Rates of Solvolysis of Bis-p-toluenesulfoxymethylcyclohexanes

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According to the previous work[1] dealing with solvolytic reactivity of a departing group such as a toluenesulfoxy group bound through a methylene linkage to a cyclohexane ring, the compound with a toluenesulfoxy group in an axial position is solvolyzed at a rate 4.2 times as fast and one half as fast as the corresponding isomer with that group in an equatorial position in acetic acid and in ethanol, respectively.

In the present work, the investigation has been extended to similar solvolysis of *cis*- and *trans*-1, 2- and 1, 4-bis-*p*-toluenesulfoxymethylcyclohexanes (described as ditosylates herein).

Experimental and Results

Samples. — All samples were prepared according to the methods by Haggis and Owen[2,3] with some modifications. The four ditosylates so obtained had the following melting points, respectively:

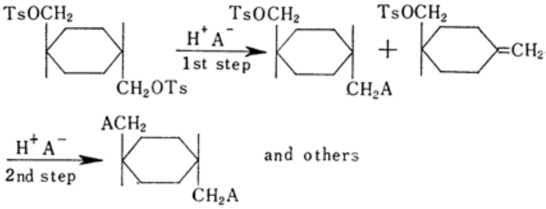
Position of $TsOCH_2$	M. p., °C	M. p. (reported)
cis-1, 2	88	84 ~85[2]
cis-1, 4	94.5~ 95	95[3]
trans-1, 2	107.5~108	108[2]
trans-1, 4	163 ~163.5	162~163[3]

Procedure for Rate Measurements. — Rate measurements were carried out in a similar manner to the previously employed method[4]. Rate constants were calculated from the formula

$$k=2.3/t\cdot\log 2a/(2a-x) \qquad (1)$$

in which a was the initial molar concentration of a ditosylate and x was the molar concentration of sulfonic acid liberated at time t.

Solvolysis was followed to 30~50% completion at 99.8±0.1°C in neutral ethanol (98.5% by weight) and in dry acetic acid containing a slight excess of sodium acetate. Concentrations were 0.01~0.015 mol./l. for the 1, 2-ditosylates and 0.002 mol./l. for the 1, 4-ditosylates, since especially the latter were difficulty soluble in these solvents. The solvolysis proceeds substantially in two steps with different rates where in the first step monotosylates are predominantly produced which in the second step are converted into final products, for example, as illustrated in the case of the *trans*-1, 4-ditosylate by the following formula:



where H^+A^- is the solvent and TsO is the toluenesulfoxy group. In all cases, however, the rate constants derived by Eq. 1 were nearly of the first order with a maximum error of 6%. Table I shows the data of a typical run with the *cis*-1, 2-ditosylate in ethanol at 99.8°C.

The acetolysis rates of the isomeric 1, 2-ditosylates were not substantially influenced by

TABLE I. ETHANOLYSIS OF *cis*-1, 2-BISTOLUENESULFOXYMETHYLCYCLOHEXANE AT 99.8°C

Time sec.	Tosylate mol./l. $\times 10^2$	$k_1\times 10^5$/sec.
0	1.06	
6000	0.955	(1.73)
10800	0.890	1.61
14400	0.835	1.65
20400	0.763	1.61
27000	0.684	1.62
		Mean 1.6

TABLE II. SUMMARY OF SOLVOLYSIS RATES AT 99.8°C

Position of $TsOCH_2$	Solvent	Tosylate mol./l. $\times 10^2$	$k_1\times 10^5$/sec.
cis-1, 2	EtOH	1.06	1.6
	AcOH*	1.00	0.31
	AcOH	1.33	0.31
trans-1, 2	EtOH	0.884	3.4
	AcOH*	1.00	0.26
	AcOH	1.33	0.27
cis-1, 4	EtOH	0.349	1.0
	AcOH**	0.530	0.49
trans-1, 4	EtOH	0.200	1.5
	AcOH**	0.530	0.21

*, ** Contained AcONa in 0.0300 and 0.0150 mol./l., respectively.

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[1] N. Mori, This Bulletin, 35, 1755 (1962).

[2] G. A. Haggis and L. N. Owen, *J. Chem. Soc.*, **1953**, 389.

[3] G. A. Haggis and L. N. Owen, ibid., **1953**, 404.

[4] N. Mori, This Bulletin, 33, 1144 (1960).

TABLE III. RELATIVE RATES

Position of $TsOCH_2$	k_{EtOH}/k_{AcOH}	k_{cis}/k_{trans}	
		EtOH	AcOH
cis-1, 2	5.1	0.47	1.2
trans-1, 2	13		
cis-1, 4	2.6	0.68	2.3
trans-1, 4	7.1		
4-*t*-Butylcyclohexylmethyl tosylate[1], *cis*	0.76	0.51	4.2
trans	6.4		

the absence of sodium acetate. The rate constants and the relative rates are summarized in Tables II and III.

Discussion

In the isomeric 1, 4-ditosylates, the trans-form may substantially exist in a diequatorial conformation while a diaxial conformation is negligible, since the energy required for moving the toluenesulfoxymethyl group from an equatorial to an axial position is 1.7 kcal./mol.[1] and therefore the free energy difference between the two conformations may be 3.4 kcal./mol. which indicates the proportion of the former conformation in the ground state to be more than 99%. On the other hand, especially in the *trans*-1, 2-ditosylate there are probably some interactions such as the steric and the electrostatic repulsion between the two bulky and polar toluenesulfoxymethyl groups, and therefore for this ditosylate a diaxial conformation may be preferable, as shown in various *trans*-1, 2-disubstituted cyclohexanes[5] containing dipolar groupings such as halogen and others, which are mainly in a diaxial conformation. Accordingly, from the considerations based on the conformational preference at the ground state and the previous results described above, it is expected that the *cis*-1, 4-ditosylate is acetolyzed more rapidly than the trans-isomer with a relatively low ratio of k_{cis}/k_{trans}, as compared with the value of 4.2 for 4-*t*-butylcyclohexylmethyl tosylate, because in the cis-form one of the two toluenesulfoxymethyl groups is always axial. On the other hand, in the 1, 2-ditosylates it may be difficult to expect their solvolysis behavior.

According to the experiments, the rate ratio in acetolysis is 2.3 for the 1, 4-ditosylate and also 1.2 for the 1, 2-ditosylate.

Further, the *cis*-1, 4-ditosylate and also the *cis*-1, 2-ditosylate are ethanolyzed more slowly than the corresponding trans-isomers with a similar trend in rate ratio to that (0.51) for the 4-*t*-butyl compound, as seen in Table III.

Further, a ratio of k_{EtOH}/k_{AcOH} is 0.76 for the *cis*-4-*t*-butyl compound and 6.4 for the trans-isomer. The high ratios of 5.1 and 2.6 for the *cis*-1, 2 and 1, 4-ditosylates should be due to one equatorial toluenesulfoxymethyl group present in them.

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[5] H. A. Smith and F. P. Byrne, *J. Am. Chem. Soc.*, 72, 4406 (1950); K. Kozima and T. Yoshino, ibid., 75, 166 (1953); M. Kilpatrick and J. G. Morse, ibid., 75, 1846 (1953); A. Tulinskie, A. D. Giacomo and C. P. Smyth, ibid., 75, 3552 (1953).