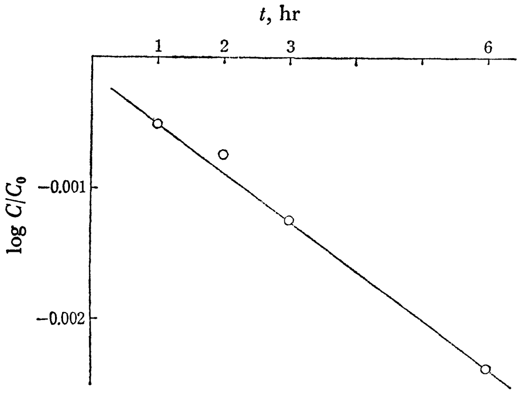

Fig. 1. Isomerization of I to II.
C_0: initial concentration of I. C: concentration of I at time t.

An isomeric change in the configuration of the substrate was found in the reaction in DMF. The El reaction of menthyl tosylate in DMF at 75°C, followed by the reduction of the reaction mixture by lithium amide, led to the isolation of neomenthol, olefins, and menthol. From the relationship of $\log C/C_0$ to the reaction time (Fig. 1), the rate of the isomerization of menthyl tosylate to neomenthyl tosylate was estimated to be 2.38×10^{-7} sec^{-1}, which is one order of magnitude smaller than the rate of the olefin formation (2.10×10^{-6} sec^{-1}). The neomenthyl derivative was not detected in the reaction mixtures obtained by reactions in any other solvents except DMF.

Experimental

Materials. DMSO and DMF were purified by drying them over calcium hydride, and they were distilled under diminished pressure. Acetonitrile was purified by the method of Coetzee *et al.*6) Methylene chloride and 1,2-dichloroethane was dried over calcium chloride and distilled. Menthyl tosylate was obtained by following the method of Winstein;4) mp 92.2—93.3°C (lit, 93.5—94.04)). Neomenthyl tosylate was prepared from neomenthol with tosyl chloride; mp 62.5—63.9°C7) (lit, 63.0—63.5°C).

Kinetic Procedure. The rates were measured by using glass tubes which could be closed by means of a polyethylene cap. The thermostats were of a conventional design and maintained the temperature within±0.05°C. The reaction mixtures were prepared from the known weight of a solute and from the solvent volumetrically. The reactions were followed by withdrawing ampoules from the thermostat at suitable intervals and by titrating them with a sodium acetate-methanol solution, using bromophenol blue as the indicator.

The Reaction in DMF. The reaction of menthyl tosylate (300 mg) was performed in the presence of two equivalent moles of lutidine in 20 m*l* of the solvent at 75°C. The reaction mixture was poured into ice water, extracted by petroleum ether, and dried over anhydrous sodium sulfate. After the evaporation of the solvent, the reaction mixture was reduced with five equivalent moles of lithium amide in ammonia at 70°C for 4 hr. The reaction mixture was hydrolysed by aq. hydrochloric acid, extracted by ether, and dried over anhydrous sodium sulfate. After the evaporation of the solvent, the products were analyzed by means of a Hitachi K-53 vpc apparatus, equipped with a flame-ionization detector on a PEG 6000 column operated at 180°C.

*The Reduction of Menthyl Tosylate.*8) Into a lithium amide-ammonia solution prepared by dissolving 0.8 g (0.05 mol) of lithium in 100 m*l* of ammonia, we added 1.6 g (0.005 mol) of menthyl tosylate dissolved in 10 m*l* of ether. After four hours methanol was added and the mixture was extracted with ether. Then the reaction mixture was treated and analyzed as has been described above; only menthol was present.

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5) S. Winstein, B. K. Morse, E. Crunwald, H. W. Jones, J. Corse D. Trifan, and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1127 (1952).

6) J. F. Coetzee, G. P. Cunningham, D. K. McGuire, and G. R. Padmanabhan, *Anal. Chem.*, **34**, 1139 (1962).

7) W. Hückel, H. Feltkamp, and S. Geiger, *Ann. Chem.*, **637**, 1 (1960).

8) W. G. Dauben and J. Z. Chitwood, *J. Amer. Chem. Soc.*, **92**, 1624 (1970).