BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1884—1890 (1968)

Solvolysis of *cis* and *trans* 2-Cyclohexylcyclohexyl, 2-Phenylcyclohexyl and 2-*p*-Anisylcyclohexyl *p*-Toluenesulfonate

Shun-Ichi MURAHASHI and Ichiro MORITANI

Department of Chemistry, Faculty of Engineering Science,
Osaka University, Machikaneyama, Toyonaka, Osaka

(Received December 21, 1967)

trans-2-*p*-Phenylcyclohexyl *p*-toluenesulfonate acetolyzes (75°C), at one-eighth of the rate of cyclohexyl *p*-toluenesulfonate, and one-sixteenth times smaller than that of the *cis* isomer. *trans*-2-*p*-Anisylcyclohexyl *p*-toluenesulfonate acetolyzes (75°C) much the same as cyclohexyl *p*-toluenesulfonate, and one-third times smaller than that of the *cis* isomer. Thus, the slow rate of the trans isomers cannot be interpreted in term of significant phenyl and *p*-anisylparticipation. This may be due to high cost in energy required to place the aryl group in the axial position where it would be in a favorable position to participate. However, it is noteworthy that the acetolysis of *trans*-2-*p*-anisylcyclohexyl *p*-toluenesulfonate gave *trans*-2-*p*-anisylcyclohexyl acetate in 70% yield, which had retention of configuration. The mechanism of this reaction is discussed. The greater reactivities of *cis* isomers are interpreted in terms of E_2 type elimination involving nucleophilic participation by the solvent as well as 2-alkylcyclohexyl *p*-toluenesulfonate.

On the cyclohexyl system the conformation of substituent might be consider to be fixed because the chair form is by far stable.[1] Thus it is very suitable to investigate the cyclohexyl system stereochemically or kinetically. Since the acceleration of rate or the stereochemistry of the reaction of aliphatic compounds is usually interpreted in terms of neighbouring participation or bridged nonclassical carbonium ion,[2] it is interesting to investigate these concepts in cyclohexyl system. The neighbouring participation of acetoxy,[3] halogen[4] and methoxy[5] groups are already investigated. In the acetolysis of *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate the reactivity of *cis* isomer is 630 times greater than that of the *trans* one, and *trans* acetate which has retention of configuration is obtained. Furthermore, the acetate which is obtained from optically active *p*-toluenesulfonate is found to be racemic. These results are reasonably explained by assuming that symmetrical bridged ion is involved as an intermediate.[3]

We have investigated on behavior of the neighboring participation of cyclohexyl, phenyl and anisyl groups in cyclohexyl system.

Results

Preparation of Materials and Infrared Spectra. The *cis* and *trans* isomers of 2-cyclohexylcyclohexanol (Ia), (IIa) and 2-phenylcyclohexanol (IIIa), (IVa) were prepared with the usual manner.[6,7] *trans*-2-*p*-Anisylcyclohexanol (VIa) was prepared by the reduction of the corresponding ketone with lithium aluminum hydride or hydrogenation-oxidation of 1-*p*-anisylcyclohexene. The latter reaction is better than the former one. On the other hand the hydrogenation of 2-*p*-anisylcyclohexanone in the presence of platinum black catalyst gave the *cis* isomer (Va).

---

[1] D. H. R. Barton, *Quart. Rev.*, **10**, 44 (1956).

[2] B. Capon, *ibid.*, **18**, 45 (1964).

[3] S. Wintein, E. Grunwald, R. E. Bruckles and C. Hanson, *J. Am. Chem. Soc.*, **70**, 816 (1948); S. Winstein, H. V. Hess and R. E. Bruckles, *ibid.*, **64**, 2796 (1942).

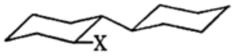
[4] S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948) ; E. Grunwald, *ibid.*, **73**, 5458 (1951).

[5] S. Winstein and R. B. Henderson, *ibid.*, **65**, 2196 (1943) ; D. S. Noyce, B. R. Thomas and B. N. Bastian, *ibid.*, **82**, 885, 1246 (1960).

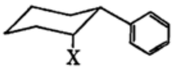
[6] W. Hückel, M. Meiel, E. Jordan and W. Seeger, *Ann.*, **616**, 46 (1958).

[7] C. C. Price and J. V. Karabinos, *J. Am. Chem. Soc.*, **62**, 1159 (1940).

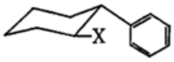
I: X=OTs
Ia: X=OH



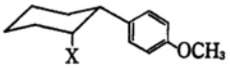
II: X=OTs
IIa: X=OH



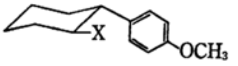
III: X=OTs
IIIa: X=OH



IV: X=OTs
IVa: X=OH



V: X=OTs
Va: X=OH



VI: X=OTs
VIa: X=OH

The infrared spectra of these isomeric alcohols obtained above are consistent with the conformational assignment. It has been pointed out that alkyl substituted cyclohexanol with an equatorial hydroxyl can be distinguished from the epimers with an axial hydroxyl by the position of C–O stretching frequency.[8] The *cis* isomer (axial) of 2-cyclohexyl, 2-phenyl and 2-*p*-anisylcyclohexanol showed absorption at 968, 964 and 965 cm^{-1} (KBr) respectively, the *trans* isomers (equatorial) at 1044, 1057 and 1056 cm^{-1}.

