insufficient (−)-phenyl-*n*-butylcarbinol available for fractionation of the product; it was simply distilled.

To 11.79 g. of phenylisobutylcarbinol, $[\alpha]^{22}\mathrm{D}$ −2.48° (neat), dissolved in 40 ml. of 9:1 methanol-glacial acetic acid, was added 0.55 g. of freshly prepared platinum oxide catalyst.[30] The mixture was shaken 24 hours in a Parr hydrogenator. After removal of catalyst and evaporation of methanol, the residual liquid was taken up in ether and shaken with 10% aqueous potassium carbonate until evolution of carbon dioxide ceased, then dried over potasssium carbonate. The infrared spectrum of the crude product after removal of ether showed none of the absorption characteristic of the phenyl group and was identical with that of the (−)-cyclohexylisobutylcarbinol from the Grignard reduction except for a weak band in the former spectrum at 5.9 μ, probably due to acetic acid. The product was fractionated at 20 mm. through a 25″ × $^3/_{16}$″ glass spiral column. The take-off was controlled automatically and the head temperature read by means of a thermocouple. The fifth and last fraction, 1.54 g., $n^{20}\mathrm{D}$ 1.4641, had a maximum rotation: $[\alpha]^{27}\mathrm{D}$ −1.74° (neat). Its infrared spectrum was superimposable on that of (−)-cyclohexylisobutylcarbinol; the band in the crude hydrogenation product at 5.9 μ had disappeared.

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STANFORD, CALIF.

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(30) Prepared from spent residues by the procedure of R. Adams, V. Voorhees and R. L. Shriner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 463, using potassium nitrate rather than sodium nitrate in the fusion step.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Studies of Configuration. VII. The Solvolysis of 3- and 4-Methoxycyclohexyl Arenesulfonates[1,2]

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The ethanolysis of *cis*- and *trans*-3-methoxycyclohexyl tosylates appears to be normal. The acetolysis of *trans*-4-methoxycyclohexyl tosylate shows evidence for internally assisted acceleration of rate. The products formed, 9% *cis*-4-methoxycyclohexyl acetate, 25% *trans*-4-methoxycyclohexyl acetate and 66% 4-methoxycyclohexene, substantiate the rate acceleration. It is suggested that a large fraction of the reaction is proceeding through the symmetrical bicyclic oxonium ion II. Such an intermediate explains the large amount of net retention of configuration in the derived acetate.

Introduction

The frequent manifestation of increased reactivity due to participation by neighboring groups is well recognized. The classical work of Winstein and his co-workers[3] has provided numerous examples, including the acetoxyl group, the methoxyl group, the halogens and the aromatic ring as participating groups. More recently, the occurrence of participating interaction has been recognized in medium ring compounds.[4-7]

On the other hand, the chemical behavior of cyclohexane systems has been adequately interpreted in general by considering only the chair conformation.

Previous examples of 1,4-interaction across a six-membered ring are sparse. The reactions of a variety of 4-substituted cyclohexyl derivatives have been studied by Owen and Robins,[8] but only meager evidence of transannular participation was obtained. The monotosylate of *trans*-1,4-cyclohexanediol failed to give any 1,4-epoxycyclohexane, but *trans*-1,4-diiodocyclohexane was obtained from both *cis*- and *trans*-1,4-di-*p*-toluenesulfonyloxycyclohexane.

Bennett and Niemann[9] have suggested that 1,4-bridged cyclic halonium ions may be involved in the reactions of 4-iodocyclohexanol and 4-bromocyclohexanol. Goering and Sims[10] have recently suggested the incursion of the 1,4-bridged bromonium ion in the rearrangement of dibromocyclohexanes with ferric bromide.

Reaction through an appropriate boat conformation has been observed in some steroids[11] and sugars.[12]

We have undertaken an investigation of interaction across 6-membered rings, which may require the incursion of a boat conformation. In a previous report Noyce and Weingarten[13] have observed such interaction in the ether–acid chloride rearrangement, but failed to find evidence for participation accompanying the solvolysis of methyl 3-tosyloxycyclohexanecarboxylate.

Since the preliminary report of the results to be discussed here was presented,[2] a further example of 1,4-interaction has been presented by Heine[14] in the hydrolysis of 4-chlorocyclohexanol. Barner,

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(1) Supported in part by the National Science Foundation, G-2387 and G-5921.

(2) A portion of this material has been presented in a preliminary Communication, D. S. Noyce and B. R. Thomas, THIS JOURNAL, **79**, 755 (1957).

