BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3298—3305 (1969)

Phenolytic Rearrangement and Isomerization of *cis*- and *trans*-4-*t*-Butylcyclohexyl *p*-Toluenesulfonates in a Phenol-Benzene Solvent*[1]

Kunio OKAMOTO, Seiki SAITÔ and Haruo SHINGU

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

(Received May 15, 1969)

As the first examples of solvolytic *cis-trans* isomerization and 1,2-rearrangement for the 4-*t*-butylcyclohexyl system, phenolytic *cis-trans* (or *trans-cis*) isomerization and 1,2-rearrangement have been found for *cis*- and *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonates in the phenol-benzene (1 : 1 by wt) solvent at 75.0°C. The tosylate, recovered after a 75% completion of the S_N1 phenolysis of the *cis*-4-tosylate, was composed of small amounts of the *trans*-4-tosylate (1%) and the *cis*-3-tosylate (11%), besides 88% of the starting *cis*-4-tosylate, clearly indicating occurrence of both the *cis-trans* isomerization and the 1,2-rearrangement of the starting *cis*-4-tosylate. In a similar fashion, starting from the *trans*-4-tosylate, small amounts of the *cis*-4-tosylate (0.7%) and the *trans*-3-tosylate (2.6%) were recovered from the tosylate after the S_N1 phenolysis was 75% complete. On the basis of the results of an examination into the influence of the added tosylate anion on the extent of isomerization and of rearrangement, it has been suggested that the *cis-trans* or *trans-cis* isomerization results largely from the external S_N2-like attack of the tosylate anion on the S_N1 ion-pair intermediate and partly as a consequence of the rotation of the *t*-butylcyclohexyl cation within the ion-pair intermediate, whereas the 1,2-rearrangement proceeds through an intramolecular 1,2-shift of hydrogen within the 4-*t*-butylcyclohexyl cation.

After the initial work of Winstein and Holness,[1] the solvolytic reactions of 4-*t*-butylcyclohexyl *p*-toluenesulfonates have been investigated by several other workers.[2-4] In these solvolyses, *t*-butylcyclohexene was the major product, while minor amounts of substitution, products were obtained as side products; as a general trend, both the olefin and the substitution product contained a considerable amount of rearranged isomers. In view of the formation of so many rearranged products, we have previously suggested[4] the possibility of the accumulation of rearranged tosylates during the course of the solvolysis of a *t*-butylcyclohexyl tosylate, since the isomerized or rearranged solvolysis intermediate, which produced an isomerized or rearranged product, will also give an isomerized or rearranged tosylate by the course of return.

In this paper, we will report on the results of the examination of such a possibility for the phenolytic *cis-trans* isomerization and the 1,2-rearrangement of *cis*-4- and *trans*-4-tosylates, and will discuss the implications of the results with the structure of the ion-pair intermediate for this system.

Results and Discussion

Recovery and Analysis of the Mixture of *t*-Butylcyclohexyl *p*-Toluenesulfonates. The phenolyses of *cis*- and *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonates were conducted in the presence of triethylamine in a 50 wt% phenol-benzene solvent at 75°C up to 75% completion. After washing with dilute aqueous sodium hydroxide and the subsequent condensation of the organic layer under reduced pressure at room temperature, the residue was treated with sodium naphthalene in THF in order to cleave the tosylate and obtain the corresponding *t*-butylcyclohexanol. The mixture of *t*-butylcyclohexanols was isolated by elution chromatography, and the composition was assayed according to the following scheme:

---

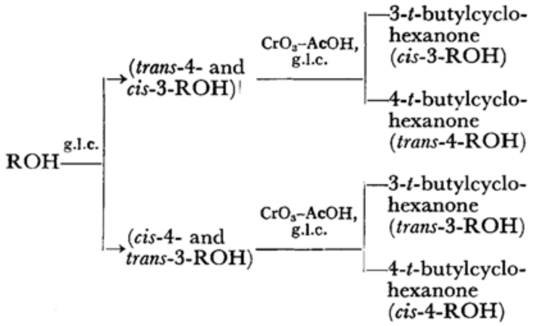
*[1] Presented at the 18th Symposium on the Organic Reaction Mechanism, Kyoto, October, 1967 (Abstract, p. 81) and at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968 (Abstract, Part III, p. 2034).

1) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).

2) V. J. Shiner, Jr., and J. G. Jewett, *ibid.*, **87**, 1382, 1383 (1965).

3) N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southan and M. C. Whiting, *J. Chem. Soc.*, *B*, **1968**, 355.

4) K. Okamoto, S. Saitô and H. Shingu, This Bulletin, **42**, 3288 (1969).



First, the mixture was separated by GLC into two fractions, *i. e.*, a mixture of the *trans*-4- and *cis*-3-alcohols and a mixture of *cis*-4- and *trans*-3-alcohols; then each fraction was oxidized by means of chromium trioxide in acetic acid, giving a mixture of 3- and 4-*t*-butylcyclohexanones, which was then assayed by GLC.

The reductive cleavage of the tosylates with sodium naphthalene was first reported by Closson, Wriede and Bank[5] as an almost ideal procedure for obtaining the alcohols without isomerization. However, the data for the *t*-butylcyclohexyl system have not been made available. Therefore, we examined the degree of isomerization for the *cis*-4-, *trans*-4-, *cis*-3-, and *trans*-3-tosylates in a series of experiments with the authentic tosylates; the results are summarized in Table 1.