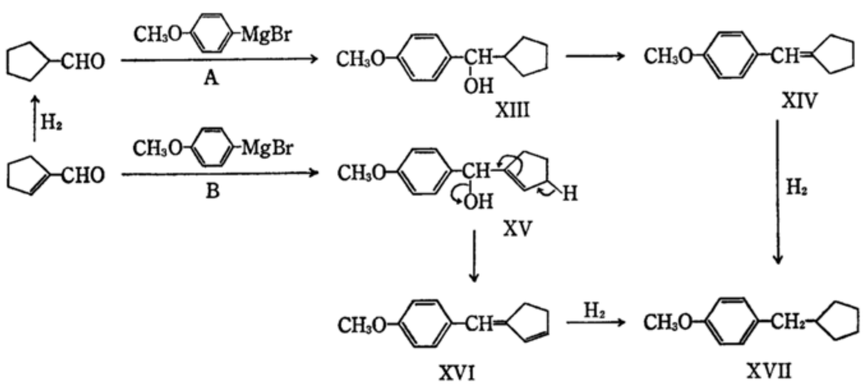
p-Methoxybenzalcyclopentane (XIV) which might be formed as the ring contraction product was obtained through the path A as shown in Scheme I. On the other hand, from the path B the alcohol XIII was not obtained, since the alcohol XV was easily dehydrated to give *p*-methoxybenzalcyclopent-1-ene (XVI).

Kinetic Experiments. The results of the kinetic measurements are listed in Table 1. Acetolyses of the isomeric *p*-toluenesulfonates in the presence of pottasium acetate are first order and the rates are increased only slightly over that observed in the absence of added acetate ion except *trans*-2-*p*-anisylcyclohexyl *p*-toluenesulfonate.[9]

The *cis* isomers are solvolyzed faster than the *trans* isomers respectively. However, the

TABLE 1. FIRST ORDER RATE CONSTANT OF 2-CYCLOHEXYL, 2-PHENYL AND 2-*p*-ANISYL *p*-TOLUENESULFONATES

Ester	Temp. °C	ROTs 10^2 M	KOAc 10^2 M	$10^5\times k_1$ sec^{-1}	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ e. u.
I	44.90	0.819	1.93	8.88 ± 0.26		
	44.91	0.819	1.93	8.92 ± 0.12		
	49.69	1.60	2.80	18.3 ± 0.2		
	59.74	1.55	2.01	51.9 ± 0.5		
	75.0			278	24.3	−0.77
II	59.84	2.21	3.04	2.46 ± 0.05		
	74.67	1.85	2.31	15.8 ± 0.3		
	75.0	2.26	2.03	16.5	28.2	+4.9
III	59.79	1.83	3.12	1.40 ± 0.04		
	74.51	1.83	3.19	7.70 ± 0.15		
	89.98	1.41	2.22	42.7 ± 0.4		
	75.0			8.38	26.5	−1.3
IV	74.73	0.684	2.28	0.455 ± 0.004		
	90.46	0.785	1.16	3.39 ± 0.07		
	99.94	0.775	2.17	10.7 ± 0.2		
	75.0			0.520	30.4	+4.3
V	74.62	1.50	2.53	12.4 ± 0.7		
	89.93	1.50	3.12	72.9 ± 0.1		
	100.09	1.60	2.53	230 ± 5		
	75.0			13.2	29.1	+6.9
VI	74.67	1.26	1.57	4.06 ± 0.19		
	89.83	1.85	3.50	21.8 ± 0.3		
	99.88	1.20	2.50	54.5 ± 0.4		
	75.0			4.31	25.7	−5.1
VI	74.62	2.49	—	2.33 ± 0.04		
	89.84	2.49	—	15.3 ± 0.2		
	99.77	2.49	—	46.7 ± 0.5		
	75.0			2.41	30.7	+6.5



Scheme I.

---

8) W. Hückel and Y. Riad, *Ann.*, **637**, 33 (1960); W. Hückel and J. Kunze, *ibid.*, **645**, 194 (1961).

9) Special salts effect has been observed about *trans*-2-*p*-anisylcyclohexyl *p*-bromobenzenesulfonate (A. N. Fainberg, G. C. Robinson and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2278 (1956)).

acetolysis rate of *trans*-2-*p*-anisylcyclohexyl *p*-toluenesulfonate is smaller than that of *cis* isomer, and the value of $\Delta H^{\neq}$ of *trans* isomer is larger than that of *cis* isomer. In the system without lyate ion, the rate is approximately half of that containing lyate ion, and showes $\Delta H^{\neq}=30.7$ kcal/mol and $\Delta S^{\neq}=6.7$ e.u.