(3) For recent papers: R. Heck and S. Winstein, *ibid.*, **79**, 3432 (1957); R. Heck, J. Corse, E. Grunwald and S. Winstein, *ibid.*, **79**, 3278 (1957); L. Goodman, S. Winstein, and R. Boschan, *ibid.*, **80**, 4312 (1958); S. Winstein and A. H. Fainberg, *ibid.*, **80**, 459 (1958), and earlier papers.

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TABLE I

ETHANOLYSIS OF 3-METHOXYCYCLOHEXYL ARENESULFONATES, 75.09°

Compounds	$k_{cis} \times 10^5$, sec.$^{-1}$	$k_{trans} \times 10^5$, sec.$^{-1}$	σ^*	k/k_H[a] Calcd.[b]	k/k_H[a] Obsd.
cis-3-Methoxycyclohexyl brosylate	2.27 ± 0.01				
Mixed 3-methoxycyclohexyl brosylate	2.47 ± .0	4.24 ± 0.2			
cis-3-Methoxycyclohexyl tosylate	0.494 ± .01		0.18	0.29	0.19
Mixed 3-methoxycyclohexyl tosylate		0.734 ± 0.02	0.18	0.29	0.285

[a] Rate relative to cyclohexyl tosylate. [b] Calcd. assuming $\rho^* = -3.00$.

Dreiding and Schmid[15] have also observed that the *p*-toluenesulfonate of *trans*-4-(*p*-hydroxyphenyl)-cyclohexanol gives a bicycloheptane derivative upon treatment with potassium *t*-butoxide.

In acyclic systems 1,4-participation is much more common. Winstein[16,17] observed substantial rate acceleration in the solvolysis of 4-methoxy-1-butyl *p*-bromobenzenesulfonate and related compounds. Oae[18] has reported rate acceleration in the formolysis of 4-bromo-1-methoxypentane. Similarly marked acceleration was observed in the hydrolysis of 4-chloro-1-butanol (with the formation of tetrahydrofuran) by Heine, Miller, Barton and Greiner.[19] Similar acceleration is observed with 4-phenylthio-1-chlorobutane.[20]

Results

Behavior of 3-Methoxycyclohexyl Arenesulfonates.—We first examined the ethanolysis of 3-methoxycyclohexyl tosylate and 3-methoxycyclohexyl brosylate. Anchimeric assistance, involving a 4-membered ring, in this system, is perhaps not to be expected, though the geometrical factors may well assist. It has previously been concluded that the ethanolysis of 3-ethoxypropyl tosylate[21] and brosylate[17] is normal.[17,22] Lindegren and Winstein[23] find no evidence of anchimeric assistance by a γ-halogen but do find evidence of assistance by a γ-hydroxyl, methylthio or acetoxy group. Doering and Young[24] have considered the "possibility of 4-membered, neighboring group interaction" in the reactions of 1,3-butanediol.

The *cis* isomer of 3-methoxycyclohexanol was separated *via* the hydrogen phthalate ester and its piperazine salt. Attempts to separate the pure *trans* isomer were not successful. The kinetic measurements were therefore made on the pure *cis* isomer and upon the mixed isomers. The results are presented in Table I.

The results are normal. It is to be noted that the rate constants agree satisfactorily with predicted values, based upon a $\rho^* \sigma^{*25}$ correlation using the data collected by Streitwieser.[22,26]

As pointed out by Streitwieser[26] such a correlation is useful in establishing the order of magnitude to be expected for such rates, but not sufficiently refined to give precise prediction. In particular no account is taken of the well known difference between axial and equatorial isomers.

From the conclusion that the solvolyses of the 3-methoxycyclohexyl tosylates are normal, derived information regarding the conformational states of the methoxycyclohexyl tosylates is forthcoming.

In the earlier report of Noyce and Weingarten[13] it was concluded that the rate ratio of 4.6 in acetic acid for the solvolysis of *trans*-3-carbomethoxycyclohexyl tosylate relative to *cis*-3-carbomethoxycyclohexyl tosylate was normal, considering the polar factors in conjunction with conformational factors.