From the *trans*-4- and *cis*-3-tosylates obtained under the reaction conditions shown in Table 1, the *t*-butylcyclohexanol contained no isomerized alcohols, whereas the *cis*-4- and *trans*-3-tosylates afforded the respective alcohols contaminated with a small quantity of isomerized alcohols, even though the cleavage was conducted at −1—2°C. The percentage of isomerization observed in the control experiments of *cis*-4- and *trans*-3-tosylates was used as a correction factor for the analysis of the tosylate mixture recovered from the phenolytic products.

Composition of the Tosylate Recovered from the Reaction Mixture for the Phenolysis of *cis*-4-*t*-Butylcyclohexyl *p*-Toluenesulfonate. The phenolysis of *cis*-4-*t*-butylcyclohexyl *p*-toluenesulfonate was carried out in the presence of an equimolar amount of triethylamine in a 50 wt% phenol-benzene solvent at 75°C up to 75% completion. A mixture of the phenolysis products and the unchanged tosylate was isolated from the phenolysis mixture, then cleaved with sodium naphthalene in THF, and subsequently separated into *t*-butylcyclohexanol and the phenolysis products by elution chromatography. The phenolysis products were not affected under the cleavage conditions.[6] The mixture of *t*-butylcyclohexanols was assayed following the scheme described above.

As is summarized in Table 2, the cleavage reaction of the recovered tosylate afforded the corresponding alcohol in a fairly good yield; the *t*-butylcyclohexanol was composed of a large portion (88—89%) of the *cis*-4-alcohol and small amounts of the *cis*-3-alcohol (10%) and the *trans*-4-alcohol (1%). This result clearly indicates that, during the phenolysis of the *cis*-4-tosylate in a phenol-benzene solvent, *cis*-*trans* isomerization and 1,2-rearrangement did occur.

In a previous paper[4] we reported that, during this phenolysis, the first-order plot gave a slight downward drift after 80% completion. In view of the fact that the solvolysis rates of the *cis*-3- and *trans*-4-tosylates are lower than those of the *cis*-4-tosylate,[1,4] this downward drift may be attributed to an accumulation of the less reactive tosylates in the unchanged tosylate with the progress of the

TABLE 1. THE CLEAVAGE OF VARIOUS *t*-BUTYLCYCLOHEXYL *p*-TOLUENESULFONATES WITH SODIUM NAPHTHALENE IN TETRAHYDROFURAN

p-Toluenesulfonate	*trans*-4-ROTs			*cis*-4-ROTs				*trans*-3-ROTs	*cis*-3-ROTs
10^3 mol, used	1.51	1.61	4.20	1.61	1.61	1.94	1.94	1.61	1.65
Na-Naphthalene[a] equivalent	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Temp., °C	32—35	32—37	2—6	28—31	0—7	−1—1	−1—1	−1—2	−1—1
Time, min	16	1	3	3	1	0.5	0.5	0.5	0.5
t-Butylcyclohexanol:									
Yield %	100	98.2	96.4	77.7	90.0	89.6	94.4	94.2	81.5
Composition %									
trans-4-ROH	100.0	100.0	100.0	0.9	1.6	1.2	1.7	—	—
cis-4-ROH	0.0	0.0	0.0	99.1	98.4	98.8	98.3	—	—
cis-3-ROH	—	—	—	—	—	—	—	1.4	100.0
trans-3-ROH	—	—	—	—	—	—	—	98.6	0.0

a) 0.30 mol/*l*

---

[5] W. D. Closson, P. Wriede and S. Bank, *J. Am. Chem. Soc.*, **88**, 1581 (1966).

[6] The results of the analysis of these phenolysis products were reported in a previous paper.[4]

TABLE 2. SUMMARY OF THE CLEAVAGE REACTION OF THE RECOVERED TOSYLATE FOR THE PHENOLYSIS OF *cis*-4-*t*-BUTYLCYCLOHEXYL *p*-TOLUENESULFONATE[a]

ROTs conversion in the phenolysis	ROTs recovered from the phenolysis mixture[b]	Ammonium tosylate added to the phenolysis mixture	*t*-Butylcyclohexanol				
			Yield %[c]	Composition %			
				trans-4-[d]	*cis*-4-	*cis*-3-	*trans*-3
75.9%	23.6%	—	91.4	1.1	88.3	10.6	0.0
72.8%	23.4%	—	84.9	1.0	88.2	10.8	0.0
75.5%	20.6%	Et_3NHOTs 0.101N	94.6	3.4	86.5	10.1	0.0
74.0%	23.2%	Et_3NHOTs 0.226N	89.5	6.7	82.4	10.9	0.0
86.5%	?[e]	Et_2NH_2OTs 0.212N	95.3[f]	4.8	76.8	14.8	0.0

a) The phenolysis was conducted in phenol-benzene (1:1 by wt) solvent at 75°C. Initial concentrations are 0.097—0.10M for the tosylate and 0.11M for triethylamine (see Table 4 in Ref. 4).

b) Analyzed by the phenolysis of the sample for the cleavage reaction; the phenyl ethers contained in the sample was not affected under the cleavage condition.

c) Based on the recovered tosylate.

d) Corrected for the *trans*-4-*t*-butylcyclohexanol produced during the cleavage reaction of *cis*-4-*t*-butylcyclohexyl *p*-toluenesulfonate (see text).

e) Not analyzed.

f) Based on the calculated value (13.5%) for the percentage of the recovered tosylate.

reaction.