Products. The lyate ion salt was present in slightly excess and the products were isolated after the reaction proceeded to ten half lives. The results are shown in Table 2. The solvolysis products were extracted followed by injecting to preparative v. p. c. The control experiments showed that the products were stable under the condition of the reactions, and fractionation during the isolation process was found to be slight and probably not significant. The analytical data by means of v. p. c. were suported by another method shown in Table 2. The acetolysis products of *trans*-2-*p*-anisylcyclohexyl *p*-toluenesulfonate were separated by column chromatography followed by reduction with lithium aluminum hydride, and it was ascertained the main product was *trans*-2-*p*-anisylcyclohexanol. It is noted that the main product is *trans*-2-*p*-anisylcyclohexyl acetate, which has the retention of configuration. Furthermore, the formation of *p*-methoxybenzalcyclopentane (2%) was detected by means of v. p. c.

TABLE 2. THE PRODUCTS FROM ACETOLYSIS OF 2-CYCLOHEXYL, 2-PHENYL AND 2-*p*-ANISYLCYCLOHEXYL *p*-TOLUENESULFONATES (%)

p-Toluene-sulfonate	1-Olefin	3-Olefin	Acetate	Undetected Product
I (*cis*)	99a)			
II (*trans*)	67a)	12	*cis*-19	2
	84b)		16	
III (*cis*)	91d)	6	3	
	93c)			
IV (*trans*)	36d)	28	*cis*-20	16
V (*cis*)	86d)	4	2	8
VI (*trans*)f)	11d)	16	*trnas*-69	2
	9e)	15	*trans*-70	4

a) Yield by v. p. c. (Carbowax 6000, 150°C).
b) Yield by column-chromatographic isolation (alumina).
c) Yield of total olefin determined by Lucas-Pressmann method.
d) Yield by v. p. c. using biphenyl as internal standard substance (Carbowax 6000, 200°C).
e) Similar to d) (Apiezon L, 250°C).
f) *p*-Methoxybenzalcyclopentane was detected as low as 2% yield.

TABLE 3. COMPARISON OF RATES FOR ACETOLYSIS OF 2-CYCLOHEXYL, 2-PHENYL AND 2-*p*-ANISYLCYCLOHEXYL *p*-TOLUENESULFONATE (75°C)

p-Toluenesulfonate	$k_1\times10^5$(sec^{-1})	*a*/*e*	Rel. Rate
I (*cis*)	278		66
II (*trans*)	16.5	17	3.9
III (*cis*)	8.38		2.0
IV (*trans*)	0.520	16	0.125
V (*cis*)	13.2		3.1
VI (*trans*)	4.31	3.1	1.0
Cyclohexyl-	4.28		1.0

Discussion of Results. The data on all of the compounds are summarized in Table 3, giving extrapolated or interpolated rate constants at 75°C. In addition, relative rates for cyclohexyl *p*-toluenesulfonate[10] are given for reference. As shown in Table 3 *cis* isomer (axial) solvolyzes faster than the *trans* isomer (equatorial) respectively.

In these substances the sizes of cyclohexyl, phenyl and *p*-anisyl groups are sterically large enough to suppose these groups occupy the equatorial position; in other words tosyl group occupies the axial position in the *cis* isomer, on the other hand the equatorial position in the *trans* isomer.

It appears that the greater reactivity of 2-cyclohexylcyclohexyl *p*-toluenesulfonate is due to steric acceleration. Scale model indicates that the 2-cyclohexylcyclohexyl system, unlike the 2-phenyl and 2-*p*-anisylcyclohexyl system, is quite congested and rotation of cyclohexyl and tosyl groups is restricted.

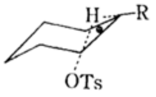
The axial-equatorial ratio of cyclohexyl *p*-toluenesulfonate is three owing to the 1,3-diaxial interaction.[11] In the case of 2-cyclohexyl and 2-phenylcyclohexyl *p*-toluenesulfonate the *cis*/*trans* ratio is respectively 16 and 17, so the *cis* isomers are more accelerated than the trans isomers. Inspection of these relative reactivities shows that in both isomers, there may be some factors to be account for the acceleration except that of 1,3-diaxial interaction. In order to aspect this factor, the products of acetolysis were investigated. As shown in Table 2 *cis* isomers gave mainly 1-olefin accompanied with a small amount of 3-olefin and acetate, although *trans* isomers gave 1-olefin and considerable large amounts of 3-olefin and *cis* acetate. Thus the formation of different products from the two

---

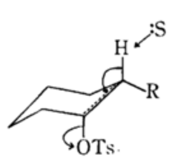
[10] H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

[11] I. Moritani, S. Nishida and M. Murakami, *ibid.*, **81**, 3420 (1959).

isomers shows that the products are not derived entirely from a dissociated 2-substituted cyclohexyl cation, since this intermediate would be common to both isomers. These results suggest that in the case of *trans* isomer, the transition state involves the classical carbonium ion. On the other hand in the *cis* isomer two explanations may offer themselves to rationalize these results; (a) E_1 type elimination involving the bridged ion XVIII or (b) E_2 type elimination by the solvent as illustrated by XIX.