For the solvolysis of the 3-methoxycyclohexyl tosylates a rate ratio for *trans:cis* of 1.5 is observed. In this instance the methoxyl group is smaller than the tosylate group and therefore the tosylate is predominantly equatorial in both the *cis* and *trans* isomers. Using a value of 1.7 for the *A*-value of the tosylate group[27] and a value of 0.74 for the methoxyl group,[28] *cis*-3-methoxycyclohexyl tosylate is 97% in the di-equatorial conformation, and *trans*-3-methoxycyclohexyl tosylate is 83% in the conformation with an equatorial tosylate group. It is then straightforward to calculate a rate ratio of 1.35, *if* one assumes that the effect of the methoxy dipole does not specifically favor one isomer. These results tend to support the higher value of 1.7[28] for the *A*-value of the tosylate group, rather than the lower value of Eliel and Ro.[32]

The solvolysis products of an isomeric mixture of *cis*- and *trans*-3-methoxycyclohexyl tosylate in acetic acid were a mixture of olefin and acetate. The olefin was entirely 4-methoxycyclohexene, and the acetate was a mixture of *cis*- and *trans*-3-methoxycyclohexyl acetate. It was demonstrated that 3-methoxycyclohexene is stable under the acetolysis conditions.

Behavior of 4-Methoxycyclohexyl Tosylate.—The rate data obtained are presented in Table II. The configurational assignment is discussed in the previous paper.[33]

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(27) S. Winstein and H. J. Holness, *ibid.*, **77**, 5562 (1955).

(28) An estimate of the *A*-value for the methoxyl group may be derived from the *A*-value of the hydroxyl group, 0.3–0.9[29-31] and the increment of a methyl group one atom from the ring, *i.e.*, the difference of *A*-values for methyl and ethyl. Recent measurements in this Laboratory support a value of 0.74 for the methoxyl group (unpublished observations of Lloyd J. Dolby).

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TABLE II

RATES OF SOLVOLYSIS OF 4-METHOXYCYCLOHEXYL TOSYLATES

	NaOAc	Ac_2O	ROTs	Temp., °C.	$k_1 \times 10^5$, sec.$^{-1}$	σ^*	k/k_H Calcd.	Obsd.
cis-								
AcOH	0.53	0.59	0.2878	75.01	2.12 ± 0.14			
	.06	.06	.030	75.09	0.766 ± .02	0.066	0.59[a]	0.18
	.54	.58	.2777	89.99	10.7 ± .5			
EtOH			.030	75.09	.654 ± .01	.066	.63[b]	.25
trans-								
AcOH	0.53	0.59	0.2932	75.00	5.71 ± 0.22			
	.20	.21	.1091	74.94	4.22 ± .23			
	.60	.06	.030	75.09	3.20 ± .11	.066	.59	.74
	.51	.58	.2632	89.97	31.7 ± 1.1			
	.53	.58	.2603	90.07	30.3 ± 0.8			
EtOH			.030	75.09	2.48 ± 0.04	.066	.63	.96

[a] $\rho^* = -3.49$.[26] [b] Assumed $\rho^* = -3.00$.

Rate acceleration is clearly observed for *trans*-4-methoxycyclohexyl tosylate, which undergoes either ethanolysis or acetolysis *faster* than the *cis* isomer. The kinetic results at 75° lead to the initial conclusion that the rate of acetolysis is 5.6 times that to be expected (1.35 × 3.20/0.766). The question of the magnitude of acceleration is considered further below. From the results it is also apparent that this ratio does not change a great deal with temperature.

Were an internal interaction by the 4-methoxyl group responsible for the acceleration, the bimolecular reaction with sodium ethoxide should give a much more normal rate ratio. Accordingly, the bimolecular rates of reaction with sodium ethoxide in ethanol were measured. The result expected is obtained, namely that the *cis* isomer undergoes reaction faster than the *trans* isomer ($k_2 \times 10^5$ mole^{-1} sec.$^{-1}$ is 303 ± 15 for the *cis* isomer and 59.1 ± 1.7 for the *trans* isomer).

The Products of Solvolysis.—The acetolyses of 4-methoxycyclohexyl tosylates give different mixtures of 4-methoxycyclohexene and 4-methoxycyclohexyl acetates. When the acetolyses are carried out at 75° in the presence of 0.6 molar sodium acetate, 0.3 molar *trans*-4-methoxycyclohexyl tosylate affords 66% 4-methoxycyclohexene, 24% *trans*-4-methoxycyclohexyl acetate and 10% *cis*-4-methoxycyclohexyl acetate. Solvolysis of the *cis*-tosylate under identical conditions yields more 4-methoxycyclohexene (83%) and only inverted *trans*-4-methoxycyclohexyl acetate (17%). These analyses were obtained using a carefully standardized extraction procedure followed by vapor phase chromatography. The accuracy of the analyses (±2%) was demonstrated by carrying standard olefin–acetate mixtures through the entire procedure under identical conditions. In addition to the characteristic vapor phase retention times for the olefin and acetates these compounds were characterized further in other product runs where the several species were isolated by chromatography on alumina.

