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The Solvolytic Isomerization and Rearrangement of *cis*-4-*t*-Butylcyclohexyl *p*-Toluenesulfonate

Kunio OKAMOTO, Seiki SAITÔ and Haruo SHINGU

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

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In a previous paper, we have demonstrated that, during the course of the phenolysis, *cis*- and *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonates (*cis*- and *trans*-4-ROTs) are isomerized into their respective geometrical isomers, and that they also undergo 1,2-rearrangement to give the 3-*t*-butylcyclohexyl toslyates (*cis*- and *trans*-3-ROTs).[1] Accordingly, such a solvolytic isomerization and rearrangement of these tosylates should occur also in common hydroxylic solvents other than phenol. The interest of the previous investigators with respect to this *t*-butylcyclohexyl system has, however, been confined only rate and product studies;[2] no papers concerned with the solvolytic isomerization and rearrangement of this system have appeared except ours.[1]

To test this prediction, we conducted acetolysis and hydrolysis on *cis*-4-ROTs at 75 and 65°C respectively; after the interruption of the solvolysis at 74 and 70% completion, we identified the four isomeric tosylates, *i.e.*, *trans*-4-, *cis*-4-, *trans*-3-, and *cis*-3-ROTs, in the recovered tosylate mixtures. The results are tabulated in Table 1, along with the results in the phenol solvent.[1] In view of the facile occurrence of the solvolytic isomerization and rearrangement in the three solvent-systems shown in Table 1, one should consider these phenomena to be general in the solvolysis of the *t*-butylcyclohexyl system.

In Fig. 1, the percentages of *trans*-4-, *cis*-3-, and *trans*-3-ROTs in the recovered tosylate mixtures in the acetolysis are plotted against the effective concentration of sodium tosylate, which is designated as one-half of the concentration of the sodium tosylate, increased until the moment when the solvolysis is interrupted.

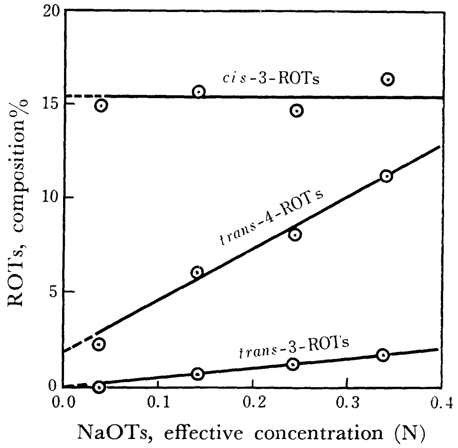
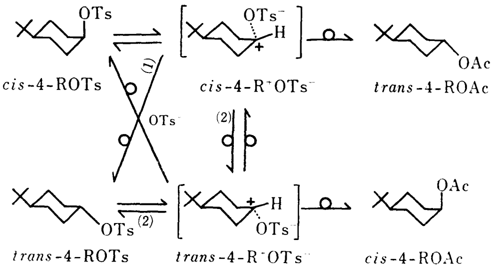


Fig. 1. The composition of the tosylate recovered at 74% completion in the acetolysis conducted in the presence of NaOAc (0.100 N) and of added NaOTs (0.00, 0.10, 0.20, and 0.30 N) at 75.0°C.

In a fashion similar to that of the explanation previously presented in the case of the phenolysis,[1] the trend of linear increase in the percentage of *trans*-4-ROTs (Fig. 1) can be explained as reflecting the following two reaction courses for the formation of *trans*-4-ROTs: (1) the S_N2-like attack of the tosylate anion on the *cis*-type ion-pair intermediate (*cis*-4-R^+OTs^-)[1]; (2) the internal return of the *trans*-type ion-pair intermediate (*trans*-4-R^+OTs^-),[1] which is "intramolecularly" formed by the rotation of the carbonium ion (R^+) in the *cis*-type ion-pair intermediate. The occurrence of the latter process is proved by the interception of the *trans*-4-ROTs line on the coordinate axis of Fig. 1. The two courses are illustrated in the following reaction scheme:



As was explained in the case of the phenolysis,[1] the invariability of the percentage of *cis*-3-ROTs (Fig. 1) indicates that the 1,2-rearrangement is almost intramolecular in nature, namely, that it

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[1] K. Okamoto, S. Saitô and H. Shingu, This Bulletin, **42**, 3298 (1969).

[2] a) S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955); b) V. J. Shiner, Jr., and J. G. Jewett, *ibid.*, **87**, 1382 (1965); c) N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam and M. C. Whiting, *J. Chem. Soc., B*, **1968**, 355.

TABLE 1. THE CCMPOSITION OF THE RECOVERED TOSYLATES IN THE PARTIAL SOLVOLYSIS OF *cis*-4-*t*-BUTYLCYCLOHEXYL *p*-TOLUENESULFONATE

Solvent	Temp. °C	Completion %	Recovered ROTs[d] %	Composition%			
				trans-4	*cis*-4	*trans*-3	*cis*-3
Acetic acid[a]	75	74.3	22.1	2.2	82.9	0.0	14.9
60% aq. acetone[b]	65	70	29.4	9.4	72.3	6.7	11.6
Phenol-benzene[c] (1 : 1 by wt)	75	75.5	23.6	1.1	88.3	0.0	10.6

a) In the presence of 0.100 N NaOAc. The initial concentration of *cis*-4-ROTs was 0.100 M.
b) In the presence of 0.048 N Et_3N. The initial concentration of *cis*-4-ROTs was 0.047 M.
c) In the presence of 0.100 N Et_3N; Cited from Ref. 1.
d) Assayed by the solvolysis.