XVIII



XIX

The high solvolysis rate of vicinally *cis* alkylcyclohexyl *p*-toluenesulfonates is due to participation of the adjacent hydrogen atom, though no details of the reaction products are given.[12] Recently this was supported by the study of β-deuterium isotope effect in solvolytic reaction.[13] However, by the systematic study of 2-alkylsubstituted cyclohexyl *p*-toluenesulfonate, it was revealed that the reaction was E_2 type elimination involving nucleophilic participation by the solvent.[14]

The acetolysis rates of *trans*-2-alkylcyclohexyl *p*-toluenesulfonates increase as the bulk of the substituent becomes larger, $CH_3 < i\text{-}C_3H_7 < C_6H_{11} < t\text{-}C_4H_9$. This may be also interpreted in terms of increasing steric effect by substituent. Nevertheless, the order of the rate ratio of *cis*/*trans* for each *p*-toluenesulfonate is found to $t\text{-}C_4H_9 < C_6H_{11} < i\text{-}C_3H_7 < CH_3$. This tendency may not be due to inductive effect but hyperconjugation. Therefore in the transition state of acetolysis of *cis* isomers the reaction may proceed through the *trans* elimination. Furthermore, it has been reported that the hydrogen participation is not effective in the solvolysis of neomenthyl,[15] 3-cyclohexyl-2-butyl[16] and 2-*t*-butylcyclohexyl *p*-toluenesulfonate.[17] Thus the accelerated rate of *cis*-2-cyclohexylcyclohexyl *p*-toluenesulfonate is considered to be arised from a predominating bimolecular solvolysis (*trans*-elimination).

TABLE 4. RATES AND RELATIVE RATES FOR ACETOLYSIS OF 2-ALKYLCYCLOHEXYL *p*-TOLUENESULFONATES (75°C)

2-Alkyl substituted cyclohexyl *p*-toluene-sulfonate	CH_3	$i\text{-}C_3H_7$-	C_6H_{11}-	$t\text{-}C_4H_9$-
k_1^{trans} (10^5)	1.56	9.22	16.5	352
k_1^{trans}/k_0^{trans}	1.00	5.91	10.6	226
k_1^{cis} (10^5)	79.5	221	278	634
k_1^{cis}/k_0^{cis}	1.00	2.78	3.50	7.98
cis(a)/*trans*(e)	51	24	17	1.8

Turing to the π-electron neighbouring system, the similar result was obtained concerning to 2-phenylcyclohexyl *p*-toluenesulfonate as shown in Tables 2 and 3. The data suggest that the reaction mechanism of acetolysis of this *p*-toluenesulfonate is same as that of 2-alkylcyclohexyl *p*-toluenesulfonate. The rate retardation observed is presumably due to the inductive effect of phenyl group.

The *trans* isomer solvolyzes not faster but slower, at one-eighth of the rate of cyclohexyl *p*-toluenesulfonate, and one-sixteenth times smaller than that of the *cis* isomer. The slow rate of the *trans* isomer cannot be interpreted in terms of significant phenyl participation. In the present case we can rationalize the failure to observe participation to the high cost in energy required to place the phenyl group in the axial position where it would be a favourable position to participate.

For the sake of comparison, rate and products of acetolysis were studied on 2-*p*-anisylcyclohexyl *p*-toluenesulfonate. In the case of *cis* isomer, the results shown in Tables 3 and 4 are similar to that of *cis*-2-phenylcyclohexyl *p*-toluenesulfonate. This indicates that *cis* isomer proceeds through *trans* elimination. On the contrary, *trans*-2-*p*-anisylcyclohexyl *p*-toluenesulfonate gave different products from those obtained from 2-alkylcyclohexyl *p*-toluenesulfonate, *viz.* the main product was not 1-olefin but acetate (70%), which was produced by retention of configuration, *trans* acetate.

The products of retention of configuration might be obtained from double inversion, that is, phenyl participation. It leads to the

---

[12] S. Winstein, B. K. Moore, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, *ibid.*, **74**, 1127 (1952); S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955); S. Winstein and J. Takahashi, *Tetrahedron*, **2**, 316 (1958); D. J. Cram and J. Tadanier, *J. Am. Chem. Soc.*, **81**, 2737 (1959).

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

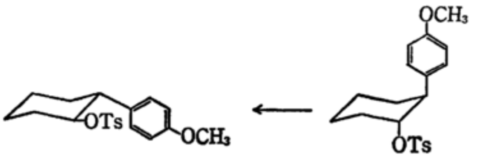
[14] I. Moritani, N. Obata and S. Nishida, to be published.