The infrared spectra of the olefinic fractions obtained from the solvolysis of either isomer were identical with that of 4-methoxycyclohexene and showed no evidence of 3-methoxycyclohexene.

The infrared spectrum of the acetate derived from *cis*-4-methoxycyclohexyl tosylate was identical with that of authentic *trans*-4-methoxycyclohexyl acetate. Hydrolysis afforded the alcohol which was converted to *trans*-4-methoxycyclohexyl-3,5-dinitrobenzoate (m.p. 125.5–126.5) which showed no depression when mixed with an authentic sample.

In the case of the acetates derived from *trans*-4-methoxycyclohexyl tosylate, hydrolysis to the alcohols afforded samples which could be analyzed easily for isomer content by infrared spectra. The infrared spectrum of the 4-methoxycyclohexanols showed that 71% of this mixture was the *trans* isomer. This is in good agreement with the value (71 ± 3%) obtained by vapor phase chromatography of the parent acetate mixture. The 3,5-dinitrobenzoate (m.p. 125.5–126.5°) of the *trans*-4-methoxycyclohexanol was isolated from this mixture.

The products of acetolysis were also examined under additional conditions (Table III).

TABLE III

PRODUCTS OF SOLVOLYSIS OF 4-METHOXYCYCLOHEXYL TOSYLATES

Temp., °C.	NaOAc	4-Methoxy-cyclohexene, %	*cis*-4-Methoxy-cyclohexyl acetate, %	*trans*-4-Methoxy-cyclohexyl acetate, %
cis				
60	0.58	80		20
75	.58	83		17
120[a]	.58	82		18
trans				
60	0.58	67.7	8.7	23.6
75	.00	69[b]	8.4	9.6[b]
75	.20	(66)	10.6	23.4
75	.58	66.4	9.6	24.0
120[a]	.58	74	7.5	18.5

[a] In refluxing acetic acid. [b] A mixture of olefins arises in the absence of sodium acetate; see text.

In the absence of sodium acetate at 75°, the ratios of the normal products are perturbed, and the reaction mixture takes on an additional complexity. Rearranged olefin is formed to the extent of 15%, 3-methoxycyclohexene being identified by its vapor phase retention time. Two additional peaks appeared, one accounting for 11% of the total reaction mixture, which showed a shorter

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(33) D. S. Noyce, G. L. Woo and B. R. Thomas, *J. Org. Chem.*, in press.

retention time than the methoxycyclohexyl acetates (possibly a cyclohexenyl acetate). A second fraction (2%) of longer retention time was also observed. Otherwise there are no striking changes in product ratios.

Discussion

Magnitude of Acceleration.—The rates of the ethanolysis and acetolysis of *cis*-4-methoxycyclohexyl tosylates both fall below the predicted values. This fact was initially troublesome. However, more recently available data provide a probable explanation.

It is difficult to assign a precise value to the polar effect of the methoxyl group. It is known that the direction of a dipole influences the ease of development of a charge in cyclic systems. For example, the dissociation constants of the *cis*- and *trans*-3-bromocyclohexanecarboxylic acid show a sensitivity to the molecular geometry,[34] although the carboxyl group is predominantly equatorial in both isomers. Noyce and Weingarten[13] have concluded that the rate ratio for the acetolysis of *cis*- and *trans*-3-methoxycarbonylcyclohexyl tosylates shows a similar sensitivity to the directional polar influences.

In recent publication, Martin and Bartlett[35] have concluded that the rigid geometry of 2-chloro-1,4-endoxocyclohexane decreases the reactivity of the halogen some 60 times more than would be expected from comparison with a simple 2-methoxycyclohexyl halide, using both the dipole interaction calculations of Winstein and Grunwald[36–38] and the $\rho^*\sigma^*$ treatment.[25,26]