In order to obtained further information about the mechanism, the phenolysis was conducted in the presence of added triethyl- or diethyl-ammonium *p*-toluenesulfonates; the composition of the tosylate thus recovered was then compared with that observed in the absence of added alkylammonium salt. In Fig. 1 the percentages of *trans*-4- and *cis*-3-tosylates in the recovered tosylate are plotted against the effective concentrations of the *p*-toluenesulfonate anion, which are defined as the sum of the concentration of the added alkylammonium tosylate and one half of the concentration of the tosylate anion liberated until the interruption of the phenolysis.

The amount of the *trans*-4-tosylate in the recovered tosylate increases linearly with an increase in the effective concentration of the tosylate anion in the reaction medium, and, within the range of experimental error, there seems to exist no isomerized tosylate in the absence of the added tosylate anion. In other words, the *cis-trans* isomerization of the *cis*-4-tosylate seems to proceed almost entirely *via* the intermolecular course including the attack of the tosylate anion on the ion-pair S_N1 intermediate, although the possibility of the intramolecular course including the rotation of the carbonium ion in the ion-pair intermediate can not be entirely eliminated (*vide infra*).

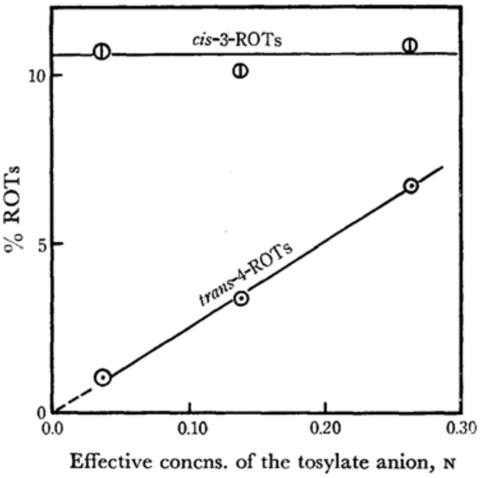
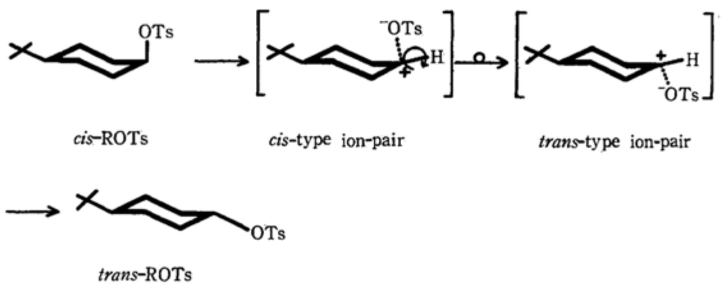
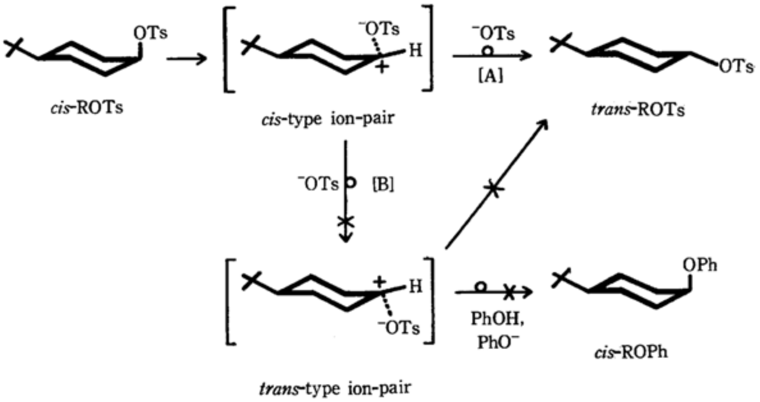


Fig. 1. The percentages of *cis-trans* isomerization and 1,2-rearrangement in the recovered tosylate for the phenolysis of *cis*-4-*t*-butylcyclohexyl *p*-toluenesulfonate in 50 wt% phenol-benzene solvent in the presence of triethylamine at 75°C.

The intramolecular course is illustrated below without considering its reversibility:

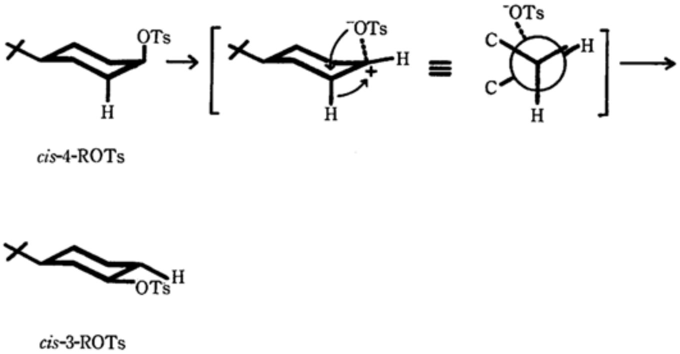


As for the intermolecular course, two pathways are possible: one is a direct return of the *cis*-type ion-pair intermediate to the *trans*-tosylate (Course A), and the other is the return *via* the *trans*-type ion-pair intermediate produced by the S_N2-like attack of the tosylate anion on the *cis*-type intermediate (Course B). These two courses may be illustrated as follows:

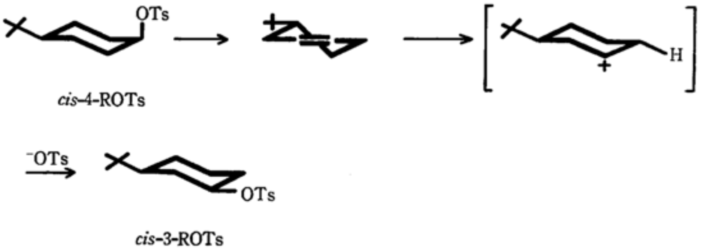


If the concentration of the *trans*-type ion-pair intermediate were increased with the increase in the S_N2-type attack of the tosylate anion on the *cis*-type intermediate (Course B), the portion of *cis*-4-*t*-butylcyclohexyl phenyl ether in the concomitant phenolysis products would also be increased. However, this is not the case; rather, the percentage of the *cis*-4-ether is slightly diminished with the increase in the added $Et_3NH^+OTs^-$.[7] Therefore, the possibility of the B course *via* the *trans*-type intermediate may be excluded.

In contrast to the *cis*-*trans* isomerization, the 1,2-rearrangement of the *cis*-4-tosylate seems to be little affected by the added tosylate anion (Fig. 1). This clearly indicates that the rearrangement is almost intramolecular in nature. Thus, the rearrangement conceivably proceeds *via* the exchange of the positions of the axial tosylate group and the axial neighboring hydrogen, as is illustrated below:



As has been mentioned in the previous paper,[4] since the initially-added *t*-butylcyclohexene does not exert any influence on the composition of the olefin product or of the phenyl ethers in the concurrent phenolysis, the possibility of 1,2-rearrangement *via* a proton addition to a stable molecule of *t*-butylcyclohexene can be eliminated. This course is as follows:



---

[7] See Table 4 in Ref. 4.

TABLE 3. SUMMARY OF THE CLEAVAGE REACTION OF THE RECOVERED TOSYLATE FOR THE PHENOLYSIS OF *trans*-4-*t*-BUTYLCYCLOHEXYL *p*-TOLUENESULFONATE[a]

ROTs conversion in the phenolysis	ROTs recovered from the phenolysis mixture[b]	Et$_3$NHOTs initially added to the phenolysis mixture, N	*t*-Butylcyclohexanol				
			Yield %[c]	Composition %			
				trans-4-	*cis*-4-	*cis*-3-	*trans*-3-
73.6%	25.2%	—	93.3	96.7	0.7	0.0	2.6
76.6%	23.4%	0.106	84.5	95.5	1.4	0.0	3.1
75.0%	25.0%	0.203	86.3	96.5	1.5	0.0	1.8

a) The phenolysis was conducted in phenol-benzene (1 : 1 by wt) solvent at 75°C. Initial concentrations are 0.099—0.10M for ROTs and 0.105—0.109N for Et$_3$N (see Table 4 in Ref. 4).

b) Analyzed by the phenolysis of the sample for the cleavage reaction; the phenyl ethers contained in the sample were not affected under the cleavage condition.

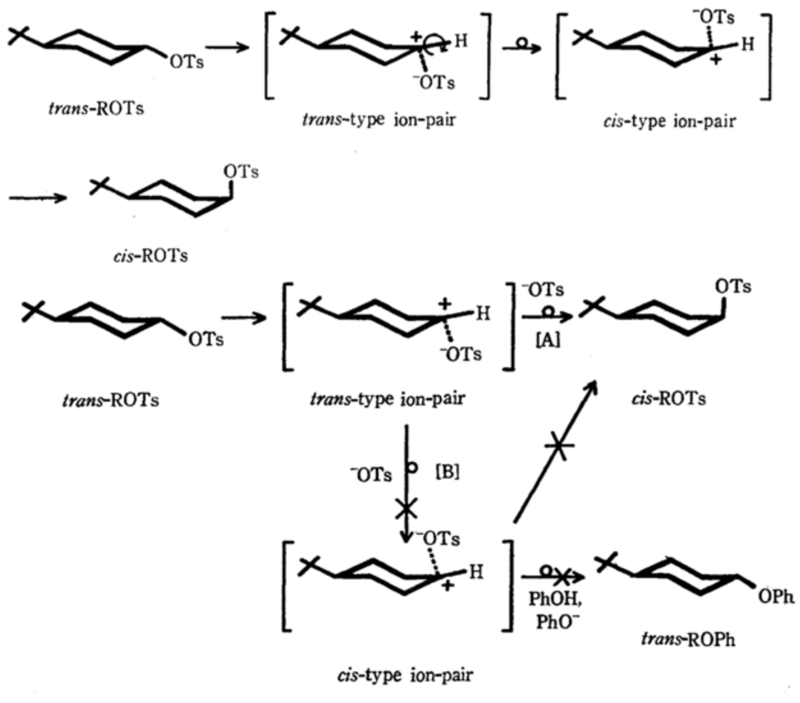
c) Based on the recovered tosylate.

Composition of the Tosylate Recovered from the Reaction for the Phenolysis of *trans*-4-*t*-Butylcyclohexyl *p*-Toluenesulfonate. The phenolysis of *trans*-4-tosylate was conducted in the presence of an equimolar amount of triethylamine in a 50 wt% phenol-benzene solvent at 75°C up to 75% completion. In a manner similar to that in the case of the *cis*-tosylate, *t*-butylcyclohexanol was isolated from the reaction mixture of the cleavage reaction of the recovered tosylate; it was assayed following the scheme described above.