[15] W. Hückel and C. M. Jennewein, *Ann.* **683**, 100 (1965).

[16] H. C. Brown, K. J. Morgan and F. J. Chloupec, *J. Am. Chem. Soc.*, **87**, 2137 (1965).

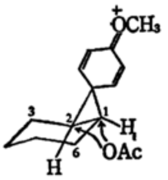
[17] K. Okamoto and K. Saito, The Abstract of the 18th Conference on the Reaction Mechanism of Organic Reaction at Kyoto 1967, page 81.

rate enhancement and retention of configuration through bridging of phenyl group. The powerful participation effect of *p*-anisyl group[18] and the formation of bridged *p*-anisonium ion in strong acid[19] have been observed. However, since the *trans* isomer VI solvolyzes slower than cyclohexyl *p*-toluenesulfonate, it seems likely that *p*-anisyl participation is not important in the reaction of this compound. This may be due to high cost in energy required to place the *p*-anisyl group in the axial position where it would be in a favourable position to participate.



XX XXI

We therefore propose the following mechanism. The rate determining step is the formation of classical carbonium ion. *p*-Anisyl group can migrate just before carbonium ion is formed at C_1, then the intermediate XXII may be formed. The newly formed bridged ion XXII may be a considerable stable intermediate of so called dienon type.[20]



XXII

When the bridged ion is opened by acetate ion, the products, which possess the same configuration as the starting materials, are obtained. Olefins might be obtained through abstraction of proton by solvent. The fact that 3-*p*-anisylcyclohexene is mainly obtained may be rationalized by suspecting the easy abstraction of proton at C_3 or C_6.

It is noteworthy that *p*-methoxybenzal cyclopentane, the rearranged ring contracted product, was detected only as low as 2% yield. The migration of methylene group may be far less than that of *p*-anisyl group in this compound.

Experimental

All melting points ware uncorrected. The IR spectrum was recorded by the use of an EPI-S2 apparatus. The UV spectrum was recorded by the use of an EPS-2U apparatus.

Materials. *2-Cyclohexylcyclohexanone.* 1-Chlorocyclohexylcyclohexanone was prepared by condensation of cyclohexanone by the method of Kunze,[21] in 70% yield, bp 115°C/6 mmHg (lit.[22] bp 140°C/18 mmHg), semicarbazone, mp 182—183°C (lit.[22] mp 182—183°C). This ketone was converted to 2-cyclohexylidenecyclohexanon by treatment with sodium methoxide in 82% yield, mp 57°C (methanol) (lit.[23] mp 57°C), semicarbazone mp 186.5—188°C. Moreover hydrogenation of 2-cyclohexylidenecyclohexanone over PdO_2-$CaCO_3$ catalysts gave 2-cyclohexylcyclohexanone in 98% yield, bp 126°C/8 mmHg (lit.[23] bp 135°C/11 mmHg), n_D^{20} 1.4913 (lit.[23] n_D^{20} 1.4915).

cis-2-Cyclohexylcyclohexanol (Ia). This material was prepared by hydrogenation of 2-cyclohexylcyclohexanone over platinum black in acetic acid in 74% yield, mp 59—60°C (petroleum ether, bp 40—50°C) (lit.[6] mp 60.8°C).

trans-2-Cyclohexylcyclohexanol (IIa). This material was prepared by reduction with lithium aluminum hydride of 2-cyclohexanone at 0°C, bp 106—107°C/6 mmHg, n_D^{20} 1.5010. This alcohol was esterificated with phthalic acid and recrystallized several times with chloroform followed by hydrolysis, and pure alcohol was obtained, mp 53—54°C (lit.[6] 52.8°C).

1-Cyclohexylcylohexene (VII). 1-Cyclohexylcylohexanol, mp 53-54°C (lit.[24] mp 51°C), bp 114—115°C/7 mmHg was dehydrated by iodine at 150°C in 50% yield, bp 64—66°C/7 mmHg, n_D^{20} 1.4965 (lit.[25] n_D^{20} 1.4949).

3-Cyclohexylcyclohexene (VIII). This material was prepared from cyclohexylmagnesium bromide and 3-cyclohexenyl bromide, bp 73—74°C/7 mmHg, n_D^{20} 1.4964 (lit.[25] n_D^{20} 1.4941).

cis-2-Phenylcyclohexanol (IIIa). *o*-Phenylphenol was hydrogenated using Raney nickel as catalyst in ethanol.[7] The oily mixture of alcohol (6.5 g) obtained was chromatographed over 100 g of activated alumina. Elution with petroleum ether (bp 40—50°C) gave 4.1 g of *cis* alcohol, mp 40—42°C (petroleum ether, bp 40—50°C) (lit.[7] mp 40—42°C).

