The Effect of Conformation on Reactivity. III[1]*. Acetolysis of the cis-Decalyl p-Toluenesulfonates*

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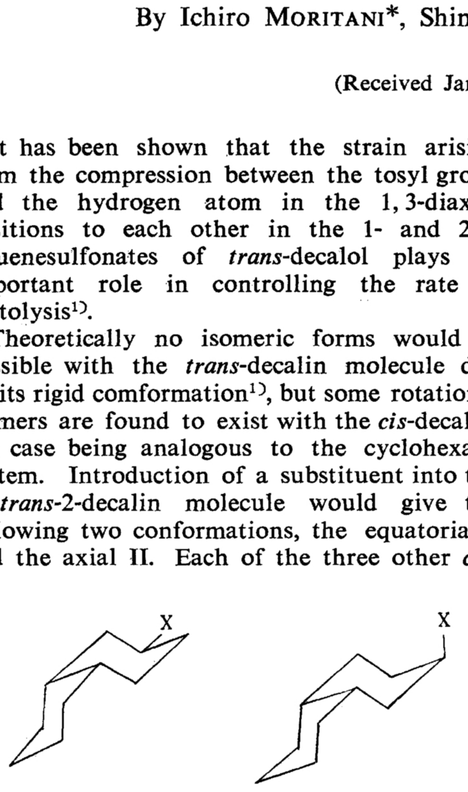
It has been shown that the strain arising from the compression between the tosyl group and the hydrogen atom in the 1, 3-diaxial positions to each other in the 1- and 2-*p*-toluenesulfonates of *trans*-decalol plays an important role in controlling the rate of acetolysis[1].

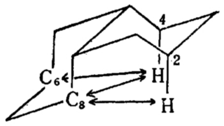
Theoretically no isomeric forms would be possible with the *trans*-decalin molecule due to its rigid comformation[1], but some rotational isomers are found to exist with the *cis*-decalin, the case being analogous to the cyclohexane system. Introduction of a substituent into the *cis*-*trans*-2-decalin molecule would give the following two conformations, the equatorial I and the axial II. Each of the three other *cis*-decalyl derivatives will give similar conformational isomers[2]. Therefore it would not be possible to utilize the interpretation given for the *trans*-decalyl system in predicting reactivities of the *cis*-decalyl derivatives.



I II

cis-*trans*-2-Decalyl derivative

The *cis*-decalin was found to be less stable than the *trans*-decalin[3]. This instability would be due to a non-bonded interaction between the atoms which constitute the *cis*-decalin ring. In other words, 1, 3-diaxial interactions are regarded as being responsible for the instabilities. This is apparent by the examination of the structure represented by III; there is a steric compression between the CH_2 group at C_6 and the hydrogen atoms in the axial position at C_2 and C_4. The group involved in giving rise to strains in the system under consideration differs therefore, as seen above, from that found to be participating in the system previously studied, i. e., the CH_2 group rather than the tosyl group. It is of considerable interest to see how this type of 1, 3-diaxial interaction will affect *cis*-decalyl derivatives.



III

cis-Decalin

Hückel[4] has made studies on the methanolysis of *cis*-decalyl *p*-toluenesulfonates[4], but has not correlated the reactivities with conformations.

It seems desirable therefore to study the reaction on a quantitative basis to find the relationships between conformation and reactivity. In this regard, we have undertaken a study on rates of acetolysis of the four isomers of the *cis*-decalyl *p*-toluenesulfonates.

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1) Parts I and II of this series: I. Moritani, S. Nishida and M. Murakami, *J. Am. Chem. Soc.*, **81**, 3420 (1959); S. Nishida, ibid., **82**, 4290 (1960).

2) Dauben [Ref. W. G. Dauben, R. C. Tweit and C. Mannerskantz, ibid., **76**, 4424 (1954)] proposed the preferred conformation of various *cis*-decalyl amines.

3) W. G. Dauben and K. S. Pitzer, "Steric Effects in Organic Chemistry", Ed. by M. S. Nerman, John Wiley & Sons, Inc., New York (1956), p. 25.

4) W. Hückel, *Ber.*, **77**., 805 (1944); W. Hückel, R. Bross, O. Fechig, H. Feltkamp, S. Geiger, M. Hanack, M. Heinzel, A. Hubele, J. Kurg, M. Maier, D. Maucher, G. Näher, R. Neidleind and R. B. Rasingkar, *Ann.*, **624**, 142 (1959).