As is shown in Table 3, the *t*-butylcyclohexanol was composed of a large amount (97%) of the *trans*-4-alcohol, derived from the starting *trans*-4-tosylate, and small amounts of the *cis*-4-alcohol (0.7%) and the *trans*-3-alcohol (2.6%). This indicates that, in a fashion similar to that in the case of the *cis*-4-tosylate, *trans-cis* isomerization and 1,2-rearrangement occur during the phenolysis of *trans*-4-tosylate, although the extent of isomerization and of rearrangement is smaller when compared with the case of the *cis*-4-tosylate.

The percentages for the isomerization and the rearrangement are set against the effective concentrations (*vide supra*) of the tosylate anion in the reaction medium in Fig. 2.

The extents of the *trans-cis* isomerization are not much affected by the increase in the effective concentrations of the tosylate anion, and there seems to exist a definite, though small, amount of *trans-cis* isomerization even in the absence of the tosylate anion. Therefore, it is conceivable that, for the *trans-cis* isomerization, there exist both the intramolecular and the intermolecular courses and that the latter course becomes predominant with the increase in the concentration of the tosylate anion. These courses are illustrated below.



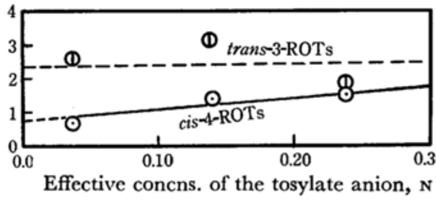
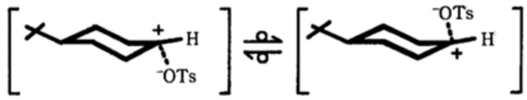


Fig. 2. The percentage of *trans-cis* isomerization and 1,2-rearrangement in the recovered tosylate for the phenolysis of *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonate in 50 wt% phenol-benzene solvent in the presence of triethylamine at 75°C.

As has been mentioned above, the intramolecular course for the *cis-trans* isomerization of the *cis*-tosylate was not observed within the range of experimental error. However, in view of the existence of the intramolecular course in the *trans-cis* isomerization, the intramolecular course should exist also in the case of the *cis*-tosylate isomerization, judging from the microscopic reversibility, as is shown below:



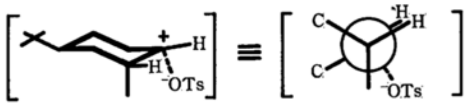
trans-type ion-pair *cis*-type ion-pair

Therefore, the apparent absence of the intramolecular course for the *cis-trans* isomerization may be attributed to the relative rapidity of the rate of the intermolecular isomerization, *i.e.*, the rate of attack of the tosylate anion on the *cis*-type ion-pair, as compared with the rate of intermolecular isomerization, *i.e.*, the rate of the internal rotation of the 4-*t*-butylcyclohexyl cation in the *cis*-type ion-pair intermediate.

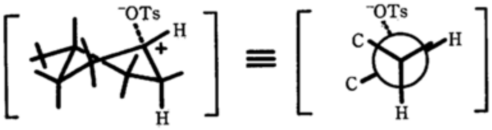
In view of the fact that the portions of *trans*-4-*t*-butylcyclohexyl phenyl ether in the products of the concomitant phenolysis decrease with an increase in the concentration of the added tosylate anion,[6] it is conceivable that the concentration of the *cis*-type ion-pair intermediate does not increase with the increase in the added tosylate anion. Consequently, the course to the *cis*-4-tosylate *via* the *cis*-type ion-pair intermediate (Course B) may be excluded.

The extent of 1,2-rearrangement for the *trans*-tosylate changes non-linearly with the increase in the effective concentration of the tosylate anion, this being shown in Fig. 2. A thorough interpretation of this trend would be difficult. However, there seems to exist no definite tendency of increase with the increase in the concentration of the tosylate anion. Consequently, we may conceive this 1,2-rearrangement to be intramolecular in nature.

Since the tosyl-group and the neighboring equatorial hydrogen atom are in the *syn*-position in the chair conformation of the ion-pair intermediate from the *trans*-4-tosylate, it seems to be rather difficult for them to exchange their positions with each other, this being illustrated as follows:



However, if a twist boat conformation is assumed for the *t*-butylcyclohexyl cation, as was first suggested in the case of the solvolysis in 50% aqueous ethanol by Shiner and Jewett,[2] a facile exchange of the two groups would be achieved because of their *anti*-position. This is illustrated as follows:



As in the case of the *cis*-tosylate, the initially added *t*-butylcyclohexenes exerted little influence on the composition of the olefin product or of the phenyl ethers in the concomitant phenolysis.[4] Thus, the possibility of 1,2-rearrangement *via* a proton addition to a stable molecule of *t*-butylcyclohexene can be excluded for the *trans*-tosylate.

The results presented in this paper clearly suggest the possibility of the solvolytic rearrangement or isomerization of the 4-*t*-butylcyclohexyl system in a solvent other than phenol. The details of the examination of the other solvents will be reported in a succeeding paper.