Found: C, 81.54; H, 9.16%. Calcd for $C_{12}H_{16}O$:

---

18) S. Winstein *et al.*, *J. Am. Chem. Soc.*, **74**, 1140 (1952); **75**, 147 (1953); **78**, 328 (1956); S. Winstein and R. Baker, *ibid.*, **86**, 2071 (1964); H. C. Brown and H. M. Bell, *ibid.*, **86**, 5003, 5006 (1964); P. von R. Schleyer, D. C. Kleinfelter and H. G. Richey, Jr., *ibid.*, **85**, 479 (1963); H. C. Brown, R. Bernheimer, C. J. Kim and S. E. Schepple, *ibid.*, **89**, 370 (1967).

19) G. A. Olah, E. Namanworth, M. B. Comisarow and B. Ramsey, *ibid.*, **89**, 711 (1967).

20) R. Baird and S. Winstein, *ibid.*, **84**, 788 (1962); A. A. Guiswold and O. L. Chapman, *J. Org. Chem.*, **29**, 2047 (1964); L. Eberson and S. Winstein, *J. Am. Chem. Soc.*, **87**, 3506 (1965).

21) K. Kunze, *Ber.*, **59**, 2085 (1926).

22) W. Hückel, O. Neuenfoeffer, A. Gerke and E. Frank, *Ann.*, **477**, 119 (1930).

23) J. Reese, *Ber.*, **75**, 384 (1942).

24) F. Signaigo and P. Cramer, *J. Am. Chem. Soc.*, **55**, 3326 (1933).

25) W. Hückel *et al.*, *Ann.*, **637**, 33 (1960).

C, 81.77; H, 9.14%. *cis*-2-phenylcyclohexyl phthalate, mp 174—175°C. Further elution with the petroleum ether (bp 40—60°C) gave small amount of *trans* isomer (IVa).

trans-2-Phenylcyclohexanol (*IVa*). This material was prepared from 2-phenylcyclohexanone[7] by lithium aluminum hydride reduction, mp 52—54°C (petroleum ether, bp 40—50°C) (lit.[7] mp 52—53°C).

Found: C, 81.60; H, 9.04%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.14%.

1-Phenylcyclohexene (*IX*). 1-Phenylcyclohexanol was dehydrated by heating with potassium acid sulfate,[26] bp 125—127°C/15 mmHg, n_D^{20} 1.5692.

3-Phenylcyclohexene. This material prepared from 3-bromocyclohexene and phenylmagnesium bromide, bp 114—115°C/15 mmHg, n_D^{20} 1.5448 (lit.[26] n_D^{20} 1.5448).

2-p-Anisylcyclohexanone. This ketone was prepared by the reaction of *p*-anisylmagnesium bromide with 2-chlorocyclohexanone in 46% yield, mp 88.0—88.5°C (lit.[27] mp 89°C).

Found: C, 76.61; H, 7.90%. Calcd for $C_{13}H_{16}O$: C, 76.44; H, 7.90%.

1-p-Anisylcyclohexene(*XI*). 1-*p*-Anisylcyclhexanol prepared from cyclohexanone and *p*-anisylmagnesium bromide was easily dehydrated during distillation, bp 138—139°C/6 mmHg. Completely dehydration by heating with potassium acid sulfate gave the pure 1-*p*-anisylcyclohexene in 52% yield, mp 32—33°C.

Found : C, 82.94 ; H, 8.60%. Calcd for $C_{13}H_{16}O_2$: C, 82.93 ; H, 8.57%. This olefin was hydrogenated with paladium black in alcohol at atmospheric pressure. After absorbing theoretical amount of hydrogen, crystalline material was obtained, which was ascertained to be *p*-anisylcyclohexene by comparison with IR spetrum and mixed melting point of the authentic sample, mp 57—58°C (lit.[27] 57—58°C).

Found: C, 81.60; H, 9.30%. Calcd for $C_{13}H_{18}O$: C, 82.08: H, 9.53%.

trans-2-p-Anisylcyclohexanol (*VIa*). This material was prepared by two methods. First, 2-*p*-anisylcyclohexanone (14 g) in dry ether (100 m*l*) was added with stirring to the ethereal solution (100 m*l*) of lithium aluminum hydride (1.5 g) below 10°C. After treatment with the usual manner, alcohol VIa (12.6 g) was obtained, mp 70—71°C (petroleum ether, bp 40—50°C).

Found: C, 75.47; H, 8.85%. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%. On the other hand, 1-*p*-anisylcyclohexene (30 g) in tetrahydrofuran (100 m*l*) was treated with diborane generated from 30 mmol of boron trifluoride ethelate.[28] After destroying excess diborane the organoborane was treated with 18.5 m*l* of 3N sodium hydroxide followed by addition of 18.5 m*l* of 30% hydrogen peroxide at 30—50°C. The reaction mixture was stirred for an additional hour, then extrated with ether. After treatment with the usual manner recrystallization by petroleum ether (bp 50—70°C) gave *trans-2-p*-ansylcyclohexanol (29 g), mp 70.8—71.2°C.

