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Kinetic Studies of Solvolysis. XVI.[*1] Phenolysis of *cis*- and *trans*-4-*t*-Butylcyclohexyl *p*-Toluenesulfonates. Rates and Product Distribution

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The rates of the phenolysis of *cis*- and *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonates have been measured in the presence of equimolar amounts of triethylamine in phenol, phenol-benzene (3 : 1 by wt), and phenol-benzene (1 : 1 by wt) solvents. At 75°C, the axial isomer, *i.e.*, the *cis* tosylate, phenolyzes more rapidly in the phenol-benzene mixture (1 : 1 by wt) than the equatorial isomer, *i.e.*, the *trans* tosylate, by a factor of 3.08; this factor is not far from the axial-equatorial rate ratios observed in other hydroxylic solvents,[2] indicating that phenol is a typical solvolytic solvent. Under the same reaction conditions as the rate measurements, the equatorial tosylate yields *t*-butylcyclohexene (72.5%), *t*-butylcyclohexyl phenyl ether (9.4%), predominantly inverted (*cis*-4-*t*-butylcyclohexyl) phenyl ether, and *t*-butylcyclohexylphenol (4.4%), whereas the axial tosylate yields *t*-butylcyclohexene (87%) and the phenyl ether (8.7%), largely inverted (*trans*-4-*t*-butylcyclohexyl) phenyl ether, but containing increasing amounts of retained (*cis*-4-*t*-butylcyclohexyl) and and rearranged (*trans*-3-*t*-butylcyclohexyl) ethers; the rest is a mixture of *t*-butylcyclohexylphenols (1.6%). The composition percentages of the retained phenyl ether obtained from the two tosylates, *i.e.*, 20.4% for the *cis* tosylate and 12.9% for the *trans* tosylate, indicate the highest extents of retention for phenol among those known for any other hydroxylic solvents.[3] The initially added *t*-butylcyclohexenes exert no influence on the olefin or on the phenyl ether composition, whereas triethylammonium and diethylammonium *p*-toluenesulfonates, when added initially, enhance the phenolysis rate and exert a small but definite influence on the composition of the phenyl ether. The hypothesis of the hydrogen-bridged cation,[2] proposed in order to explain the enhanced rate of the *cis* isomer and in order to elucidate the retained solvolysis product, has been questioned by a consideration of the mechanism on the basis of the results of this phenolysis.

In previous studies[1] of the retentive solvolysis, it has been demonstrated that phenol is a notable

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[*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); Part XV: K. Okamoto, I. Nitta and H. Shingu, This Bulletin, **41**, 1433 (1968).

[1] a) Part XI: K. Okamoto, H. Yamada, I. Nitta and H. Shingu, This Bulletin, **39**, 299 (1966); b) K. Okamoto, K. Komatsu and H. Shingu, *ibid.*, **39**, 2785 (1966); c) Part XIII: K. Okamoto, M. Hayashi, K. Komatsu and H. Shingu, *ibid.*, **40**, 624 (1967); d) Part XIV: K. Okamoto, K. Komatsu and H. Shingu, *ibid.*, **40**, 1677 (1967).

solvent in which the S_N1 solvolysis of optically-active α-phenylethyl chloride gives a partially-retained phenyl ether. However, for the systems other than α-phenylethyl, it was not clear whether or not such retentive phenolysis is common. Therefore, it is obviously desirable to have more information about the structural factors of the substrate with regard to the retention of the configuration in phenolysis. As one of works of this line, we have considered it of interest to extend the rate and the product studies to the 4-*t*-butylcyclohexyl system, because this system has a rigid conformation fixing the *t*-butyl group in the equatorial position; also, the kinetic[2] and the product analysis[2,3] data have already been made available for various solvents other than phenol. In this paper we will describe our findings on the rate and the products in the phenolysis of *cis*- and *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonates in the presence of triethylamine, and will discuss the bearing of the results on the characteristics of phenol as an ionizing solvent and as a retentive solvent.

Results and Discussion

Phenolysis Rates of *cis*- and *trans*-4-*t*-Butylcyclohexyl *p*-Toluenesulfonates in the Presence of Triethylamine. The phenolysis of *cis*- and *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonates was carried out in phenol-benzene solvents at 75°C and the rate constants were determined titrimetrically. In spite of the presence of equimolar amounts of triethylamine, the *trans* tosylate displayed good first-order behavior, whereas the first-order plot for the *cis* tosylate shows a downward drift after about 80% completion (Fig. 1). Initially-added triethylammonium *p*-toluenesulfonate gave rise to a small rate enhancement for both tosylates (Table 1), probably due to the normal salt effect.[4]

There is a decided trend towards markedly enhanced rates in solvents with higher phenol contents; at 75°C for the *trans* tosylate a one and half-fold increase in the phenol concentration gave rise to rate enhancement by a factor of three (Table 1).

In Fig. 2 the solvolysis rates of 4-*t*-butylcyclohexyl *p*-toluenesulfonates in phenol-benzene (1 : 1 by wt), phenol-benzene (3 : 1 by wt), phenol, acetic acid,[2] formic acid,[2] and ethanol[2] at 75°C are plotted on a logarithmic scale against the *Y* scale of Grunwald and Winstein.[5,6] There is a general tendency towards higher rates in solvents of higher *Y* values, but the proportionality is far from exact. This result is not unexpected if one considers that the rate measured for the *t*-butylcyclohexyl system might not reflect the true ionization rate of the system (*vide infra*).

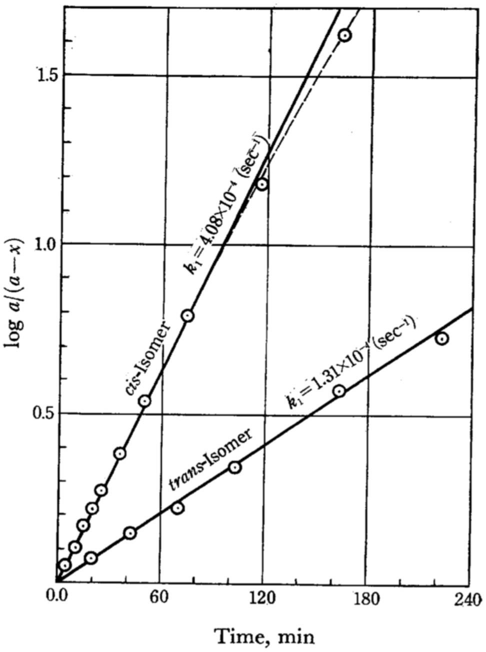

Fig. 1. First-order plots for phenolysis of *cis*- and *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonates in the presence of triethylamine in 50 wt% phenol-benzene solvent at 75.0°C.

The *cis* tosylate, *i. e.*, the axial isomer, phenolyzed more rapidly than the *trans* (equatorial) tosylate by a factor of 3.08 in phenol-benzene (1 : 1 by wt) at 75°C, indicating, as far as the axial-equatorial rate ratio is concerned, that the phenolic solvent[7] is not specifically different from such other solvents as formic acid, acetic acid, and ethanol, in which the axial tosylate solvolyzes more rapidly than the equatorial isomer by factors of 2.51, 2.85, and 3.05 respectively (Table 1).