TABLE I. SUMMARY OF THE RATE CONSTANTS OF THE ACETOLYSIS OF *cis*-DECALYL *p*-TOLUENESULFONATES

Decalyl *p*-toluene sulfonate	Temp. °C	$10^5 \cdot k_1$ sec^{-1}	$\Delta H^{\neq}$ kcal./mol.	$\Delta S^{\neq}$ e. u.
cis-cis-1	75.0	73.3		
	64.77	25.3±0.01	23.6	−5.3
	51.04	5.39±0.06		
	41.32	1.70±0.03		
cis-trans-1	95.42	41.4±0.3	28.2	−2.1
	85.08	13.3±0.1		
	75.0	4.08		
	70.45	2.33±0.02		
	60.26	0.647±0.014		
cis-cis-2	90.21	42.5±0.4	27.3	+0.6
	75.36	7.84±0.02		
	75.0	7.15		
	60.33	1.32±0.01		
cis-trans-2	90.29	45.4±0.2	27.4	+1.3
	75.61	8.88+0.04		
	75.0	8.53		
	60.33	1.34±0.004		

TABLE II. RELATIVE RATES OF ACETOLYSIS OF *cis*- AND *trans*-DECALYL *p*-TOLUENESULFONATES AT 75.0°C

Decalyl *p*-toluene-sulfonate	Rel. rate 75.0°C	Decalyl *p*-toluene-sulfonate	Rel. rate 75.0°C	cis/trans
cis-trans-1	2.1	*trans-trans*-1	0.53	3.9
cis-cis-1	36.9	*trans-cis*-1	27.6	1.3
cis-trans-2	4.3	*trans-trans*-2	3.1	1.4
cis-cis-2	3.6	*trans-cis*-2	1.0	3.6

TABLE III. PERCENTAGE OF OLEFIN FORMED ON THE ACETOLYSIS OF DECALYL *p*-TOLUENESULFONATES at 100°C

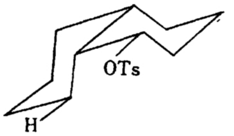
Decalyl *p*-toluenesulfonate	Conformation	Percentage of Olefin, %
trans-trans-1	1 e	66
trans-cis-1	1 a	90
trans-cis-2	2 e	68
trans-trans-2	2 a	80
cis-trans-1		81
cis-cis-1		100
cis-cis-2		79
cis-trans-2		74

The rates of acetolysis of *cis-cis*-1, *cis-trans*-1, *cis-cis*-2, *cis-trans*-2-decalyl *p*-toluenesulfonate were measured at several temperatures. The results are given in Table I. Straight-line relationships between the rate constants and reciprocal of the absolute temperatures were obtained.

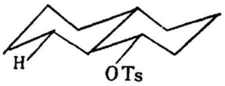
The rates of acetolysis of the *cis*-decalyl derivatives were found to be always faster than those of the *trans*-decalyl derivatives. The rate acceleration in the *cis*-decalyl system appears to be due to 1, 3-diaxial interaction, consisting of a strain between ring A and B (Table II).

To provide further evidence, the products formed in the acetolysis of the *p*-toluenesulfonates were determined and the results are summarized in Table III. The acetolysis of *cis-cis*-1-decalyl *p*-toluenesulfonate yielded—octalin as the principal product. The olefin obtained gave only the white nitroso chloride, m. p. 138°C (decomp.), of $\Delta^{1,9}$-octalin[5] by treatment with amyl nitrite and concentrated hydrochloric acid. The olefin was also identified by the infrared and ultraviolet absorption spectra* (Figs. 1 and 2).

On the other hand, *cis-cis*-2-decalyl *p*-toluenesulfonate gave 80% of an olefin which was identified to be disubstituted by the ultraviolet absorption spectrum, Fig. 2 and 20% of acetate. The rate of acetolysis of *cis-cis*-1-decalyl *p*-toluenesulfonate is expected to be comparable to that of *trans-trans*-1-decalyl *p*-toluenesulfonate as illustrated in IV and V.