Found: C, 75.77; H, 8.88%. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%. These two alcohols obtained above showed the same IR spectra and mixed melting points.

cis-2-p-Anisylcyclohexanol (*Va*). A mixture of 2-*p*-anisylcyclohexanone (6.7 g), acetic acid (70 m*l*) and conc. hydrochloric acid (1 m*l*) was hydrogenated over platin-mohr catalysis at atmospheric pressure until the theoretical amount of hydrogen had been absorved. After treatment with the usual manner *cis*-2-*p*-anisylcyclohexyl acetate (Vb) was obtained, mp 81—82°C.

Found: C, 72.49; H, 8.05%. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12%. *cis-p*-Anisylcyclohexanol was prepared by hydrolysis of the acetate in 66% yield (from ketone), mp 53—54°C (petroleum ether, bp 40—50°C).

Found: C, 75.82; H, 8.73%, Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%. This alcohol was identical with the one obtained from the reduction of 2-*p*-anisylcyclohexanone by aluminum isopropoxide.[27]

trans-2-p-Anisylcyclohexyl Acetate (*VIb*). This material was prepared from *trans*-2-*p*-anisylcyclohexanol and acetic acid anhydride in dry pyridine in 98% yield, mp 58—59°C (petroleum ether, bp 40—50°C).

Found: C, 71, 94; H, 8.00%. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12%.

3-p-Anisylcylohexene (*XII*). This material was obtained from 3-bromocyclohexene and *p*-anisylmagnesium bromide in 40% yield, n_D^{25} 1.5498 (lit.[29] 1.5500).

Cyclopentyl Aldehyde. 1-Cyclopent-1-ene aldehyde[30] was prepared from oxidation of *trans*-cyclohexane-1, 2-diol by sodium paraperiodate followed by condensation by potassium hydroxide solution at pH 4, bp 57°C/25 mmHg, ν 1640 (C=C), 1679 cm^{-1} (C=O), λ_{max}^{EtOH} 234.5 mμ. A solution of this aldehyde (40 g) in ether (50 m*l*) was hydrogenated over 8% paradium-charcoal catalyst (8 g). After absorption of the theoretical amount of hydrogen (10 *l*), the catalysts were filtered off, and the distillation of the filtrate gave cyclopentyl aldehyde[31] (20 g), bp 34°C/24 mmHg, ν 1720 cm^{-1}.

p-Anisylcylopentylcarbinol (*XIII*). To a solution of *p*-anisylmagnesium bromide (0.23 mol) in ether (400 m l) was added a solution of cyclopentyl aldehyde (20 g) in ether (200 m*l*) with reflux. After treatment with the usual manner *p*-anisylcyclopentylcarbinol (20 g) was obtained. Phenyl urethane, mp 237—238°C.

p-Methoxybenzalcyclopentane (*XIV*). *p*-Anisylcyclopentylcarbinol was dehydrated by heating with aqueous oxalic acid, bp 82—84°C/0.001 mmHg, n_D^{20} 1.5710.

Found: C, 82.94; H, 8.54%. Calcd for $C_{13}H_{16}O$:

---

26) E. L. Eliel, J. W. McCoy and C. C. Price, *J. Org. Chem.*, **22**, 1533 (1957).

27) W. E. Bachmann, G. I. Fujimoto and L. B. Wick, *J. Am. Chem. Soc.*, **72**, 1995 (1950).

28) H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961).

29) W. R. Biggerstaff, A. P. Menditto and I. Yokoyama, *J. Org. Chem.*, **19**, 934 (1954).

30) J. B. Brown, H. B. Herbest and E. H. Jones, *J. Chem. Soc.*, 3634 (1950).

31) P. M. Union, *Ann. chim.*, [11] **43**, 1 (1934).

C, 82.93; H, 8.57%.

p-Methoxybenzalcyclopentene (*XVI*). To a solution of *p*-anisylmagnesium bromide (0.42 mole) in ether (350 m*l*) a solution of 1-cyclopent-1-ene aldehyde (38 g) in ether (100 m*l*) was added slowly with stirring at 0°C. After reflux for additional half of hour, the mixture was poured into a cold saturated aqueous solution of ammonium chloride. The organic layer was washed with water and dried over magnesium sulfate, and the ether was removed. The residual oil was distilled, bp 118—119°C/0.15 mmHg, mp 70—71°C (ethanol) (56%).

Found: C, 83.35; H, 7.40%. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58%. ν_{Nujol} 1255, 1247 ($-OCH_3$), 1606, 1537, 1510, 1179, 814 (phenyl), 1306 cm^{-1}, λ_{max}^{EtOH} 297.5 mμ. The olefin (mp 70—71°C) above obtained was hydrogenated by absorbing two moles of hydrogen, and *p*-anisylcyclopentylmethane was obtained, n_D^{20} 1.5238.

Found: C, 81.86; H, 9.49%. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54%. This material was also obtained by hydrogenation of *p*-methoxybenzal cyclopentane by the absorption of one mole of hydrogen.