In the extreme that the higher rate of the axial over the equatorial tosylate is attributed only to steric acceleration caused by the higher initial

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

[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] For the normal salt effect in the acetolysis, see A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2763 (1956).

[5] a) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); b) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

[6] The *Y* values for phenol-benzene (1 : 1 by wt) and phenol-benzene (3 : 1 by wt) were determined in this laboratory; K. Okamoto and S. Saitô, unpublished work.

[7] Phenol is an especially powerful solvolytic solvent despite its low dielectric constant (9.78 at 60°C); the *Y* value for phenol was estimated to be about 1.77 (*cf.* Footnote 6).

TABLE 1. RATES OF SOLVOLYSIS OF *cis*- AND *trans*-4-*t*-BUTYLCYCLOHEXYL *p*-TOLUENESULFONATES AT 75°C

Solvent	ROTs	Base	$10^4 k_1$ (sec^{-1})	k_1 *cis*/k_1 *trans*
PhOH-Benzene (1:1 by wt)	*cis*	Et_3N		
	0.0972 M	0.106 N	4.08 } 4.00	3.08
	0.0980 M	0.111 N	3.91	
	0.0990 M	0.105 N	4.13[a)]	(3.15[b,d)])
	0.0978 M	0.111 N	4.88[b)]	
	trans	Et_3N		
	0.0833 M	0.110 N	1.31 } 1.30	
	0.103 M	0.106 N	1.29	
	0.0989 M	0.105 N	1.38[c)]	
	0.0997 M	0.106 N	1.55[d)]	
PhOH-Benzene (3:1 by wt)	*trans*	Et_3N		
	0.0999 M	0.106 N	4.00	—
PhOH	*trans*	Et_3N		
	0.100 M	0.109 N	11.0	—
Formic acid[e)]	*cis*	NaO_2CH	354[f)]	2.51
	trans	NaO_2CH	141[f)]	
Acetic acid[e)]	*cis*	NaOAc	1.03	2.85
	trans	NaOAc	0.362	
Ethanol[e)]	*cis*	—	0.703[g)]	3.05
	trans	—	0.230[g)]	

a) With added $Et_3NH^+OTs^-$ (0.101 N).
b) With added $Et_2NH_2^+OTs^-$ (0.198 N).
c) With added $Et_3NH^+OTs^-$ (0.203 N).
d) With added $Et_2NH_2^+OTs^-$ (0.191 N).
e) S. Winstein and N. J. Holness, Ref. 2.
f) Extrapolated from data at 25 and 50°C.
g) Probably contaminated with the S_N2 type ethanolysis.

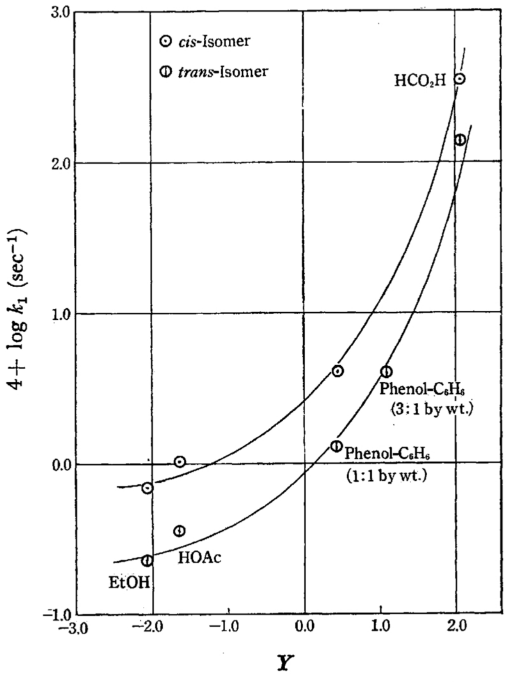

Fig. 2. Plots of log k_1's for solvolysis in various solvents against Y-values.

state energy of the axial isomer, the rate enhancement for the axial isomer is calculated to be a factor of 2.1 at 75°C, since a reliable value for the energy difference in ΔF between the two isomers has recently given as 0.515 kcal/mol.[8)]

The gap between the calculated (2.1) and the observed factor (2.51—3.08) can be ascribed to the lowering of the free energy for the transition state of the axial isomer; the value is estimated to be about 0.12—0.27 kcal/mol (Fig. 3).

As regard to the elucidation of this decrease in the free-energy of the transition state for the *cis* tosylate, the neighboring hydrogen participation hypothesis has prevailed, especially in the cases of the 4-*t*-butylcyclohexyl[2,9)] and 3-cyclohexyl-2-butyl[10)] systems. However, it seems difficult to deduce the formation of a bridged ethylene-protonium-ion-type intermediate[2)] on the basis of such a small stabilization of the transition state.[11)]

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8) F. R. Jensen, C. H. Bushweller and B. H. Beck, *J. Am. Chem. Soc.*, **91**, 344 (1969).

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

10) D. J. Cram and J. Tadanier, *ibid.*, **81**, 2737 (1959).

11) The question of the existence of a hydrogen-bridged cation intermediate for the solvolysis of the 4-*t*-butylcyclohexyl system will be the subiect of a subsequent publication.

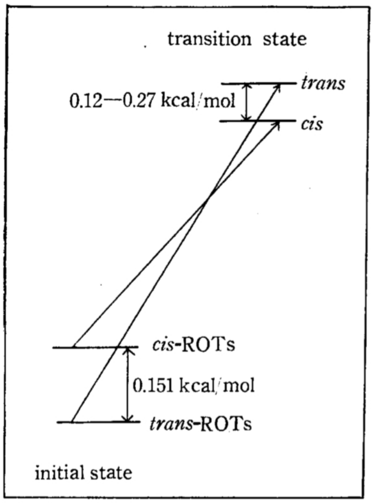
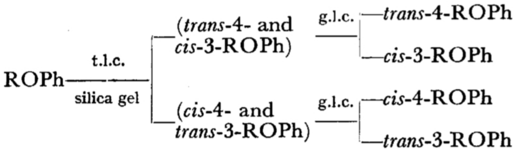


Fig. 3. Free-energy diagram for the solvolysis of *cis*- and *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonates.