IV
cis-cis-1-Decalyl
tosylate
70



V
trans-trans-1-Decalyl
tosylate
1

70 : 1

However, the rate of the former was found to be 70 times faster than that of the latter. This marked difference in reactivity would then be ascribed to characteristics inherent to the ring systems or their conformation, since it has been known that *cis*-decalin is less stable than the *trans*-decalin by 2.2 kcal./mol.[3]. It would then be reasonable to suppose that the 1, 3-diaxial interaction present in the ground state of *cis*-decalin ring system is responsible for the exceedingly fast rate of the *cis*-decalyl derivatives. The mechanism involved contains obviously a weakening of the strain in the course of attaining the transition state by loosening the carbon-hydrogen bond at C_9 with simultaneous formation of a partial double bond between C_1 and C_9. This decrease in strain is due to a displacement of C_9 from the axial to the equatorial position with respect to the A ring as shown in

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[5] A. C. Cope and G. Holzman, *J. Am. Chem. Soc.*, 72, 3062 (1952).

* An olefin obtained from an acetolysis of *trans-cis*-1-decalyl *p*-toluenesulfonate showed exactly the same infrared and ultraviolet absorption spectra as those of the olefin obtained in this study.

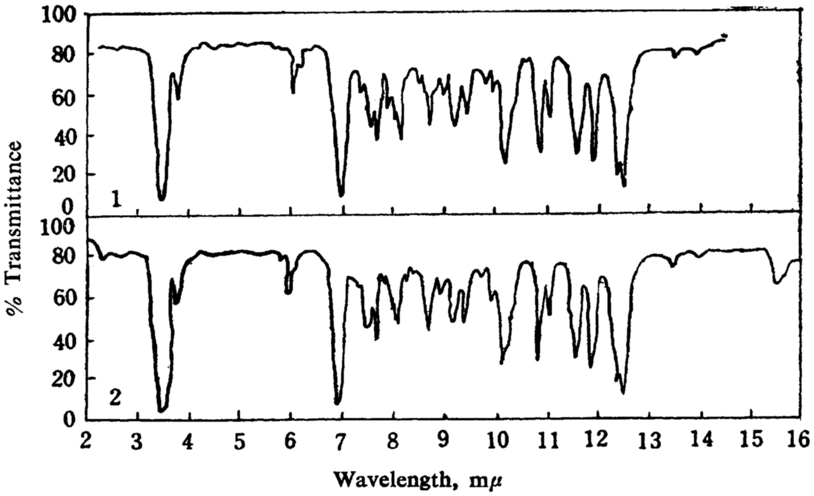


Fig. 1. ------ Infrared absorption spectra; curve 1, the olefin obtained on the acetolysis of *cis-cis*-1-decalyl *p*-toluenesulfonate; curve 2, $\triangle^{1,9}$-octalin6).

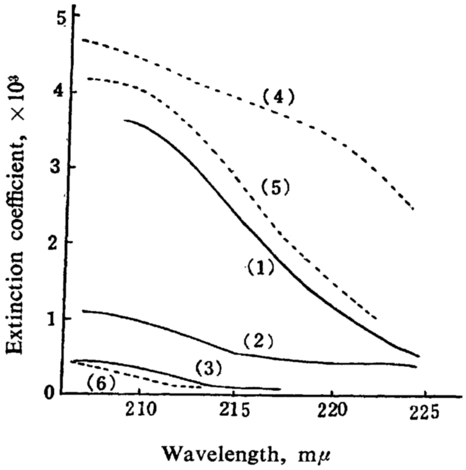
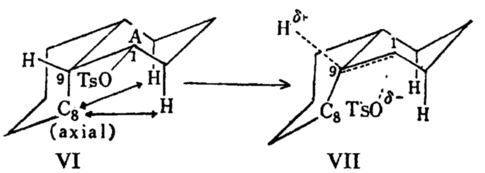


Fig. 2. Ultraviolet absorption spectra; curve 1, the olefin obtained on the acetolysis of *cis-cis*-1-decalyl *p*-toluenesulfonate; curve 2, the olefin obtained on the acetolysis of *cis-trans*-1-decalyl *p*-toluenesulfonate; curve 3, the olefin obtained on the acetolysis of *cis-cis*-2-decalyl *p*-toluenesulfonate; curve 4, tetrasubstituted olefin7); curve 5, trisubstituted olefin (exo-double bond)7); curve 6, disubstituted olefin7).