Kinetic Measurements. Solvolysis kinetics were measured by our previous methods.[11] In the solvolysis of the *p*-toluenesulfonates, no unusual feature was noted in the kinetic behavior except *trans*-2-*p*-anisylcyclohexyl *p*-toluenesulfonate. In this case special salt effect was found.[32]

Acetolysis products. *Acetolysis of cis and trans-2-Cyclohexylcyclohexyl p-Toluenesulfonate. a*) *Vapor Phase Chromatography.* The mixture of *trans*-2-cyclohexylcyclohexyl *p*-toluenesulfonate (4.95 g) and potassium acetate (2.25 g) was acetolyzed at 99.8°C until the reaction proceeded to ten-half lives. The reaction mixture was poured into cold water followed by continuous extraction by petroleum ether (bp 40—50°C). After washing with sodium bicarbonate solution and water, the petroleum ether solution was dried, concentrated and injected to v. p. c. (Carbowax 6000, 3 m, 150°C). The data obtained is shown in Table 2. For the acetolysis of *cis*-2-cyclohexylcyclohexyl *p*-toluenesulfonate the data was obtained by the same treatment.

b) *Product Isolation.* A solution of *trans*-2-cyclohexylcyclohexyl *p*-toluenesulfonate (3.36 g) and potassium acetate (1.10 g) in acetic acid (100 m*l*) was acetolyzed and treated similarly as described above. The concentrated petroleum ether solution was chromatographed over alumina. Elution with petroleum ether gave olefins (1.99 g) selectively and further elution with benzene gave acetate (0.32 g). Treatment of the acetate with lithium aluminum hydride gave an alcohol, which was identified to be *cis*-2-cyclohexylcyclohexanol by comparison of IR spectrum with that of an authentic sample.

Acetolysis of cis and trans-2-Phenylcyclohexyl p-Toluenesulfonates. The acetolysis products were determined by v. p. c. (Carbowax 6000, 3 m, 200°C).

Acetolysis of cis and trans-2-p-Anisylcyclohexyl p-Toluenesulfonates. a) *Vapor Phase Chromatography.* A solution of *trans*-2-*p*-anisylcyclohexyl *p*-toluenesulfonate (5.02 g) in acetic acid (140 m*l*) and potassium acetate (2.20 g) was heated at 99.8 °C until the reaction proceeded to ten-half lives. Further work up essentially as above for the *cis*-2-cyclohexyl *p*-toluenesulfonate yielded oily liquid (3.81 g), this was submitted to v. p. c. (Apiezon L, 2 m, 250°C, and Carbowax 6000, 2 m, 200°C, biphenyl was used as an internal standard substance). *p*-Methoxybenzalcyclopentane which was formed through ring contraction was identified, but *p*-anisylcyclopentylcarbinyl acetate and *p*-anisylmethylcyclopentene-1 were not detected.

A solution of *cis*-2-*p*-anisylcyclohexyl *p*-toluenesulfonate (0.788 g) in acetic acid (140 m*l*) and potassiun acetate (0.457 g) was solvolyzed. The reaction products (0.408 g) was analyzed by v. p. c.

b) *Product Isolation.* A solution of *trans*-2-*p*-anisylcyclohexyl *p*-toluenesulfonate (250g) in acetic acid (100 m*l*) potassium acetate (1.02 g) were heated at 99.8°C until ten half lives. After treatment as described above the oily reation products (1.42 g) obtained were dissolved in petroleum ether and submited to v. p. c. Elution with benzene gave olefins and further elution with benzene-methanol gave acetate. Treatment of the acetate with lithium aluminum hydride gave alcohol (mp 70—71°C), which was identified to be *trans*-2-*p*-anisylcyclohexanol by comparison with IR spectrum and mixed mp. The ratio of olefin and *trans* acetate is 12/88.

TABLE 5. DECOMPOSITION TEMPERATURE, ANALYTICAL DATA AND YIELDS OF 2-SUBSTITUTED CYCLOHEXYL *p*-TOLUENESULFONATES[a]

Ester	Decompt. point (°C)	Found C%	Found H%	Calcd C%	Calcd H%	Yield %
I	84.5 (84.2)[8]	67.88	8.34	67.80	8.39	68
II	122 (125.8)[8]	67.49	8.21	67.80	8.39	84
III	114 (102—103)[33]	68.96	6.77	69.06	6.71	60
IV	129 (126—128)[33]	69.36	6.78	69.06	6.71	69
V	117	66.61	6.65	66.64	6.65	81
VI	119	66.69	6.62	66.64	6.65	94

a) *p*-Toluenesulfonates were prepared from the method of Tipson.[34]

---

32) S. Winstein and R. M. Roberts, *J. Am. Chem. Soc.*, **75**, 2297 (1953).

33) S. J. Cristol and F. R, Stermitz, *ibid.*, **82**, 4692 (1960).

34) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).