TABLE 2. PRODUCT COMPOSITION OF THE PARTIAL SOLVOLYSIS OF *cic*-4-*t*-BUTYLCYCLOHEXYL *p*-TOLUENESULFONATE

Solvent and temp.	Cyclohexenes composition			RY (Y=OAc, OH, and OPh) Composition				Ref.
	4-*t*-Bu	3-*t*-Bn	1-*t*-Bu	*trans*-4	*cis*-4	*trans*-3	*cis*-3	
Acetic acid[a] 75.0°C	98.3	1.7	trace	67.5	5.4	25.6	1.5	This paper
Acetic acid[b] 100°C	96.8	3.1	0.1	56.7	5.8	34.2	3.3	Ref. 2c
60% aq. acetone[c] 65°C (reflux temp.)	96.5	1.3	2.2	86.1	2.7	10.3	0.9	This paper
Phenol-benzene[d] (1 : 1 by wt.) 75°C	97.4	2.6	trace	55.0	20.4	13.7	10.9	Previous paper[d]

a) See footnote a in Table 1. Products were assayed by glc.
b) In the presence of 0.05 N NaOAc; the result of the complete acetolysis.
c) See footnote b in Table 1. Products were assayed by glc.
d) In the presence of 0.100 N Et_3N; the result of the complete phenolysis. Cited from our previous paper (K. Okamoto *et al.*, This Bulletin, **42**, 3288 (1969)).

may be caused by the 1,2-hydride shift in the *cis*-type ion-pair intermediate (*cis*-4-R^+OTs^-); the linear increase in the percentage of *trans*-3-ROTs with an increase in the concentration of the added tosylate anion (Fig. 1) indicates that *trans*-3-ROTs is formed mostly by the intermolecular S_N2-like attack of the tosylate anion on the *cis*-3-R^+OTs^--type ion-pair intermediate, which can be formed intramolecularly from the *cis*-4-R^+OTs^--type ion-pair intermediate.

In Table 2, the compositions of the reaction products are presented; they show that, of the three solvents, the phenol solvent is the most effective for the formation of the retained substitution product, *i.e.*, *cis*-4-RY; the composition of olefins is not so much affected by the nature of the solvent.

The hypothesis[2a] that the retained product (*cis*-4-RY) comes from the hydrogen bridged ion-pair intermediate may be considered to be unnecessary, since the considerable solvolytic isomerization of *cis*-4-ROTs into *trans*-4-ROTs clearly indicates that, in these solvolyses, the appreciable part of the retained product (*cis*-4-RY) is actually produced by the course of the inversion of *trans*-4-ROTs or the trans-type ion-pair intermediate (*trans*-4-R^+OTs^-); this is illustrated in the above scheme. Furthermore, the interpretation[2b] that the isotope effect caused by the introduction of the deuterium atom into the 2-positions of *cis*-4-ROBs is to be ascribed to the formation of the hydrogen-bridged ion-pair intermediate seems unreasonable, because the isotope effect measured for *cis*-4-ROBs[2b] is seemingly not the effect of a single *cis*-4-ROBs but the composite effect of a brosylate mixture, *viz.*, a mixture of *cis*-4-, *trans*-4-, *cis*-3-, and *trans*-3-ROBs.

Experimental

Recovery of the Unchanged Tosylate from the Solvolysis Mixture and the Analysis of Its Composition. The solvolysis was interrupted after the desired time; then, after the evaporation of the solvent at 0—10°C, the mixture of the solvolysis product and the unchanged tosylate was distilled under 0.1—0.05 mmHg at room temperature to give the product as the distillate and to leave the tosylate as the residual solid; the IR spectra of the recovered tosylate showed that neither acetate nor alcohol was present ($<0.5\%$). The recovered tosylate was cleaved into the parent alcohol using sodium-naphthalene in THF according to the method of Closson *et al.*[3] The alcohol was converted to the corresponding acetate by the method of Rickborn and Quartucci;[4] the analysis of the acetate was performed by glc using a 2 m×4 mm column with 30% PEG 6000 on selite 545 (Yanagimoto) at 130°C.

Product Analysis. The mixture of olefins obtained by the solvolysis was analyzed at 70°C by glc using the column described above. The mixture of the alcohol obtained by the hydrolysis was gas-chromatographically analyzed after its conversion to the corresponding acetate (see above).

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[3] W. D. Closson, P. Wriede and S. Bank, *J. Amer. Chem. Soc.*, **88**, 1581 (1966); see also Ref. 1.

[4] B. Rickborn and J. Quartucci, *J. Org. Chem.*, **29**, 3185 (1964).