VI
cis-cis-1-Decalyl tosylate
(more strained)

VII
(transition state)
(less strained)

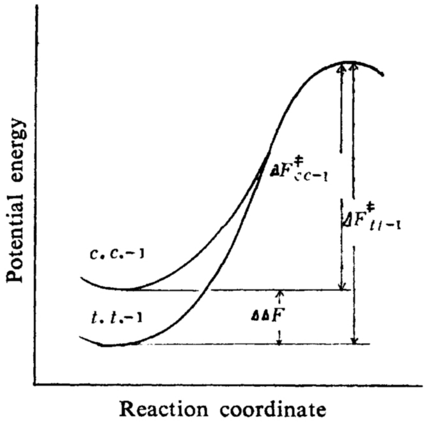


Fig. 3

VI and VII. Supposing the conformation of the transition state of *trans-trans*-1- to be similar to that of *cis-cis*-1-, the free energy of activation which controls reactivity can be represented as shown in Fig. 3, in which $\Delta F^{\ddagger}_{cc-1}$ indicates the free energy of activation for *cis-cis*-1- and $\Delta F^{\ddagger}_{tt-1}$ for *trans-trans*-1-decalyl *p*-toluenesulfonate. The energy difference between *cis*- and *trans*-decalin in the ground state would then be $\Delta\Delta F$. Thus *cis-cis*-1-decalyl *p*-toluenesulfonate should contain less free energy of activation than does the *trans-trans*-1-decalyl *p*-toluenesulfonate by $\Delta\Delta F$ indicating a higher reactivity of the former.

This rate-accelerating factor participates only in the elimination reaction. In other words, the rate-accelerating factor is operating only when $\Delta^{1,9}$-octalin is formed as a result of the cleavage of the *cis*-decalin ring. Our result that the acetolysis of *cis-cis*-1-1-decalyl *p*-toluenesulfonate yielded only $\Delta^{1,9}$-octalin is

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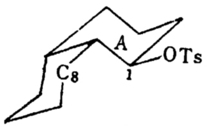
6) A. C. Cope, R. J. Cotter and G. G. Roller, *J. Am. Chem. Soc.*, **77**, 3594 (1955).

7) P. Bladon, H. B. Henbest and G. W. Wood, *J. Chem. Soc.*, **1952**, 2737.

well in accord with the interpretation based on the above consideration.

cis-trans-1-Decalyl *p*-toluenesulfonate, an epimer of *cis-cis*-decalyl *p*-toluenesulfonate, was found to be less reactive than the *cis-cis*-1-decalyl derivative, the former being 17 times less reactive than the latter.

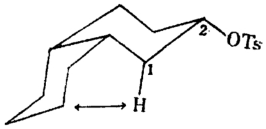
The preferred conformation of the *cis-trans*-1-decalyl derivative is represented by VIII and it will be seen that the C_8 is in the equatorial position with respect to ring A*). Accordingly, in the transition state a partial double bond should be formed between C_1 and C_9, in conformity with the explanation given for the *cis-cis*-1-decalyl derivative. But the decrease of the strain of the *cis*-decalin ring will be expected to be much smaller than that observed with the *cis-cis*-1-decalyl derivative. Thus, the contribution of strain in the acceleration of the reaction rate would be exceedingly small. This prediction was well supported by our experimental results, which showed that reactivity of *cis-trans*-1-decalyl *p*-toluenesulfonate was smaller than that of *cis-cis*-1-decalyl *p*-toluenesulfonate but greater than that of *trans-trans*-1-decalyl *p*-toluenesulfonate by a factor of 3.9, and that the olefin obtained in 80% yield consisted of a mixture of tri- and disubstituted octalin instead of trisubstituted $\Delta^{1,9}$-octalin as a major product (Fig. 2).



VIII
cis-trans-1-Decalyl tosylate

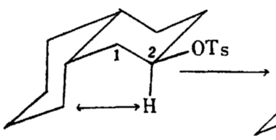
The distance between the carbon atom at the reaction center and the site of the ring fusion at C_9-C_{10} in the *cis*-2-decalyl derivatives is not sufficiently small to affect their reaction rates, as observed with the 1-decalyl derivatives, but strains of the type we have proposed are considered to participate in giving higher reactivities compared with the *trans-cis*-2-decalyl derivative (2-equatorial).