Products of Phenolysis of *cis*- and *trans*-4-*t*-Butylcyclohexyl *p*-Toluenesulfonates in the Presence of Triethylamine. The products of phenolysis were investigated for both *trans*- and *cis*-4-*t*-butylcyclohexyl *p*-toluenesulfonates in a 50 wt% phenol-benzene solvent containing equimolar amounts of triethylamine at 75°C. The reaction mixture was worked up in the usual manner and then chromatographed over silica gel, giving *t*-butylcyclohexenes (a mixture of 4-, 3- and 1-*t*-butyl isomers), *t*-butylcyclohexyl phenyl ethers (a mixture of *cis*-4-, *trans*-4-, *cis*-3- and *trans*-3-*t*-butylcyclohexyl isomers), and a mixture of *t*-butylcyclohexylphenols. After the run with added triethyl- or diethylammonium *p*-toluenesulfonate had been conducted up to about 75% completion, the reaction mixture was treated with sodium naphthalene in tetrahydrofufan in order to cleave the unchanged tosylate into *t*-butylcyclohexanols; then, from the reaction mixture *t*-butylcyclohexanols,[12] *t*-butylcyclohexyl phenyl ethers and *t*-butylcyclohexylphenols were separated by elution chromatography.

The compositions of *t*-butylcyclohexenes and *t*-butylcyclohexyl phenyl ethers were determined by GLC; in some cases the latter mixture was separated into two components by means of TLC prior to the GLC analysis. The analysis scheme for the composition of *t*-butylcyclohexyl phenyl ethers is as follows:



$$\text{ROPh} \xrightarrow[\text{Apiezon grease, 200°C}]{\text{g.l.c.}} \textit{trans}\text{-3-ROPh} + (\textit{cis}\text{-3- and } \textit{cis}\text{-4-ROPh}) + \textit{trans}\text{-4-ROPh}$$

(three peaks)

The composition of *t*-butylcyclohexanols, separated as a fraction of chromatography, was not analyzed.

Much as with the trend observed for other solvents,[3] the main product of the phenolysis for both tosylates is a mixture of *t*-butylcyclohexenes. The yield (%) of olefin formed from the equatorial (*trans*) tosylate is not far below that obtained from the axial (*cis*) tosylate (Table 2); this seems also a general tendency for the 4-*t*-butylcyclohexyl system irrespective of the nature of the solvent employed (*cf.* Ref. 3 and Table 2).

TABLE 2. SOLVOLYSIS PRODUCTS FROM 4-*t*-BUTYLCYCLOHEXYL *p*-TOLUENESULFONATES

Solvent:	Phenol-Benzene (1:1 by wt) (Present work)		HOAc (Whiting *et al.*[a])	
Temp.:	75°C	75°C	100°C	100°C
ROTs:	*cis*	*trans*	*cis*	*trans*
	0.0913 M	0.0987 M		
Base:	Et_3N	Et_3N	NaOAc	NaOAc
	0.123 N	0.106 N	0.05 N	0.05 N
Time:	6.0 hr	18.7 hr		
Cyclohexenes:				
Yield %	87.0	72.5	87.0	79.2
Composition %				
4-*t*-Butyl	97.4	95.3	96.6	93.0
3-*t*-Butyl	2.6	4.1	3.2	6.3
1-*t*-Butyl	trace	0.6	0.2	0.7
Cyclohexyl Phenyl Ethers or Cyclohexyl Acetates:				
Yield %	8.7	9.4	12.8	21.9
Composition %				
trans-4-*t*-Butyl	55.0	12.9	57.0	1.8
cis-4-*t*-Butyl	20.4	69.2	5.5	89.0
trans-3-*t*-Butyl	13.7	12.8	35.2	2.3
cis-3-*t*-Butyl	10.9	5.1	2.3	6.9
t-Butylcyclohexylphenols:				
Yield %	1.6	4.4	—	—

a) Ref. 3.

Since olefin formation from the equatorial (*trans*) tosylate cannot be attributed to a usual E2-type anti-elimination,[13] the production of so much olefin from the equatorial isomer may indicate the contribution of a considerable amount of *cis-syn*-elimination in the E1 or S_N1 ion-pair intermediate.[14]

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12) A mixture of *cis*-4-, *trans*-4-, *cis*-3-, and *trans*-3-*t*-butylcyclohexanols; the analysis of the composition will be described in a subsequent paper.

13) J. Sicher, J. Závada and M. Pánková, *Chem. Commun.*, **1968**, 1147.

14) For *cis*-elimination *via* the carbonium-ion intermediate for the deamination of *cis*-4-*t*-butylcyclohexylamine and *trans*-2-decalylamine, see, respectively, G. Lamaty, C. Tapiero and R. Wylde, *Bull. Soc. Chim. France*, **1968**, 2039, and T. Cohen and A. R. Daniewski, *J. Am. Chem. Soc.*, **91**, 532 (1969).

The composition of the olefin formed in phenol is compared with that in acetic acid[3] in Table 2; the compositions for the two solvents are quite similar. Besides 4-*t*-butylcyclohexene, there exists a small amount of rearranged olefins in the cases of both solvents, indicating the presence of rearranged ion-pair intermediates during the solvolysis.

The substitution products for both tosylates are composed of a major proportion of *t*-butylcyclohexyl phenyl ether and a minor amount of *t*-butylcyclohexylphenol; among the isomers of the phenyl ether, the inverted ether is the predominant component, the rest being the retained and the rearranged or isomerized ether (Table 2). This trend has also been found in the distribution of substitution products for acetolysis[3] (Table 2) and other solvolyses.[3]

However, the composition percentage of the retained phenyl ether in phenolysis for both tosylates is the highest among those of the retained products in other solvents.[3] This probably means that the front-side attack of the phenol molecule may play an important part in increasing the retentive course for the substitution; the fact that, even in the phenolic solvent, the yield of the retentive product never exceeds that of the inverted product for 4-*t*-butylcyclohexyl system is in marked contrast to the α-phenylethyl system, for which the retentive course is predominant in the phenolic solvents.[1]

As has been observed in the cases of other solvents,[2,3] in the phenolic solvent a substantial quantity of rearranged products is also present in the substitution products; the proportions of 3-*t*-butylcyclohexyl phenyl ethers are 24.6% from the *cis* tosylate and 17.9% from the *trans* tosylate.

Since initially-added *t*-butylcyclohexenes did not exert any influence on the composition of olefins and phenyl ethers for both tosylates within essentially the experimental error of analysis (Table 3), the possibility of the formation of rearranged products *via* a proton addition to a stable molecule of *t*-butylcyclohexene can be eliminated. This course is illustrated in Fig. 4.

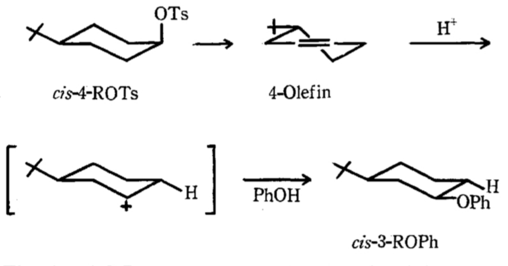

Fig. 4. 1,2-Rearrangement *via* *t*-butylcyclohexene.

The initial addition of the *p*-toluenesulfonate anion in the form of triethyl- or diethyl-ammonium salt, which is also produced as the phenolysis proceeds, has a small but definite influence on the composition of the phenyl ether (Table 4).