Experimental[8]

Materials. The *t*-butylcyclohexanols (*cis*-4, *trans*-4, *cis*-3 and *trans*-3), *t*-butylcyclohexyl tosylates (*cis*-4, *trans*-4, *cis*-3 and *trans*-3), 3- and 4-*t*-butylcyclohexanones, and triethylammonium and diethylammonium tosylates were synthesized as described in a previous paper.[4] Benzene, phenol, triethylamine, and tetrahydrofuran (each of a reagent grade) were dried and purified by fractional distillation: benzene, bp 80.2—80.5°C; phenol, bp 181—182°C; triethylamine, bp 89—89.8°C; tetrahydrofuran, bp 66.7—66.9°C. The naphthalene (reagent grade) was used without further purification.

Gas-liquid Chromatography of *t*-Butylcyclohexanols. The gas-liquid chromatography of isomeric *t*-butylcyclohexanols was performed on a 2 m×4 mm copper-tubing column packed with 30 wt% PEG 6000 on selite (80—100 mesh) at 150°C, and the hydrogen flow rate was adjusted to 60 m*l*/min; benzene solutions (15—25 μl) of *t*-butylcyclohexanols (5—10 wt%) were injected. Retention times: *cis*-4-OH, 18.0 min; *trans*-4-OH, 20.5 min; *cis*-3-OH, 20.3 min; *trans*-3-OH, 17.9 min. We could not separate the mixture of the *trans*-4- and

---

[8] The melting points are not corrected. The infrared spectra were determined with a Shimadzu Model IR-27 spectrophotometer. All the GLC studies were made with a Shimadzu Model GC-2B dual-column gas chromatograph.

cis-3- (equatorial) isomers or the mixture of the *trans*-3- and *cis*-4- (axial) isomers under these conditions.

Gas-liquid Chromatography of *t*-Butylcyclohexanones. A mixture of 3- and 4-*t*-butylcyclohexanones was separated on a 2-m column packed with 30% PEG 6000 on selite at 110°C, using hydrogen as the carrier gas (70 m*l*/min). Benzene solutions (40—50 μl) of ketones (5 wt%) were injected. The retention times of the 3- and 4-*t*-butylcyclohexanones were 51.9 min and 56.8 min respectively; calibration was carried out with ketones of known compositions.

Analysis of *t*-Butylcyclohexanols. Mixtures of the *cis*-4- and *trans*-3-alcohols and of the *trans*-4- and *cis*-3-alcohols were separated gas-chromatographically, using a 5-m column and two liquid-nitrogen traps; then each fraction was converted into a mixture of 3- and 4-ketones by treating it with chromium trioxide in acetic acid according to the method of Winstein and Holness.[1] This 3- and 4-ketone mixture was gas-chromatographically analyzed. The calibration was performed by the oxidation of mixtures of the respective alcohols of known compositions.

The Cleavage of *t*-Butylcyclohexyl *p*-Toluenesulfonates into the Parent Alcohols Using Sodium Naphthalene in Tetrahydrofuran. *A) Cleavage of trans-4-t-Butylcyclohexyl p-Toluenesulfonate.* In 100-m*l* four-necked flask, equipped with a mechanical stirrer, a thermometer, a dropping funnel and a calcium chloride tube, there were placed successively 3.42 g (0.0267 mol) of naphthalene, 84 m*l* of THF, and 0.580 g of matallic sodium, which has been cut in small pieces, all under a nitrogen atomosphere at room temperature. The mixture was then stirred for 1 hr to produce a dark green solution of sodium naphthalene.

To this sodium naphthalene solution there was added a solution of 1.30 g (0.0042 mol) of the *trans*-4-tosylate in 7 m*l* of THF at 0°C through a dropping funnel over a period of 1 min. Then, the sodium naphthalene solution was immediately decomposed by the addition of aqueous THF. The reaction mixture was treated with 100 m*l* of water and 30 g of sodium chloride. The water layer was extracted with three 50-m*l* portions of ether, and the combined ether extracts were washed with 10% aqueous sodium chloride solution and then dried over anhydrous magnesium sulfate. The ether solution was concentrated to give 4.0 g of a crystalline material, which was chromatographed over 100 g of silica gel (Nakarai, No. II-A. 100—200 mesh). The column was eluted successively with benzene, *n*-hexane-ether (9 : 1 by vol), *n*-hexane-ether (4 : 1 by vol), and *n*-hexane-ether (1 : 1 by vol), 25-m*l* portions being taken. The fractions 3—8, obtained using benzene, gave 3.07 g of naphthalene. The fractions 9—16, obtained using *n*-hexane-ether (9 : 1 by vol), did not give anything. The fractions 17—24, obtained using *n*-hexane-ether (4 : 1 by vol), gave 162 mg of a viscous oil the infrared spectrum of which exhibited a strong absorption at 1060 cm^{-1}; no attempt was made to characterize this material further. The fractions 25—31, obtained using *n*-hexane-ether (4 : 1 by vol), gave 67.1 mg of an oily material. The evaporation of this material under 4 mmHg at 80°C gave, in a dry-ice-methanol trap, 4-*t*-butylcyclohexanone (20.6 mg, 3.2% yield; mp 46—49°C; mp 48—51°C on admixture with an authentic sample of 4-*t*-butylcyclohexanone; the infrared spectrum was identical with that of an authentic sample of 4-*t*-butylcyclohexanone). The infrared spectrum of the remaining high-boiling material was identical with that of the viscous oil given by the preceding fractions 17—24. The fractions 48—57, obtained using *n*-hexane-ether (1 : 1 by vol), gave 630 mg of *trans*-4-*t*-butylcyclohexanol (96.4% yield). The GLC analysis of the alcohol of the fraction 48 (27.4 mg) indicated one peak with a retention time of 21.1 min (an authentic *trans*-4-alcohol, 20.5 min). The results of this run are listed in Table 1, along with the results of other runs under different reaction conditions.