The preferred conformation of the *cis-cis*-2-decalyl *p*-toluenesulfonate shows that the hydrogen in the axial position at C_1 or C_3 is involved in giving rise to 1, 3-diaxial interaction. In the transition state, there will be a decrease in strain by partial breaking away of the hydrogen in the axial on either C_1 or C_3 after having formed a partial double bond between C_1 and C_2 or C_3. This requires less free energy of activation and consequently *cis-cis*-2-decalyl *p*-toluenesulfonate is expected to be more reactive than *trans-cis*-2-decalyl *p*-toluenesulfonate with which no such situation is possible. The prediction is well supported by the results that *trans-cis*-2-decalyl *p*-toluenesulfonate gives the olefin in only 68% while *cis-cis*-2-decalyl *p*-toluenesulfonate 80%.

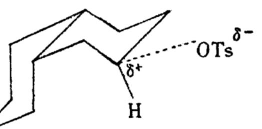


IX
cis-cis-2-Decalyl tosylate
(more strained)

Since the C_2 in the *cis-trans*-2-decalyl *p*-toluenesulfonate molecule, represented by X as the preferred conformation, takes a planar structure in the transition state in both the substitution and elimination reactions, a decrease of 1, 3-diaxial interaction which has been present in the ground state would be expected, resulting in the increased reactivity. This is well demonstrated by the results of the kinetic studies; the *cis-trans*-2-decalyl derivative is 4.3 and 1.4 times more reactive than *trans-cis*-2-decalyl *p*-toluenesulfonate (2-equatorial) and *trans-trans*-decalyl *p*-toluenesulfonate (2-axial), respectively.



X
cis-trans-2-Decalyl
tosylate (more strained)



XI
(transition state)
(less strained)

The present study with the *cis*-decalyl *p*-toluenesulfonates and the previous one with the *trans*-decalyl sulfonates point to the fact that 1, 3-diaxial arrangement, rather than the nature of the atoms or groups, is important in giving rise to strain. The data presented here and the foregoing discussion have provided further evidence to support the importance of 1, 3-diaxial interaction in controlling reactivities of the conformational isomers of the decalin derivatives.

Experimental

Materials. — *cis-cis-1-Decalol.* — α-Naphthol was reduced with Raney nickel and the crystalline material formed in the reaction mixture after

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* The other conformation (Ref. 2) of *cis-trans*-1-decalyl *p*-toluenesulfonate is expected to show a reactivity comparable to that of *cis-cis*-1-derivative. This is not the case however. Our results were not in agreement with this.

collection and recrystallization from petroleum ether, had m. p. 92~93°C⁽⁸⁾.

cis-trans-1-Decalol.—The last fraction collected from the distillation of the reduction product of α-naphthol was distilled through a 45-cm. distilling column, under reduced pressure and the fraction boiling at 130~132°C/20 mmHg was collected. *cis-cis*-1-Decalol was removed by collecting crystalline material from a solution of the distillate in petroleum ether (50~60°C) and also crystals formed on concentrating the mother liquor. The oily filtrate weighing 6 g. was allowed to react with 5.8 g. of phthalic anhydride for 6 hr. at 135~140°C. The solid product obtained on cooling was recrystallized three times from benzene, twice from carbon tetrachloride and once from benzene, to give 7 g., m. p. 140~142°C⁽⁹⁾.

The ester weighing 7 g. was hydrolyzed with 100 ml. of a 5% alcoholic solution of potassium hydroxide under reflux for one hour. After addition of water, it was extracted five times with 50 ml. portion of ether. The combined ether extracts were washed with water and dried over anhydrous magnesium sulfate. The ether was removed by distillation and the residue distilled to give 3 g. (83% yield), b. p. 116~117°C/20 mmHg.

cis-cis-2-Decalol.—A solution of 300 g. of β-naphthol in 300 ml. of ethanol was hydrogenated at 140~145°C under 200 atmospheric pressure, using 25 g. of Raney nickel as catalyst. The reaction mixture contained some crystalline material. The product was liquified by warming and the catalyst separated by filtration while warm. After cooling solution, the crystalline needles were collected and recrystallized once from alcohol and once from petroleum ether to give 80 g. of *cis-cis*-2-decalol, m. p. 104~105°C⁽¹⁰⁾.