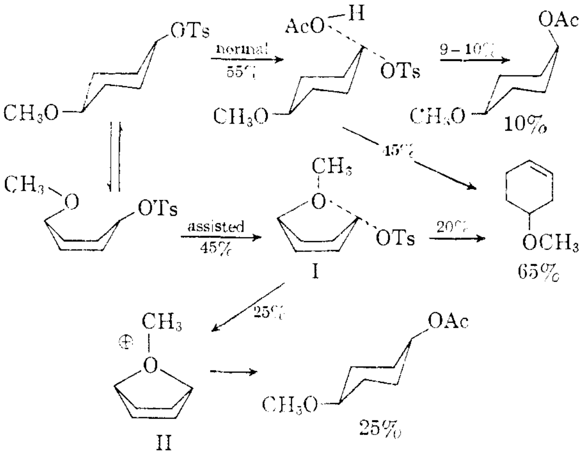
We conclude that the rate ratio of the *cis*- and *trans*-4-methoxycyclohexyl tosylates provides substantial evidence for an internally assisted reaction pathway for the *trans* isomer. The *trans* isomer undergoes solvolysis faster than the *cis* isomer. Normal expectation would be for the *cis* isomer, in which there is a higher proportion of the axial tosylate, to undergo solvolysis more rapidly than the *trans* isomer. It is also to be noted that the activation parameters ($\Delta H^{\ddagger}$ = 26.5 kcal./mole and $\Delta S^{\ddagger}$ = −5.80 e.u. for *cis*-4-methoxycyclohexyl tosylate and $\Delta H^{\ddagger}$ = 27.2 kcal./mole and $\Delta S^{\ddagger}$ = −0.3 e.u. for *trans*-4-methoxycyclohexyl tosylate) are consistent with the proposal of an internally assisted pathway.

The product studies indicate that about one-third of the 4-methoxycyclohexyl acetate formed in the solvolysis of the *trans*-tosylate has the inverted *cis* configuration. This represents one of the products of normal solvolysis. Since the geometry of the *cis*-tosylate is unfavorable for methoxyl participation we have assumed that it undergoes normal solvolysis and that therefore a normal solvolytic process in this system leads to a 5:1 olefin–acetate ratio. On this basis one may calculate that about 55% of the products in the acetolysis of *trans*-4-methoxycyclohexyl tosylate arise from a "normal" solvolytic process. It follows that the assisted solvolysis of *trans*-4-methoxycyclohexyl tosylate affords 25% *trans*-4-methoxycyclohexyl acetate and in addition about 20% 4-methoxycyclohexene.

The previous discussion leads us to propose the following reaction sequence (Chart I). The initial reaction for the assisted pathway is to the internally solvated ion pair I, which then may react further to give the bridged bicyclic oxonium ion II.

CHART I

REACTION SCHEME FOR THE ACETOLYSIS OF 4-METHOXYCYCLOHEXYL TOSYLATE



It is interesting to compare the magnitude of the anchimeric assistance in the present instance with the results obtained for δ-methoxyalkyl benzenesulfonate by Winstein, Allred, Heck and Glick.[17]

The rate of solvolysis of 5-methoxy-2-hexyl bromobenzenesulfonate relative to *sec*-butyl brosylate is 163.[17] In the present instance the normal and assisted rates are very nearly equal. Thus, for 4-methoxycyclohexyl tosylate the driving force for participation almost exactly counterbalances the energy required for the chair–boat transformation. In the acylic examples of Winstein, Allred, Heck and Glick the 5-membered oxonium intermediate involves the eclipsing of the groups about 3 C–C bonds. Thus, the driving force for the methoxyl group is approximately 6 kcal. for the eclipsing energy + 3.5 kcal. (representing the net acceleration in the acyclic system). In the cyclohexyl case the assisted rate almost exactly counterbalances the chair to boat change, plus some additional strain energy. Thus, the present data appear to place an upper limit on the chair–boat conformational energy difference of somewhat less than 9 kcal.

Experimental[39]

***cis*-3-Methoxycyclohexanol.**—The mixture of *cis*- and *trans*-3-methoxycyclohexanols, prepared by hydrogenation of resorcinol monomethyl ether over Raney nickel, was converted to the hydrogen phthalate.[40] The initial product was a viscous oil which failed to crystallize. 3-Methoxycyclohexyl hydrogen phthalate (2.0 g.) was treated with a solution of 0.98 g. of piperazine hydrate in acetone. On cooling

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[34] S. Siegel and J. G. Morse, THIS JOURNAL, **75**, 3857 (1953).

[35] J. C. Martin and P. D. Bartlett, *ibid.*, **79**, 2533 (1957).

[36] S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

[37] S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).

[38] E. Grunwald, *ibid.*, **73**, 5458 (1951).

[39] All melting points are corrected. The infrared spectra were recorded with a Baird Infrared Spectrophotometer Model B. Analyses are by the Microanalytical Laboratory, University of California.

[40] J. Kenyon, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 418.

overnight, the solution deposited crystals, m.p. 114–118°. Three crystallizations from acetone afforded 0.4 g. of the piperazine salt, m.p. 125.5–126.5°. Regeneration of *cis*-3-methoxycyclohexyl hydrogen phthalate afforded crystals from acetone–petroleum ether, m.p. 103.5–104.5°.

Anal. Calcd. for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52. Found: C, 65.01; H, 6.70.