B) Cleavage of cis-4-t-Butylcyclohexyl p-Toluenesulfonate. To a sodium naphthalene solution in THF, prepared from 1.50 g (0.0116 mol) of naphthalene, 40 m*l* of THF, and 0.270 g (0.0116 mol) of metallic sodium, there was added a solution of 0.602 g (0.00194 mol) of the *cis*-4-tosylate in 3 m*l* of THF at −1—3°C over a period of 0.5 min. Working-up in the usual way gave a residual crystalline material (1.5 g), which was then chromatographed over 50 g of silica gel (Nakarai, No. II-A. 100—200 mesh). The column was eluted successively with benzene, *n*-hexane-ether (4 : 1 by vol), and *n*-hexane-ether (3 : 2 by vol), 25-m*l* portions being taken. The fractions 1—5, obtained using benzene, 1.39 g of naphthalene. The fractions 12—17, obtained using *n*-hexane-ether (4 : 1 by vol), gave 126.3 mg of a viscous oil from which, by means of the working-up described in section A, 4-*t*-butylcyclohexanone (19.0 mg, 6.4% yield) was collected in the trap. The fractions 18—29, obtained using *n*-hexane-ether (3 : 2 by vol), gave 289.3 mg of 4-*t*-butylcyclohexanol (94.4% yield). Analysis of the alcohol of the fraction 25 by GLC showed one peak corresponding to *cis*-4-*t*-butylcyclohexanol. Analysis of the combined alcohol fractions from 26 to 29 by GLC showed two peaks, corresponding to *cis*- and *trans*-4-*t*-butylcyclohexanol respectively. The percentage of the *trans*-4-alcohol produced during the cleavage reaction of the *cis*-4-tosylate was calculated to be 1.70% of the total alcohol. The results of the cleavage reactions of *cis*-4-tosylate under various reaction conditions are summarized in Table 1.

C) Cleavage of cis- and trans-3-t-Butylcyclohexyl p-Toluenesulfonates. The cleavage reactions for *cis*- and *trans*-3-tosylates were carried out in the same way as above. These results are summarized in Table 1.

D) Cleavage of a Mixture of Tosylates with a Known Composition. A mixture of *cis*-4- (0.339 g), *trans*-4- (0.0723 g), *cis*-3- (0.0306 g), and *trans*-3-tosylates (0.0691 g) was cleaved in the same way as above. A mixture of four isomeric alcohols was obtained in a 90% yield; the analysis of the composition according to the analysis scheme described above gave the following results, after correction for the rearrangement of axial (*cis*-4 and *trans*-3) compounds to equatorial (*trans*-4 and *cis*-3) compounds during the cleavage reaction (see Table 1): *cis*-4, 66.3%; *trans*-4, 14.7%; *cis*-3, 5.0%; *trans*-3, 14.0%. On the other hand, the composition of the starting tosylate mixture was as follows: *cis*-4, 66.3%; *trans*-4, 14.1%; *cis*-3, 6.0%; *trans*-3, 13.5%.

Cleavage of the Tosylate Recovered from the Reaction Mixture for the Phenolysis of *cis*-4-*t*-Butylcyclohexyl *p*-Toluenesulfonate. The phenolysis of *cis*-4-*t*-butylcyclohexyl *p*-toluenesulfonate (3.11 g) in phenol-benzene (1 : 1 by wt) (100 m*l*) in the presence of triethylamine (0.103N) was conducted following a previously-described method[4]; the phenolysis mixture (1.002 g), containing unchanged tosylate, was recovered after 1.0 hr (72.8% completion), by employing the procedure reported in a previous paper.[4] A part of the recovered phenolysis mixture (0.139 g) was further phenolyzed, and the composition of the tosylate present in the mixture was determined to be 72.5 wt% (23.6% based on starting tosylate) from the infinity titers. The rest of the recovered phenolysis mixture (0.863 g) was treated with sodium naphthalene in THF, prepared from 1.85 g of naphthalene, 0.325 g of metallic sodium, and 43 m*l* of THF; working-up in the usual way gave 2.2 g of a crystalline material, which was then chromatographed over silica gel (60 g, Nakarai, No. II-A. 100—200 mesh) to give *t*-butylcyclohexanone (11.1 mg, 3.6% yield) from fractions 13—17 (25-m*l* per one fraction), obtained using *n*-hexane-ether (4 : 1 by vol), and *t*-butylcyclohexanol (267 mg, 84.9% yield) from fractions 22—37, obtained using *n*-hexane-ether (3 : 2 by vol); besides these fractions, fractions containing naphthalene, *t*-butylcyclohexyl phenyl ether, and *t*-butylcyclohexylphenol were eluted. The infrared spectrum of the alcohol of fraction 22 in CCl_4 was identical with that of an authentic sample of *cis*-4-*t*-butylcyclohexanol. The crystalline alcohols from the fractions from 22 to 27 (total 190 mg) were each examined in turn by GLC to show one peak corresponding in retention time to *cis*-4-alcohol. These results show that the alcohol of the fractions from 22 to 27 is exclusively *cis*-4-*t*-butylcyclohexanol and does not contain any *trans*-3-*t*-butylcyclohexanol.[9] The oily alcohol from fractions 28—37 (total 77 mg) was submitted to GLC, which showed two peaks with retention times of 17.3 min and 20.4 min; 55.0% and 45.0% respectively. Then the fractions for both the peaks were collected as eluted in liquid-nitrogen traps by GLC (5-m column at 150°C) to give 20.0 mg of crystalline alcohol for the first peak and 22.4 mg of oily alcohol for the succeeding peak; these substance were then each oxidized with chromium trioxide in acetic acid. The GLC examination for the ketone derived from the crystalline alcohol showed one peak corresponding in retention time to 4-*t*-butylcyclohexanone; from this the first peak was confirmed to be the *cis*-4-alcohol. The ketone derived from the oily alcohol was analyzed by GLC, showing two peaks corresponding in retention time to 3- and 4-*t*-butylcyclohexanones. The calibration, carried out with a mixture of ketones derived from a mixture of *trans*-4- and *cis*-3-alcohols of known compositions, gave the following results: *trans*-4-OH, 16.6%; *cis*-3-OH, 83.4%. The composition of the *t*-butylcyclohexanol given by the cleavage reaction of the unchanged tosylate was calculated to be as follows: *cis*-4-OTs, 88.2%; *trans*-4-OTs, 1.0%; *cis*-3-OTs, 10.8%; *trans*-3-OTs, 0.0%. The results of this run are listed in Table 2, along with the results of the other runs.