cis-2-Decalone⁽¹⁰⁾.—To a solution of 30 g. (0.19 mol.) of *cis-cis*-2-decalol in 120 ml. of glacial acetic acid was added cautiously 15 g. (0.15 mol.) of chromium trioxide in a concentrated aqueous solution so that the temperature did not rise above 50°C. After allowing the reaction mixture to stand for two days at room temperature, it was heated on a water bath for two hours. It was cooled and a solution of 40 g. of potassium hydroxide in 200 ml. of water was added dropwise under ice cooling. The reaction mixture was extracted four times with ether and the ether solution washed with a saturated solution of sodium bicarbonate, followed by a saturated solution of sodium chloride. After drying the ether solution over anhydrous magnesium sulfate, the ether was removed and the residue distilled to give 24 g. (81% yield) of material, b. p. 124.5~125.5°C/20 mmHg, n_D^{41}: 1.4945.

cis-trans-2-Decalol⁽¹¹⁾.—To a solution of 5.3 g. (0.035 mol.) of *cis-2*-decalone in 100 ml. ethanol was added 5 g. (0.22 mol.) of metallic sodium. When the reaction was complete, water was added and the oil which had separated was extracted five times with ether. The combined ether extracts were washed with water, dried over anhydrous magnesium sulfate, the ether removed, and the residue distilled to give 4 g. (75% yield) of material, b. p. 120~121°C/13 mmHg. After standing overnight the distillate, *cis-cis*-2-decalol in crystalline form (2.5 g.) was separated from the oil (1.5 g).

A reaction product formed by treating 4.3 g. of the oil with 4.3 g. of phthalic anhydride for six hours at 135~140°C was treated with petroleum ether to give a solid product. It was dissolved in a small amount of acetone to remove some insoluble material and the crystalline material obtained upon adding some petroleum ether was recrystallized from ethyl acetate to give 7.7 g. of the phthalate of *cis-trans*-2-decalol, m. p. 151~152°C⁽¹²⁾.

The fraction boiling at 134~135°C/20 mmHg, 13.5 g., obtained from the reduction product of β-naphthol was treated with 13 g. of phthalic anhydride for six hours at 135~140°C. After treating the reaction product in the manner described above, 11 g. of the ester was obtained, m. p. 146~150°C.

Upon hydrolysis of the phthalic acid ester as described previously, 4.3 g. (75% yield) of the fraction boiling at 120~123°C/12 mmHg was obtained.

cis-trans-2-Decalyl *p*-nitrobenzoate⁽¹²⁾ was prepared by the reaction of the fraction obtained above with *p*-nitrobenzoyl chloride in dry pyridine, m. p. 73~74.5°C.

Found: C, 67.35; H, 7.26; N, 4.49. Calcd. for $C_{17}H_{21}O_4N$: C, 67.31; H, 6.98; N, 4.62%.

A solution of 7 g. (0.023 mol.) of the *p*-nitrobenzoate in 100 ml. anhydrous ether was added dropwise to a mixture of 3.5 g. (0.092 mol.) of lithium aluminum hydride in 50 ml. anhydrous ether and the reaction mixture refluxed for six hours. After allowing it to stand overnight, the excess hydride was decomposed by adding a small piece of ice and 100 ml. of 6 N hydrochloric acid. The ether layer was separated, washed with water, and dried over anhydrous magnesium sulfate. After removing the ether, the residue was distilled to give 3 g. (84% yield) of material, b. p. 121~123°C/12 mmHg.

cis-Decalyl p-Toluenesulfonates⁽⁴⁾. — The method employed was identical with that described for the preparation of the *trans*-decalyl *p*-toluenesulfonates. However, for the preparation of *cis-cis*-2-decalyl *p*-toluenesulfonate, it was found necessary to use 1.5 mol. equivalent of *p*-toluenesulfonyl chloride for one mole of the decalol in order to obtain a pure product. *cis-cis*-1-Decalyl *p*-toluenesulfonate was found to be very unstable and the analytical results obtained did not check closely with the calculated values, but the melting point of the decalol and the *p*-toluenesulfonate were in good agreement with those reported.

cis-trans-1-Decalyl *p*-toluenesulfonate was purified by recrystallizing from methanol to remove *cis-cis*-1-decalyl-*p*-toluenesulfonate, which was readily

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8) W. Hückel and E. Brinkmann, *Ann.*, **441**, 21 (1925).