With these seed crystals, larger quantities of *cis*-3-methoxycylohexyl hydrogen phthalate were obtained by fractional crystallization, m.p. 104–105°.

***cis*-3-Methoxycyclohexyl Tosylate.**—A cold solution of 10 g. of *cis*-3-methoxycyclohexanol in 30 ml. of pyridine was rapidly added to 16 g. of *p*-toluenesulfonyl chloride. After 12 hours the reaction mixture was diluted with water, extracted with chloroform, and the chloroform extracts washed successively with dilute sulfuric acid, sodium bicarbonate and water. After drying the chloroform solution over anhydrous magnesium sulfate, the chloroform was removed under reduced pressure to afford *cis*-3-methoxycyclohexyl tosylate as a clear colorless liquid, 13.9 g. (64%).

Anal. Calcd. for $C_{14}H_{20}O_4S$: C, 59.13; H, 7.09; S, 11.27. Found: C, 58.90; H, 7.14; S, 11.34.

Similarly the tosylate of the mixed isomer was prepared.

Anal. Found: C, 59.09; H, 7.18; S, 11.47.

***cis*-3-Methoxycyclohexyl-*p*-Bromobenzenesulfonate.**—The brosylate was prepared in a similar fashion, and crystallized from petroleum ether, m.p. 34–35°.

Anal. Calcd. for $C_{13}H_{17}O_4BrS$: C, 44.70; H, 4.91; Br, 22.88; S, 9.18. Found: C, 44.50; H, 5.03; Br, 22.72; S, 9.33.

The brosylate of the mixed isomers was a liquid.

Anal. Found: C, 44.98; H, 5.13; Br, 22.67; S, 9.01.

cis- and *trans*-4-methoxycyclohexyl tosylates were described previously,[33] m.p. 87–88.4° and 66.5–67.5°, respectively. Other preparations of *trans*-4-methoxycyclohexyl tosylates after careful purification showed m.p. of 65.5–66.2° and 67.2–68.2°.

Product Isolation from Acetolysis. A. *cis*-4-Methoxycyclohexyl Tosylate.—A solution of 2.0 g. of *cis*-4-methoxycyclohexyl tosylate and 1.10 g. of sodium acetate in 200 ml. of dry acetic acid were heated at 87° for 3 days. The diluted reaction mixture was extracted with pentane, and the pentane extracts washed with sodium bicarbonate. Total recovery was 0.9 g. of products. The mixture of olefin and acetate was separated by chromatography on alumina (Merck). There was obtained from the early fractions 0.33 g. (41% yield) of 4-methoxycyclohexene, identified by infrared spectrum. There was no indication of the presence of 3-methoxycyclohexene (absence of band at 10.80 μ). The later fractions afforded 0.5 g. (41% yield) of crude *trans*-4-methoxycyclohexyl acetate, identified by infrared spectrum. A small sample was hydrolyzed to the alcohol, and converted to *trans*-4-methoxycyclohexyl 3,5-dinitrobenzoate, m.p. and m.m.p. 125.5–126.5°.

B. *Trans*-4-Methoxycyclohexyl Tosylate.—Similarly 2.0 g. of *trans*-4-methoxycyclohexyl tosylate was heated on the steam-bath for two days in acetic acid with a slight excess of sodium acetate. Chromatography afforded 0.55 g. (76%) 4-methoxycyclohexene, and 0.7 g. (22%) of 4-methoxycyclohexyl acetate, which appeared to be largely *trans* isomer upon comparison of infrared spectra. The alcohol, obtained by hydrolysis was converted to the 3,5-dinitrobenzoate, m.p. and mixed m.p. 125.5–126.5°. A small quantity of lower melting material, m.p. 90–117°, was isolated from the mother liquors.

C. 3-Methoxycyclohexyl Tosylate.—Acetolysis at 90° of 9.1 g. of the mixed *cis*- and *trans*-3-methoxycyclohexyl tosylate afforded on fractionation 30% of mixed *cis*- and *trans*-3-methoxycyclohexyl acetate, and 50% of olefin identified by infrared spectrum as 4-methoxycyclohexene. It was also demonstrated that 3-methoxycyclohexene was stable under the reaction conditions.

Kinetic Methods.—Volumetric equipment was calibrated in the usual manner. A 5-ml. automatic pipet was calibrated under the actual conditions of the kinetic run by pipetting aliquots of acetic acid (at 75°) into a weighed flask at room temperature. Temperature control was maintained ±0.02° by a mercury thermoregulator and electronic relay. Potentiometer titration, employing a Beckman *p*H meter, model H, with standard glass and calomel electrodes was used to follow all acetolyses, using 0.03 *N* *p*-toluenesulfonic acid in acetic acid as titrant. Five-ml. aliquots of the reaction mixture were removed for titration and the end-point was determined to ±0.03 ml.