Cleavage of the Tosylate Recovered from the Reaction Mixture for the Phenolysis of *trans*-4-*t*-Butylcyclohexyl *p*-Toluenesulfonate. The *trans*-4-tosylate (6.23 g) was phenolyzed in 50 wt% phenol-benzene (200 m*l*), containing triethylamine (0.107 N), for two half-lives; the unchanged tosylate was then recovered following the method described in a previous paper.[4] The recovered material (2.181 g) was divided into two parts by means of the ether solution. A part of the recovered material (0.387 g) was further phenolyzed, and the measurements of the infinity titers gave the composition of the tosylate present in the recovered material. The rest of the recovered material (1.794 g) was treated with sodium naphthalene in THF much as in the working-up described above; the resulting crystalline material was chromatographed over silica gel (100 g, Nakarai, No. II-A. 100—200 mesh). Successive elution with the indicated solvents gave the following fractions (25-m*l* portions being taken): the fractions 9—57, obtained using *n*-hexane, naphthalene; the fractions 63—79, obtained using *n*-hexane-benzene (7 : 3 by vol), *t*-butylcyclohexyl phenyl ether; the fractions 84—102, obtained using benzene, *t*-butylcyclohexylphenol; the fractions 129—137, obtained using *n*-hexane-ether (4 : 1 by vol), *t*-butylcyclohexanone (29.8 mg, 4.6% yield); the fractions 138—151, obtained using *n*-hexane-ether (4 : 1 by vol), oily *t*-butylcyclohexanol (27.4 mg); the fractions 152—171, obtained using *n*-hexane-ether (1 : 1 by vol), crystalline *t*-butylcyclohexanol (554.9 mg).

The crystalline alcohol from the fractions from 152 to 171 was proved to be *trans*-4-*t*-butylcyclohexanol on the basis of its melting point (mp 80—81°C) and infrared spectrum and on the basis of the results of a GLC examination.

The oily alcohol from the fractions from 138 to 151 was submitted to GLC showing two peaks corresponding in retention times to the axial and the equatorial alcohols; the compositions were 47.2% and 52.8% respectively. Then the fractions were collected as eluted in liquid-nitrogen traps by GLC (5-m column at 150°C) to give an oily alcohol for the first peak and a crystalline alcohol for the second peak; these substances were each treated with chromium trioxide in acetic acid. The GLC examination for the ketone from the oily alcohol showed two peaks corresponding in retention times to 3- and 4-*t*-butylcyclohexanone; when the ratio was calibrated with ketones derived from a mixture of *cis*-4-OH and *trans*-3-OH of known compositions, the *cis*-4-OH/*trans*-3-OH ratio was determined to be 0.263. The GLC examination for the ketone produced from crystalline alcohol showed one peak corresponding in retention time to 4-*t*-butylcyclohexanone; from this the crystalline alcohol was confirmed to be pure *trans*-4-alcohol. From these results, the composition of the recovered tosylate was calculated to be as follows: *cis*-4-OTs, 0.7%; *trans*-4-OTs, 96.7%; *cis*-3-OTs, 0.0%, *trans*-3-OTs, 2.6%.

Cleavage of the Tosylate Recovered from the Reaction Mixture for the Phenolyses Conducted in the Presence of Triethylammonium or Diethylammonium *p*-Toluenesulfonate. The phenolysis was conducted in the presence of added triethylamine and triethyl- or diethyl-ammonium tosylate, and the composition of the recovered tosylate was analyzed in a manner similar to that described in a previous paper[4] and in the preceding sections; The results are summarized in Table 2 for the *cis*-4-tosylate and in Table 3 for the *trans*-4-tosylate.

---

[9] When the phenolysis of the *cis*-4-tosylate was conducted in the presence of added triethylammonium tosylate, the last fraction of the crystalline alcohol, corresponding to fraction 27 in the case of this run, was converted into ketone; the ketone was then analyzed by GLC to show one peak corresponding in retention time to 4-*t*-butylcyclohexanone. On the basis of this result, the fraction 27 was considered to be pure *cis*-4-*t*-butylcyclohexanol.