TABLE 3. RESULTS OF PHENOLYSIS OF 4-*t*-BUTYLCYCLOHEXYL *p*-TOLUENESULFONATES IN THE PRESENCE OF ADDED *t*-BUTYLCYCLOHEXENES AND TRIETHYLAMINE[a]

	cis	*cis*	*trans*	*trans*
ROTs:	0.0913 M	0.0970 M	0.0987 M	0.105 M
Et_3N:	0.123 N	0.110 N	0.106 N	0.107 N
t-Butylcyclohexenes:	—	0.101 M[b]	—	0.272 M[c]
Time:	6.0 hr	5.4 hr	18.7 hr	19.0 hr
Cyclohexenes:				
Yield %	87.0	?[d]	72.5	?[d]
Composition %				
4-*t*-Butyl	97.4	95.9	95.3	95.3
3-*t*-Butyl	2.6	2.9	4.1	4.1
1-*t*-Butyl	trace	1.2	0.6	0.6
Cyclohexyl Phenyl Ethers:				
Yield %	8.7	9.4	9.4	9.9
Composition %				
trans-4-*t*-Butyl	55.0	54.3	12.9	12.9
cis-4-*t*-Butyl	20.4	20.5	69.2	67.3
trans-3-*t*-Butyl	13.7	14.3	12.8	13.0
cis-3-*t*-Butyl	10.9	10.8	5.1	6.9
t-Butylcyclohexylphenols:				
Yield %	1.6	2.0	4.4	5.3

a) In phenol-benzene (1:1 by wt) at 75.0°C.

b) A mixture of 4-*t*-butyl-, 3-*t*-butyl- and 1-*t*-butylcyclohexenes (Composition: 95.3, 3.2 and 1.5%).

c) A mixture of 4-*t*-butyl-, 3-*t*-butyl- and 1-*t*-butylcyclohexenes (Composition: 95.3, 4.1 and 0.6%).

d) The yield was not determined.

A thorough explanation of the variation in the composition with an increase in the concentrations of the *p*-toluenesulfonate anion would be difficult because of the presence of at least four probably interconvertible ion-pair intermediates, corresponding to the four substitution products. However, it can be conservatively pointed out that the retained substitution need not be derived by only a front-side attack of a molecule of phenol, but may also be produced by the isomeric intermediate. For instance, the *cis* ion-pair intermediate may be formed by an internal rotation of the *t*-butyl cyclohexyl cation from the *trans* ion-pair intermediate; consequently, starting from the *trans* tosylate, the retained substitution product may also be produced *via* a double inversion course, following the course illustrated in Fig. 5.

Thus, conceivably there exists a possibility of the accumulation of isomerized or rearranged tosylates during the phenolysis of the 4-*t*-butylcyclohexyl system by means of the internal return of the isomerized or rearranged intermediate or by an inversive attack of the *p*-toluenesulfonate anion on the unrearranged intermediate.

The downward drift of the first-order plot for

TABLE 4. RESULTS OF PHENOLYSIS OF 4-*t*-BUTYLCYCLOHEXYL *p*-TOLUENESULFONATES IN THE PRESENCE OF ADDED TRIETHYLAMMONIUM *p*-TOLUENESULFONATE AND TRIETHYLAMINE[a]

ROTs:	*cis*	*cis*	*cis*	*cis*	*trans*	*trans*	*trans*	*trans*
	0.0913M	0.0990M	0.103M	0.0974M	0.100M	0.0987M	0.0989M	0.100M
Et_3N:	0.123N	0.105N	0.105N	0.111N	0.107N	0.106N	0.105N	0.109N
$Et_3NH^+OTs^-$:	—	0.101N	0.226N	0.212N[b]	—	—	0.203N	0.106N[b]
Time:	6.0 hr	0.95 hr	0.88 hr	1.0 hr	2.8 hr	18.7 hr	2.6 hr	2.8 hr
Conversion:	100%	75.5%	74.0%	86.5%	73.6%	100%	75.0%	76.6%
Cyclohexenes:								
Yield %	87.0	?[c]	?[c]	?[c]	?[c]	72.5	?[c]	?[c]
Composition %								
4-*t*-Butyl	97.4	98.8	?[c]	?[c]	?[c]	95.3	?[c]	?[c]
3-*t*-Butyl	2.6	1.2	?[c]	?[c]	?[c]	4.1	?[c]	?[c]
1-*t*-Butyl	trace	trace	?[c]	?[c]	?[c]	0.6	?[c]	?[c]
Cyclohexyl Phenyl Ethers:								
Yield %	8.7	11.6	10.4	8.6	10.9	9.4	11.0	12.5
Composition %								
trans-4-*t*-Butyl	55.0	60.9	63.6	60.8	12.2	12.9	10.4	10.6
cis-4-*t*-Butyl	20.4	19.5	17.6	17.6	70.3	69.2	70.9	72.9
trans-3-*t*-Butyl	13.7	12.1	12.0	14.0	12.8	12.8	10.6	11.4
cis-3-*t*-Butyl	10.9	7.5	6.8	7.6	4.7	5.1	8.1	5.1
t-Butylcyclohexylphenols:								
Yield %	2.0	2.1	2.3	1.8	5.7	4.4	3.3	5.2

a) In phenol-benzene (1:1 by wt) solvent at 75.0°C.
b) Instead of $Et_3NH^+OTs^-$, $Et_2NH_2^+OTs^-$ was used.
c) The yield or composition was not determined.

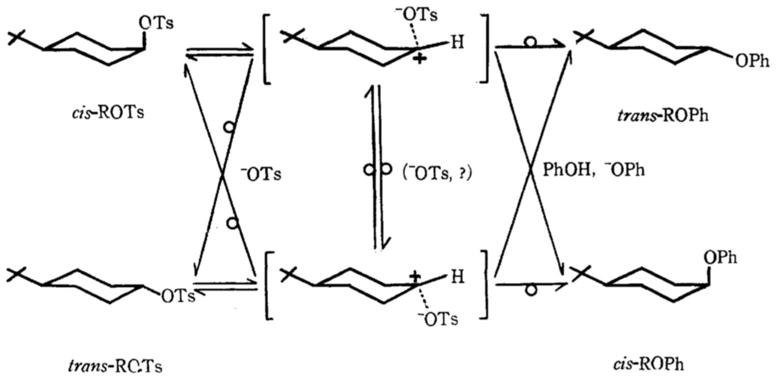

Fig. 5. Possible courses for the formation of retained 4-*t*-butylcyclohexyl phenyl ethers in phenolysis.

the *cis* tosylate, illustrated in Fig. 1, might be due to the accumulation of the *trans* tosylate, which is phenolyzed slower than the *cis* isomer.

On the basis of these considerations of the course for the retained products, the necessity of the hypothesis of a hydrogen-bridged cation intermediate[2] for the 4-*t*-butylcyclohexyl system, proposed as an explanation of the formation of the retained substitution product, may well be questioned, as it may also be questioned on the basis of the rate data presented above. Further discussion of this problem will be the subject of a subsequent paper.