At higher concentrations (0.1–0.3 *M* tosylate) the kinetic method was altered. Aliquots of the reaction mixture were withdrawn and quickly cooled to 20°. A 3.00-ml. sample was withdrawn and the excess sodium acetate titrated with 0.13–0.14 *N* perchloric acid in glacial acetic acid using brom phenol blue as indicator.

Acetic acid was fractionated from a slight excess of acetic anhydride. The water content was 0.05 ml./liter by Karl Fischer titration. Acetic anhydride, 0.6 g./liter, was added and the acetic acid was used in this form.

Ethanol was dried by the diethyl phthalate procedure, and the water content was below the limits of the Karl Fischer method (less than 0.01%). Ethanolic sodium ethoxide was prepared by dissolving clean sodium in the above ethanol. It was standardized by adding a weighed excess of potassium hydrogen phthalate, and titration with 0.01 *N* hydrochloric acid. Ethanolic sodium ethoxide showed no variation in titer under the conditions of a kinetic run during the first 24 hours. Over more extended periods of time the titer changed, necessitating the use of calculated rather than experimental infinity titers.

Kinetic Calculations.—The rate constant for ethanolysis of *trans*-3-methoxycyclohexyl brosylate was calculated from the rate of solvolysis of a mixture of *cis*- and *trans*-3 methoxycyclohexyl brosylate. From infrared spectral data an estimate of the compositions of the isomeric alcohols (70% *cis*) was obtained. From the kinetic data (Table IV) the rate constant at the end of the run (2.45 × 10^{-5} sec.$^{-1}$) agrees satisfactorily with the independently determined value (2.27 × 10^{-5} sec.$^{-1}$) for the *cis* isomer. Assuming that only *cis*-3-methoxycyclohexyl tosylate remains, one obtains the result that 66% of *cis*-3-methoxycyclohexyl brosylate is present in the original mixture and that the rate constant for the ethanolysis of *trans*-3-methoxycyclohexyl brosylate is 4.2 × 10^{-5} sec.$^{-1}$ by a procedure very similar to that used by Brown and Fletcher.[41] Data for a typical experiment are given in Table IV.

TABLE IV

ETHANOLYSIS OF AN EPIMERIC MIXTURE OF *cis*- AND *trans*-3-METHOXYCYCLOHEXYL BROSYLATE AT 75.09°

Time, sec. × 10^{-3}	Titer, ml. of NaOH (0.1156 *N*)	Concentration × 10^2 isomer *cis*[a]	*trans*	Integrated rate for *trans* isomer, k_1 × 10^5 sec.$^{-1}$
0	0.770	1.532	0.848	..
1.47	1.195	1.482	.800	2.96
3.60	1.745	1.412	.743	3.67
6.71	2.608	1.316	.639	4.22
12.2	3.820	1.160	.515	4.12
21.3	5.485	0.9447	.345	4.22
31.2	6.890	.7540	.211	4.45
39.1	7.753	.6309	.135	4.71
64.3	9.395	.3555	.0306	4.21
77.2	9.875	.2649	.0102	4.52
97.8	10.348	.1658	.0000	....
			Av.	4.24 ± 0.22

[a] Calculated using 2.303 log $(C_a/C_b) = k(t_b - t_a)$, where t_b = 97.8 sec. × 10^3, C_b = total concentration, and k = 2.27 × 10^{-5} sec.$^{-1}$ from previous run.

Refinement leads to the data reported in Table I.

The second-order rate constants for the reaction of 4-methoxycyclohexyl tosylate with sodium ethoxide were calculated from the integrated rate equation, and also by the approximate formula of Ingold.[42]

Corrections were made for the volume expansion of ethanol at 75°.

Product Analysis by Vapor Phase Chromatography.—Both *cis*- and *trans*-4-methoxycyclohexyl tosylates were solvolyzed as 0.3 molar solutions in acetic acid under the conditions of the kinetic experiments. After 13 half-lives at 75° the products were isolated by a standardized pentane–ether extrac-

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(41) H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949).

(42) C. K. Ingold, *J. Chem. Soc.*, 225 (1936).

tion from an aqueous solution of the reaction mixture. Solvent was removed with a modified Podbielniak distillation column. The products were analyzed using an Aerograph A-100 gas phase chromatograph equipped with a five-foot Silicone oil–chromosorb column.

