Rates of Solvolysis of 2-Hydroxycyclohexyl Brosylates

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In the present paper there will be reported the preparation and the solvolysis rates of *cis*- and *trans*-2-hydroxycyclohexyl brosylates. The *cis* isomer used for solvolysis is a new substance and could not be prepared by the usual method[1]. The *cis* isomer has now been obtained in a good yield by the reaction of *cis*-cyclohexane-1, 2-diol with 2 to 3 equivalent quantities of *p*-bromobenzenesulfonyl chloride in dry pyridine.

The solvolysis rates were measured at 99.8°C in ethanol (98.5% by weight) and also in acetic acid containing a slight excess of acetic anhydride. In all cases, the observed rates, especially in ethanol, were of the first order and the error of the measurements was always lower than 5%. In acetolysis, one free hydroxyl group in each of the isomers will react with acetic acid to form 2-acetoxycyclohexyl brosylate, especially in the presence of *p*-bromobenzenesulfonic acid liberated during the solvolysis. Therefore, a calculated first order rate constant in a run in acetic acid will change continuously and gradually. However, the rates were nearly of the first order. Table I lists the data for a run with *trans*-2-hydroxycyclohexyl brosylate in acetic acid. It is seen that in the run the first order rate constant is almost constant. The slight increase of the rate the during run is probably attributed to the accompanying acetolysis of the corresponding acetoxy cyclohexyl brosylate formed.

TABLE I. ACETOLYSIS OF *trans*-2-HYDROXYCYCLOHEXYL BROSYLATE IN ACETIC ACID AT 99.8°C

Time (min.)	Brosylate (mol./l.)		$k_1 \times 10^2$ (min^{-1})
0.0	6.16×10^3		
30	3.36		2.02
50	2.20		2.06
70	1.49		2.02
90	0.91		2.12
110	0.051		2.26
150	0.016		2.44
		Mean	2.15

The rate constants and the relative rates for the isomeric brosylates are summarized in Table II.

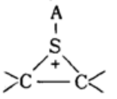
TABLE II. RATE CONSTANTS AND RELATIVE RATES FOR BROSYLATES AT 99.8°C

	$k_1 \times 10^2$, min^{-1}		k_{cis}/k_{trans}	
2-Substituent	EtOH	AcOH	EtOH	AcOH
cis-OH	9.5	2.23	1.1	1.03
trans-OH	8.5	2.15		
cis-OAc		0.0058*		
trans-OAc		3.1*		
H	ca. 11**			

* From data in Ref. 1

** Calculated from data at lower temperatures in Ref. 1

Generally, in solvolysis of 2-functionally substituted cyclohexyl brosylates and tosylates, the reaction rate of the *trans*-forms is larger than that of the *cis*-form. For example, the relative rates of acetolysis (at 75°C) of 2-acetoxycyclohexyl *p*-brosylates are in the following sequence[1]: unsubstituted (1.0) > *trans* (0.3) ≪ *cis* (1.31×10^{-4}). In those cases, with the *trans*-group, the reaction proceeds substantially by way of cyclic ion I, and with the *cis*-group, probably carbonium ion II.



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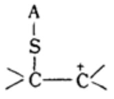

II

However, unlike those compounds, the reactivity of *cis*-2-hydroxycyclohexyl brosylate is slightly greater than that of the *trans*-isomer. Further, the rate constants for the brosylates are in the same order as that for unsubstituted cyclohexyl *p*-brosylate (see Table II). The slightly higher reactivity of the *cis*-isomer and the very small difference in reactivity between the *cis*- and *trans*-isomers can not be explained on the basis of the participation of hydroxyl group alone. The high reactivity of the isomers is probably due to the participation of the hydrogen atom in β-position similar to unsubstituted cyclohexyl brosylate, rather than due to that of hydroxyl group. The fact that the reactivity of the *cis*-isomer is higher than that of the *trans*-isomer is mainly due to steric acceleration based on 1*a*, 3*a*-interaction (or B-strain). Those facts are in good agreement

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[1] S. Winstein, E. Grundwald and L. L. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948).

with the behavior in solvolysis of 2-*tert*.-butylcyclohexyl *p*-tosylate[2].

Experimental

Samples and Solvents. ***cis*-2-Hydroxycyclohexyl *p*-Brosylate.**—A solution of 0.5g. of *cis*-cyclohexane-1,2-diol (m. p. 97°C., prepared from cyclohexene in *tert*.-butanol with OsO_4[3]) in 2 cc. of dry pyridine was treated with 2.5 g. of *p*-bromobenzenesulfonyl chloride at 5 to 10°C. After 30 to 40 min. the mixture was diluted with cold 6N HCl and the oily product precipitated was triturated with dil. HCl repeatedly to solidify. After recrystallization from benzene and ligroin (b. p. 75~120°C), 0.7 g. of the *cis*-brosylate was obtained as brittle needles, m. p. 110.6°C.

Found: C, 42.93; H, 4.80. Calcd. for $C_{12}H_{15}O_4SBr$: C, 42.99; H, 4.51%.

***trans*-2--Hydroxycyclohexyl *p*-Brosylate** was obtained with a good yield from *trans*-cyclohexane-1,2-diol (m. p. 102~104°C., prepared from cyclohexene and hydrogen peroxide in formic acid[4]) in an analogous way to the *cis*-isomer. After recrystallization from benzene and ligroin, the *trans*-brosylate was obtained as needles, m. p. 108°C (reported 106.9~108.8°C[1]).

Ethanol (98.5% by weight).—Commercial reagent grade absolute ethanol was fractionally distilled.

Acetic Acid.—Reagent grade glacial acetic acid was crystallized twice by the freezing method, refluxed with 2% by weight of acetic anhydride and 1% by weight of anhydrous sodium acetate for 3 hr., and distilled.

Procedure for Rate Measurements[5].—The sample was weighed out and made up to volume in the solvent at 15~20°C. About 6~7 cc. portions were sealed in tubes and immersed in vapor over boiling water (99.8°C). Time was counted from immersion of the tube to its removal and quenching in ice-water. After being cooled the tube was allowed to come to room temperature and then opened, a 5 cc. aliquot was pippetted out and titrated with standard base from a 2 cc. microburet. Concentrations of brosylates (all given at room temperature) were in the range from 0.02 to 0.07 mol./l. and titrations in acetic acid were carried out with a 0.05 N standard solution of AcONa in acetic acid with Bromophenol Blue as indicator, and in ethanol, a 0.05 N standard aquous solution of NaOH was used for titration with phenolphthalein as indicator. Rate constants were calculated from the formula

$$k_1 = 1/t \cdot \ln a/(a-x)$$

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

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2) H. L. Goering and R. L. Reeves, *J. Am. Chem. Soc.*, **78**, 4931 (1956).

3) N. A. Milas and S. Sussman, ibid., **59**, 2345 (1937).

4) Organic Synthesis, Vol. 28, p. 35 (1948).

5) N. Mori, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 1458 (1959).