Experimental[15]

Materials. ***trans*-4-*t*-Butylcyclohexanol** was obtained from the hydrogenphthalate of a mixture of 4-*t*-butylcyclohexanol, which had itself been prepared by means of the catalytic hydrogenation of *p*-*t*-butyl-

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15) The melting points are not corrected. The microanalyses were done by the Microanalytical Center, Kyoto University. The infrared spectra were determined with a Shimadzu Model IR-27 spectrophotometer. All the gas-liquid chromatographical studies were made with a Shimadzu Model GC-2B dual-column gas chromatograph.

phenol, employing the same reaction conditions as those of the hydrogenation of *p*-isopropylphenol.[16]

p-*t*-Butylphenol (30 g, 0.20 mol) was hydrogenated using 1.6 g of a Raney nickel catalyst (W-2)[17] and 41 m*l* of absolute ethanol as a solvent in a 300-m*l* autoclave at 150°C for five hours (initial hydrogen press, 100 kg/cm^2). The catalyst was removed by filtration and washed with ethanol. The combined ethanol solutions were evaporated to dryness to give 31.0 g of 4-*t*-butylcyclohexanol (97% yield, mp 62—68°C); the infrared spectrum of the carbon tetrachloride solution showed no absorptions in the aromatic regions.

Several crystallizations of the hydrogenphthalate and subsequent saponification afforded *trans*-4-*t*-butylcyclohexanol; mp 80.1—81.1°C (lit, mp 81—82°C,[2] 80—80.5°C[18] and 82°C[19]).

***cis*-4-*t*-Butylcyclohexanol** was obtained by the elution chromatography of a mixture of 4-*t*-butylcyclohexanols; this mixture had been prepared by the reduction of 4-*t*-butylcyclohexanone with Raney nickel (W-2)[17] in ethanol. *cis*-4-*t*-Butylcyclohexanol, obtained by chromatography over alumina (Nakarai 200), melted at 81—82°C (lit, mp 82—83°C,[2] 82.5—83.5°C[20] and 83—83.5°C[19]).

4-*t*-Butylcyclohexanone was prepared following the method of Winstein and Holness[2]; the chromic acid oxidation of a mixture of 4-*t*-butylcyclohexanols in acetic acid gave 4-*t*-butylcyclohexanone in an 82% yield. This ketone melted at 48—50°C (lit, mp 47.5—48.5°C[2] and 49—50°C[21]) and boiled at 85—86°C/7 mmHg (lit, bp 90—92°C/9 mmHg[2] and 106—108°C/19 mmHg[21]).

The Tosylate of *trans*- and *cis*-4-*t*-Butylcyclohexanols was prepared according to the usual Tipson procedure.[22] *trans*-4-*t*-Butylcyclohexyl *p*-toluenesulfonate melted at 88.5—89.5°C (lit, mp 89.4—90.0°C[2] and 89—90°C[23]). *cis*-4-*t*-Butylcyclohexyl *p*-toluenesulfonate melted at 78—79°C (lit, mp 79—80°C[2] and 78—79°C[23]).

3-*t*-Butylcyclohexanone was prepared by means of the reaction of 2-cyclohexen-1-one with *t*-butylmagnesium chloride using a modification of the method of Whitmore and Pedlow[24]: oxidation of cyclohexene with chromium trioxide in acetic acid gave 2-cyclohexen-1-one (27% yield); bp 64—65°C/20 mmHg, n_D^{20} 1.4870 (lit, bp 65—66°C/20 mmHg[2] and 67°C/25 mmHg,[24] n_D^{25} 1.4824,[2] n_D^{20} 1.4879[24]). The Grignard reaction of 2-cyclohexen-1-one with *t*-butylmagnesium chloride in the presence of cuprous chloride[25] gave 3-*t*-butylcyclohexanone (39% yield); bp 69—72°C/4 mmHg, n_D^{25} 1.4601 (lit, bp 92—95°C/10 mmHg[2] and 96—98°C/20 mmHg,[24] n_D^{25} 1.4611,[2] n_D^{20} 1.4615[24]).

***cis*-3-*t*-Butyl- and *trans*-3-*t*-Butyl-cyclohexanols** were prepared in good yields by the reduction of 3-*t*-butylcyclohexanone with, respectively, lithium aluminum hydride[2] and Raney nickel in ethanol.[2] Each alcohol was purified by several recrystallizations of the hydrogenphthalate and by subsequent saponification. *trans*-3-*t*-Butylcyclohexanol melted at 64—66°C (lit, mp 48—49°C,[2] 48°C[3] and 64°C[3]), and *cis*-3-*t*-butylcyclohexanol melted at 41—43°C; bp 105—106°C/10 mmHg, n_D^{25} 1.4670 (lit,[2] mp 40—41°C, bp 103°C/10 mmHg, n_D^{25} 1.4660).

***cis*-3-*t*-Butyl- and *trans*-3-*t*-Butyl-cyclohexyl *p*-Toluenesulfonates** were prepared according to the method of Tipson.[22] *cis*-3-*t*-Butylcyclohexyl *p*-toluenesulfonate melted at 58—59°C (lit, mp 58—59.5°C[2]). *trans*-3-*t*-Butylcyclohexyl *p*-toluenesulfonate melted at 44—45°C (lit, mp 33—35°C[2]).

4-*t*-Butylcyclohexene was prepared by means of the E2 reaction of *cis*- or *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonate with sodium phenoxide in acetone at 80°C for 20.9 hr (for the reaction of the *cis*-tosylate) or 17.3 hr (for the *trans*-tosylate). After working up in the usual way, the residual oily material was chromatographed over silica gel (Nakarai, No. II-A. 100—200 mesh). 4-*t*-Butylcyclohexene was eluted by using *n*-hexane as an eluant (see the section describing the preparation of *cis*-4-*t*-butylcyclohexyl phenyl ether).

3-*t*-Butylcyclohexene was prepared by treating 3-bromocyclohexene with *t*-butylmagnesium chloride. The bromination of cyclohexene with *N*-bromosuccinimide, following the method of Ziegler *et al.*,[26] gave 3-bromocyclohexene, bp 71—73°C/29 mmHg, in an 81% yield. The 3-bromocyclohexene was treated with *t*-butylmagnesium chloride by the method of Goering *et al.*[27] to produce 3-*t*-butylcyclohexene, bp 68.5—69°C/29 mmHg, n_D^{25} 1.4579, in a 50% yield (lit, bp 170.5°C/746 mmHg,[27] n_D^{25} 1.4568[27]).

Triethylammonium *p*-Toluenesulfonate and Diethylammonium *p*-Toluenesulfonate were prepared by dissolving slight excess of the corresponding amine and *p*-toluenesulfonic acid (Nakarai reagent-grade, monohydrate) in acetone; then, after the evaporation of the acetone and the excess of amine, the ammonium salts were dried to a constant weight *in vacuo* at 90—100°C.