9) W. Hückel, R. Danneel, A. Gross and H. Naab, ibid., **502**, 99 (1933).

10) W. Hückel, *Nach. Ges. Wiss. Göttingen Math.-Phys. Klasse*, 1923, No. 1, 43-56; W. Hückel and R. Mentzel, *Ann.*, **441**, 8 (1925).

11) W. Hückel, R. Mentzel, E. Brinkmann and E. Kamenz, ibid., **451**, 109 (1926).

12) W. Hückel and K. Kumetat, *Ber.*, **67**, 1890 (1934).

decomposed by this treatment. Other *p*-toluenesulfonates were recrystallized from petroleum ether of appropriate boiling point.

The melting points and analytical results of the *cis*-decalyl *p*-toluenesulfonates prepared are given in Table IV.

TABLE IV. THE MELTING POINTS AND ANALYTICAL DATA OF THE *cis*-DECALYL *p*-TOLUENESULFONATES

Decalyl *p*-toluenesulfonate	M. p.[3], °C	Found: %	%
cis-trans-1	88~89	C: 66.13	H: 7.98
cis-cis-1	96	C: 65.85	H: 7.79
cis-trans-2	88~89.5	C: 65.94	H: 7.83
cis-cis-2	76~77	C: 66.14	H: 8.05
		Calcd. for $C_{17}H_{24}O_3S$	
		C: 66.20	H: 7.84

TABLE V. REPRESENTATIVE KINETIC DATA FOR THE ACETOLYSIS OF 0.0179 mol./l. *cis-cis*-2-DECALYL *p*-TOLUENESULFONATE WITH 0.0185 mol./l. POTASSIUM ACETATE AT 90.21°C

Time sec.	$HClO_4$ ml.	$10^4 \cdot k_1$ sec^{-1}
0	3.661	—
600	2.894	4.24
1500	2.073	4.17
2100	1.644	4.26
2400	1.476	4.26
2700	1.316	4.30
3120	1.175	4.18
3660	0.963	4.27
4200	0.828	4.22
5520	0.562	4.32
—	—	—
∞	0.248	
	Mean	4.25±0.04

Rate Measurements.—The rate determinations were made by the procedure previously described[1]. A typical kinetic run is shown in Table V.

Determination of the Proportion of Unsaturated Products. — Amounts of unsaturated substances formed in the reaction were determined by the bromide-bromate method[13].

Acetolysis of *cis-cis*-1-Decalyl *p*-Toluenesulfonate.—Twelve grams of *cis-cis*-1-decalyl *p*-toluenesulfonate were dissolved in 290 ml. of an acetic acid solution of 14 g. of potassium acetate. This solution was warmed for fifteen minutes at 100°C on a steam bath. After cooling 250 ml. of 25% aqueous solution of sodium hydroxide was added to the above solution. The solution was extracted with ether, dried over anhydrous magnesium sulfate, the ether was removed and distilled to give 4 g. (76% yield) of material, b.p. 84~86°C/23 mmHg. The acetate was not obtained.

One gram of this product was mixed with 3 ml. of acetic acid solution of two grams of isoamyl nitrite. Cooling the solution, 2 ml. of concentrated hydrochloric acid was added dropwise with swirling. The white precipitate was separated by filtration and washed with a few milliliters of acetone. The residual white nitrosochloride of $\Delta^{1,9}$-octalin (0.9 g.) had 128~130°C (decomp.)[14]. Two recrystallizations of this white nitrosochloride from acetone gave an analytically pure substance, 138°C (decomp.)[14]. The blue nitrosochloride of $\Delta^{1,9}$-octalin was not obtained from the acetone filtrate.

Found: C, 59.16; H, 7.88; N, 6.98. Calcd. for $C_{10}H_{16}NOCl$: C, 59.55; H, 8.00; N, 6.95%.

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[13] J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, 73, 5039 (1951); H. G. Lucas and D. Pressman, *Ind. Eng. Chem., Anal. Ed.*, 10, 140 (1938).

[14] R. A. Bendeser, R. E. Robinson, D. M. Sauve and O. H. Thomas, *J. Am. Chem. Soc.*, 77, 3230 (1955).