Sodium Phenoxide was prepared from metallic sodium and phenol in dry toluene. A solution with a slight excess of phenol in toluene was mixed with metallic sodium, and then refluxed. The sodium phenoxide was filtered out, washed with benzene, and then dried *in vacuo* to a constant weight at 100—110°C.

The benzene, phenol, triethylamine, acetone, dimethylformamide, and tetrahydrofuran (each of a reagent grade) were dried and purified by fractional distillation; bps 80.2—80.5°C, 181—182°C, 56.5—56.7°C, 151.5—153°C, and 66.7—66.9°C respectively. The naphthalene (reagent grade) was used without further purification.

***cis*-4-*t*-Butylcyclohexyl Phenyl Ether.** A solution of 3.10 g (0.15 mol) of *trans*-4-*t*-butylcyclohexyl *p*-

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toluenesulfonate in 67 m*l* of an acetone solution of sodium phenoxide (0.396M) was sealed in an ampoule, and then the ampoule was kept at 80°C for 17.3 hr. To the reaction mixture there were then added 120 m*l* of water, 70 m*l* of benzene, and 23 g of sodium chloride. The water layer was extracted several times with benzene, and the combined benzene solutions were washed with a 10% aqueous sodium chloride solution. After drying over anhydrous magnesium sulfate, the benzene solution was concentrated in a rotatory evaporator to give 9.68 g of a brown oil. A part of the brown oil (6.21 g) was chromatographed over 100 g of silica gel (Nakarai, No. II-A. 100—200 mesh). The column was eluted successively with *n*-hexane, *n*-hexane-benzene (4 : 1 by vol), and benzene. The fractions 1—22, obtained using *n*-hexane, gave 342 mg of 4-*t*-butylcyclohexene (37.3% yield); bp 49—50°C/14 mmHg, n_D^{20} 1.4597, n_D^{30} 1.4569 (lit, bp 65—66°C/20 mmHg,[2] n_D^{20} 1.4583,[2] 1.4581[28] and 1.4587[29]). The fractions 24—30, obtained using *n*-hexane-benzene (4 : 1 by vol), gave 465 mg of *cis*-4-*t*-butylcyclohexyl phenyl ether (30.2% yield); bp 88—90°C/0.13 mmHg, n_D^{30} 1.5093.

Found: C, 82.88; H, 10.34%. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41%.

The fractions 31—40, obtained using benzene, gave 90.9 mg of 4-*t*-butylcyclohexylphenol.

***trans*-4-*t*-Butylcyclohexyl Phenyl Ether.** *trans*-4-*t*-Butylcyclohexyl phenyl ether was prepared by the reaction of *cis*-4-*t*-butylcyclohexyl *p*-toluenesulfonate with sodium phenoxide in acetone at 80°C for 20.9 hr. The *trans*-ether was separated as has been described in the case of the *cis*-ether; it melted at 71—72°C after recrystallization from *n*-hexane.

Found: C, 82.96; H, 10.50%. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41%.

***trans*-3-*t*-Butylcyclohexyl Phenyl Ether.** *trans*-3-*t*-Butylcyclohexyl phenyl ether was prepared by treating *cis*-3-*t*-butylcyclohexyl *p*-toluenesulfonate with sodium phenoxide in dimethylformamide at 90°C. A mixture of 3.10 g (0.01 mol) of *cis*-3-*t*-butylcyclohexyl *p*-toluenesulfonate and 100 m*l* of a solution of sodium phenoxide (0.215M) in dimethylformamide was kept at 90°C for 17 hr in a glass-stoppered, round-bottomed 200-m*l* flask. After 900 m*l* of water had been added to the reaction mixture, the mixture was extracted with 100-m*l* portions of ether. The ether extracts were washed successively with a 10% aqueous sodium chloride solution, a 10% aqueous sodium hydroxide solution, and a 10% aqueous sodium chloride solution until the washings became neutral to litmus. After drying over anhydrous magnesium sulfate, the ether was removed by rotatory evaporation to give 1.70 g of a brown oil as a residue; this was chromatographed using an elution column packed with 50 g of silica gel (Nakarai, No. II-A. 100—200 mesh). The column was eluted successively with *n*-hexane, *n*-hexane-benzene (7 : 3 by vol), and benzene, 20-m*l* portions being taken. The fractions 1—7, obtained using *n*-hexane, gave 615 mg of *t*-butylcyclohexene (46.7% yield); bp 64°C/18 mmHg. Analysis by GLC indicated two components with retention times of 22.3 min (authentic 3-*t*-butylcyclohexene, 22.7 min) and 25.6 min (authentic 4-*t*-butylcyclohexene, 25.5 min). The fractions 8—16, obtained using *n*-hexane-benzene (7 : 3 by vol), gave 612 mg of *trans*-3-*t*-butylcyclohexyl phenyl ether (26.4% yield); bp 105°C/0.3 mmHg, n_D^{20} 1.5110, n_D^{30} 1.5091.

Found: C, 82.74; H, 10.59%. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41%.

The fractions 21—28, obtained using benzene, gave 63 mg of 3-*t*-butylcyclohexylphenol.

***cis*-3-*t*-Butylcyclohexyl Phenyl Ether.** *cis*-3-*t*-Butylcyclohexyl phenyl ether was prepared by treating *trans*-3-*t*-butylcyclohexyl *p*-toluenesulfonate with sodium phenoxide in dimethylformamide at 90°C for 16.5 hr. The *cis*-3-ether was separated in a manner similar to that described in the case of the *trans*-3-ether; bp 105°C/0.3 mmHg (27.1% yield).

Found: C, 82.72; H, 10.52%. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41%.

Gas-Liquid Chromatography of *t*-Butylcyclohexyl Derivatives. *A) Analysis of t-Butylcyclohexenes.* A complete separation was achieved on a column (5 m) packed with 30 wt% polyethylene glycol 6000 on selite 545 (Yanagimoto Co.), at 80°C using hydrogen as the carrier gas (60 m*l*/min). Analysis was carried out using peak-height and half-width measurements. The retention times of the three olefins are summarized in Table 5.

TABLE 5. RETENTION TIMES OF *t*-BUTYLCYCLOHEXENES

	1-*t*-Butyl-cyclohexene	3-*t*-Butyl-cyclohexene	4-*t*-Butyl-cyclohexene
Retention time (min)	20.1[a)]	22.7	25.5

a) The retention time of the first peak which was showed by g.l.c. examination for the mixture of *t*-butylcyclohexenes, prepared by treating 4- or 3-*t*-butylcyclohexene with *N*-lithioethylenediamine in ethylenediamine solution at 100—110°C for 3 hr. It had been confirmed by Campbell *et al.* (N. C. G. Campbell, J. R. P. Clark, R. R. Hill, P. Oberhänsli, J. H. Parish, R. M. Southan and M. C. Whiting, *J. Chem. Soc., B*, **1968**, 349) that this first peak corresponds to 1-*t*-butylcyclohexene.

B) Analysis of t-Butylcyclohexyl Phenyl Ethers. All the gas-liquid chromatographical studies of the isomeric *t*-butylcyclohexyl phenyl ethers were made at 200°C (column and detector temperature). A coiled column was made of 4-mm-i. d.×2-m annealed copper tubing packed with 20% apiezon grease L on neosorb NC (60—80 mesh: Nishio Co.). Hydrogen was used as the carrier gas (50 m*l*/min). Benzene solutions (15—25 *μl*) of *t*-butylcyclohexyl phenyl ethers (5 wt%) were then injected. The retention times of the four ethers are summarized in Table 6. It was difficult to separate the *cis*-4- and *cis*-3-isomers.

TABLE 6. RETENTION TIMES OF *t*-BUTYLCYCLOHEXYL PHENYL ETHERS

	trans-3	*cis*-3	*cis*-4	*trans*-4
Retention time (min)	15.4	17.9	17.9	22.3

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Thin-Layer Chromatography of *t*-Butylcyclohexyl Phenyl Ethers. A mixture of the *cis*-4-ether and *cis*-3-ether, the separation of which was not successful by means of GLC, was separated by TLC on silica gel GF 254 (E. Merck, Darmstadt) using *n*-hexane - benzene (9 : 1 by vol) as the developing solvent, the spots being detected by means of a UV lamp. In this case, we did not succeed in separating a mixture of the *trans*-4- and *cis*-3-(equatorial) isomers or the *trans*-3- and *cis*-4-(axial) isomers. The R_f values of the *t*-butylcyclohexyl phenyl ethers are listed in Table 7.

TABLE 7. R_f VALUES OF *t*-BUTYLCYCLOHEXYL PHENYL ETHERS

	trans-3	*cis*-3	*cis*-4	*trans*-4
R_f Value	0.54—0.66	0.41—0.51	0.56—0.66	0.35—0.46

On the basis of these results, it can be concluded that the composition of a mixture of four ethers could be analyzed according to the analysis scheme presented above.

Rate Measurements. *A) Solvolysis in a Phenol-benzene Mixture.* A sealed-ampoule technique was employed. The reaction mixture was prepared by mixing a weighed amount of the tosylate and the solution of triethylamine (of a known concentration) in a phenol-benzene mixture at room temperature. Each ampoule contained 1 m*l* of an aliquot of the reaction mixture. The thermostat was controlled to ± 0.05 at 75°C. After reaction for appropriate lengths of time, the content of the ampoule was run into acetic acid. The unchanged triethylamine was titrated with a 0.05N perchloric acid solution in acetic acid, with crystal violet as the indicator. The infinity titers were determined after at least ten half-lives. The rate constant was calculated graphically by a plot of $\log a/(a-x)$ against the time. The rate data are shown in Table 1.

B) Solvolysis in Phenol. A weighed amount of *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonate and an aliquot of a solution of a known concentration of triethylamine in melted phenol were placed in a measuring flask placed in a thermostated bath kept at 75.0±0.05°C. At appropriate time intervals, aliquot portions (1.000 m*l*) were pipetted into 5 m*l* of cold acetic acid; the solutions were then titrated according to the method described in section A. The rate constant was calculated from the first-order rate equation by a graphical method, the results being illustrated in Table 1.

Phenolyses of *cis*- and *trans*-4-*t*-Butylcyclohexyl *p*-Toluenesulfonates in a 50 wt% Phenol-Benzene Solvent in the Presence of Triethylamine. The results of the phenolyses of *cis*- and *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonates in a 50 wt% phenol-benzene solvent are summarized in Table 2. The details of the procedures can be illustrated by the following description of the phenolysis of *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonate.

A weighed amount (65 m*l*) of a 50 wt% phenol-benzene mixture containing triethylamine (0.106M) was preheated in a glass-stoppered, round-bottomed 100-m*l* flask at 75±0.05°C for 20 min; then *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonate (1.989 g) was added in one portion. After 18.7 hr (13 half-lives), the reaction mixture was diluted with 120 m*l* of ether and extracted with five 50-m*l* portions of a 10% aqueous sodium hydroxide solution. The organic layer was washed successively with 50 m*l* of a 10% aqueous sodium chloride solution, two 50-m*l* of a 10% aqueous hydrochloric acid solution, and three 50-m*l* portions of a 10% aqueous sodium chloride solution until the washings became neutral to litmus. The ether solution was then dried with anhydrous magnesium sulfate and the solvent removed by fractional distillation to give *ca.* 1 g of an oily material; this material was chromatographed using an elution column packed with 25 g of silica gel (Nakarai, No. II-A. 100—200 mesh). The column was eluted successively with *n*-hexane, *n*-hexane - benzene (7 : 3 by vol), and benzene, 20-m*l* portions being taken.

The fractions 2—5, obtained using *n*-hexane, gave 642 mg of *t*-butylcyclohexene (bp 68—69°C/29 mmHg; 72.5% yield); this substance showed, when submitted to GLC, three peaks with retention times of 20.0 min (authentic 1-*t*-butylcyclohexene, 20.1 min), 22.3 min (authentic 3-*t*-butylcyclohexene, 22.7 min), and 25.9 min (authentic 4-*t*-butylcyclohexene, 25.5 min). The composition analysis was carried out by peak-height and half-width measurements, giving the following results: 1-olefin, 0.6%; 3-olefin, 4.1%; 4-olefin, 95.3%. The fractions 9—17, obtained using *n*-hexane - benzene (7 : 3 by vol), gave 137 mg of *t*-butylcyclohexyl phenyl ether (9.4% yield). The GLC of this material showed three peaks, with retention times of 15.6 min (authentic *trans*-3-ether, 15.4 min), 18.4 min (a mixture of *cis*-3- and *cis*-4-ethers), and 22.3 min (authentic *trans*-4-ether, 22.3 min). The analysis by peak-height and half-width measurements gave 12.8%, 74.3% and 12.9% for the respective peaks. Then, the rest of the resulting phenyl ether was separated by TLC on a silica-gel layer (GF 254 E. Merck, 1 mm), using *n*-hexane - benzene (9 : 1 by vol) as the developing solvent; the spots were detected by means of a UV lamp. A mixture of the phenyl ethers (A) (*cis*-4+*trans*-3) was extracted from the layer of the R_f=0.54—0.66 by the use of benzene; another mixture of the phenyl ethers (B) (*cis*-3+*trans*-4) was similarly collected from the layer of the R_f=0.37—0.50. These ether mixtures were submitted directly to the GLC; from each mixture (A or B), two peaks were observed. The retention times were 15.4 min (authentic *trans*-3-ether, 15.4 min) (15.6%) and 18.2 min (authentic *cis*-4-ether, 17.9 min) (84.4%) for A, and 17.8 min (authentic *cis*-3-ether, 17.9 min) (30.7%) and 22.3 min (authentic *trans*-4-ether, 22.3 min) (69.3%) for B. From these results, the composition of the resulting *t*-butylcyclohexyl phenyl ether was calculated to be as follows: *trans*-3-ether, 12.8%; *cis*-3-ether, 5.1%; *cis*-4-ether, 69.2%; *trans*-4-ether, 12.9%. The fractions 20—36, obtained using benzene, gave 64.3 mg of *t*-butylcyclohexylphenol (4.4% yield); the infrared spectrum in chloroform had characteristic bands in the hydroxylic regions: $\nu_{\max}$ 3700 cm^{-1} and 3500 cm^{-1}, due to nonbonded OH and bonded OH respectively. No attempt was made to determine the composition of this *t*-butylcyclohexylphenol.

The Phenolyses Conducted in the Presence of Added *t*-Butylcyclohexene. The results of the phenolyses of *cis*- and *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonates in 50 wt% phenol-benzene, in the presence of added *t*-butylcyclohexene and triethylamine at 75°C are summarized in Table 3.

A weighed amount of a 50 wt% phenol-benzene solvent, containing triethylamine and *t*-butylcyclohexene, was preheated in a glass-stoppered flask at 75°C for 20 min. The products were isolated and separated in a manner similar to that described in the preceding section. The composition analyses of the olefin and the phenyl ether were conducted by GLC and by the combined use of GLC and TLC respectively, as has been described above.

Phenolyses Conducted in the Presence of Added Triethylammonium or Diethylammonium *p*-Toluenesulfonate. The results of the phenolyses of *cis*- and *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonates in a 50 wt% phenol-benzene solvent in the presence of initially-added triethylamine and triethylammonium (or diethylammonium) *p*-toluenesulfonate at 75.0°C are shown in Table 4. The following description of the phenolysis of *cis*-4-*t*-butylcyclohexyl *p*-toluenesulfonate in the presence of triethylamine and triethylammonium *p*-toluenesulfonate will serve to illustrate the details of the procedure.

A two-necked, round-bottomed 200-m*l* flask, placed in a dry box, was charged with 120 m*l* of a 50 wt% phenol-benzene solvent containing 0.105M triethylamine, and 3.31 g of triethylammonium *p*-toluenesulfonate (0.101M). Then the mixture was preheated at 75.0± 0.05°C for 20 min. To this mixture there was added a 3.69-g portion of *cis*-4-*t*-butylcyclohexyl *p*-toluenesulfonate (0.0990M), and then the reaction vessel was kept in a thermostated bath for 57 min. The reaction mixture was cooled in an ice bath to room temperature. The titration of 1 m*l* of an aliquot with a standard 0.05N perchloric acid solution in acetic acid, using crystal violet as the indicator, showed that phenolysis proceeded up to 75.5% completion.

A 200-m*l* portion of ether was added to the reaction mixture; the ether solution was extracted with seven 50-m*l* portions of a 20% aqueous sodium hydroxide solution which had been cooled in ice water. The ether layer was washed with a 10% aqueous hydrochloric acid solution and a 10% aqueous sodium chloride solution successively, and then dried over anhydrous magnesium sulfate. The dried ether solution was concentrated using an efficient fractionating column; during this period the bath temperature was kept below 55°C. The residual benzene solution was concentrated in a rotatory evaporator equipped with an ice-sodium chloride trap to give *ca.* 1.9 g of a colorless liquid as the residue and *ca.* 45 m*l* of a condensate in the trap. The colorless residual liquid was then condensed further under 4 mmHg at 50°C in a rotatory evaporator equipped with a dry ice-methanol trap. A wet, pale yellow crystal (0.982 g) was recovered as the residue, and in the trap 0.906 g of a colorless liquid condensed. This liquid was analyzed by GLC (5-m column, 30% PEG 6000 on selite 545 at 80°C; the same analytical conditions as that of olefin). There were observed four peaks with retention times of 1.9 min (benzene), 20.6 min (authentic 1-*t*-butylcyclohexene, 20.1 min) (a trace), 22.7 min (authentic 3-*t*-butylcyclohexene, 22.7 min) (1.2%), and 26.7 min (authentic 4-*t*-butylcyclohexene, 25.5 min) (98.8%).

The recovered pale yellow crystal, which was a mixture of phenolysis products other than olefin, was treated with sodium naphthalene in tetrahydrofuran in order to cleave the unchanged tosylate into the corresponding alcohol. In a 100-m*l* four-necked flask, equipped with a mechanical stirrer, a thermometer, a dropping funnel and a calcium chloride tube, there were successively placed 1.62 g (0.0127 mol) of naphthalene, 38 m*l* of purified THF and 0.280 g of metallic sodium, which had been cut in small pieces, under a nitrogen atmosphere and at room temperature. The mixture was stirred for 1 hr to produce a dark green solution of sodium naphthalene. Then the reaction vessel was cooled in an ice bath, and a solution of 0.800 g of pale yellow crystal in 8 m*l* of THF was added to the sodium naphthalene solution over a period of 0.8 min (reaction temperature, 0—4°C). The sodium naphthalene solution was then immediately decomposed by the addition of aqueous THF. The reaction mixture was treated with 50 m*l* of water and 15 g of sodium chloride. The water layer was extracted with three 20-m*l* portions of ether, and the combined ether extracts were washed with a 10% aqueous sodium chloride solution and then dried with anhydrous magnesium sulfate. The ether was removed by means of a rotatory evaporator to give 2.0 g of a crystalline material, which was chromatographed using an elution column packed with 60 g of silica gel (Nakarai, No. II-A. 100—200 mesh). The column was eluted successively with *n*-hexane, *n*-hexane-benzene (1 : 1 by vol), benzene, *n*-hexane-ether (9 : 1 by vol), and *n*-hexane-ether (4 : 1 by vol), 50-m*l* portions being taken. The fractions 1—12, obtained using *n*-hexane, gave 1.39 g of naphthalene. The fractions 14—17, obtained using *n*-hexane-benzene (1 : 1 by vol), gave 191.3 mg of *t*-butylcyclohexyl phenyl ether (11.6% yield), contained in the phenolysis products (it was confirmed by means of a control experiment that *t*-butylcyclohexyl phenyl ether was not affected during the cleavage reaction). The composition of the resulting *t*-butylcyclohexyl phenyl ether was determined following the analysis scheme described above: *trans*-4-ether, 60.9%; *cis*-4-ether, 19.5%; *cis*-3-ether, 7.5%; *trans*-3-ether, 12.1%. The fractions 20—22, obtained using benzene, gave 34.4 mg of *t*-butylcyclohexylphenol (2.1% yield), the infrared spectrum of which in chloroform had characteristic bands at 3700 cm^{-1} and 3500 cm^{-1}. No attempt was made to determine the composition of this material.

The fractions 33—36, obtained using *n*-hexane-ether (9 : 1 by vol), gave *t*-butylcyclohexanone, while the fractions 37—50, obtained using *n*-hexane-ether (4 : 1 by vol), gave *t*-butylcyclohexanol (products of the cleavage reaction). The details of the analyses of these materials will be reported in a subsequent paper.