The accuracy of the technique was demonstrated by extracting known mixtures of the solvolysis products from acetic acid–sodium acetate–acetic anhydride mixtures. Concentration and volume conditions were identical, with only the relative proportions of olefin and acetate being varied. A direct relationship between area under the effluent peaks and mole fraction was observed.

From *trans*-4-methoxycyclohexyl tosylate there was obtained 67.2 ± 1.2% 4-methoxycylohexene (retention time 1 minute 10 seconds) and 32.8 ± 1.2% 4-methoxycyclohexyl acetate (retention time 5 minutes 5 seconds). A duplicate run gave 65.6 ± 0.3% and 34.4 ± 0.3% olefin and acetate, respectively. The acetate fraction gave on hydrolysis a mixture of *cis*- and *trans*-4-methoxycyclohexanols, which by infrared analysis contained 71.4% *trans* isomer. The acetate fraction showed on a second vapor phase chromatographic analysis 70.9% *trans*-4-methoxycyclohexyl acetate (retention time 28 minutes) and 29.1% *cis*-4-methoxycyclohexyl acetate (retention time 30 minutes). There is thus indicated 66.4 ± 2% 4-methoxycyclohexene, 24.0 ± 2% *trans*-4-methoxycyclohexyl acetate and 9.6 ± 2% *cis*-4-methoxycyclohexyl acetate.

In like fashion, *cis*-4-methoxycyclohexyl tosylate afforded 83.0 ± 2% (82.4 ± 1, 83.6 ± 1) 4-methoxycyclohexene and 17 ± 2% (17.6 ± 1, 16.4 ± 1) *trans*-4-methoxycyclohexyl acetate, both identified by infrared spectrum. The infrared spectrum of the latter showed *only trans* isomer to be present.

A similar procedure was used for product runs at other temperatures.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Diacyl Peroxides. V.[1] Reaction of Phthaloyl Peroxide with Norbornylene

BY FREDERICK D. GREENE AND WILLIAM W. REES[2]

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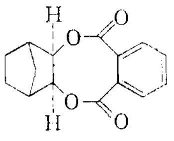
The reaction of phthaloyl peroxide and norbornylene in carbon tetrachloride solution affords the cyclic phthalate of *cis-exo*-2,3-bicyclo[2,2,1]heptanediol (I) in 20% yield, the cyclic phthalate of *exo*-2-*syn*-7-bicyclo[2,2,1]heptanediol (II) in 10% yield, phthalic anhydride in 10% yield and the addition product of carbon tetrachloride to norbornylene(IV, 2-chloro-3-trichloromethylbicyclo[2,2,1]heptane). Kinetic data indicate peroxide consumption by bimolecular reaction with norbornylene and establish that peroxide consumption by free radical chain decomposition is unimportant under these conditions. The formation of the 2,7-norbornyl phthalate (II) and earlier data are suggestive of the intervention between reactants and products of configurations possessing considerable positive charge at a carbon atom of the original double bond.

In a previous study[3] the reaction of the cyclic diacyl peroxide, phthaloyl peroxide, with olefins was shown to be general and to obey second-order kinetics. The marked similarity observed in the relative reactivity of phthaloyl peroxide, peracetic acid and dibromocarbene toward aliphatic olefins and the available data on product compositions were interpreted in terms of bimolecular reaction of neutral peroxide with olefin. Additional evidence on the nature of the phthaloyl peroxide–olefin reaction is provided by the present study employing norbornylene.

Results

Reaction of phthaloyl peroxide with norbornylene in carbon tetrachloride at reflux affords a mixture of products, four of which were obtained in pure form. The major product, isolated in 20% yield of purified material, is a one-to-one adduct of the peroxide and the olefin, m.p. 204–205°. This compound is assigned structure I, cyclic phthalate of *cis-exo*-2,3-bicyclo[2,2,1]heptanediol, on the basis of the phthalate absorption in the infrared at 1735, 1300 and 1130 cm.$^{-1}$; the close similarity in ultraviolet spectrum, λ_{max} 272 (log ϵ, 3.07), to that of dibutyl phthalate; and alkaline hydrolysis to phthalic acid and *cis-exo*-2,3-bicyclo[2,2,1]heptanediol, identified by direct comparison with an authentic sample. A second one-to-one adduct, II, m.p. 142–143°, was isolated from the reaction mixture in 10% yield. The infrared spectrum showed a strong twin-peaked carbonyl band (1737 and 1712 cm.$^{-1}$) and absorption in the carbon–oxygen region at 1300, 1148 and 1125 cm.$^{-1}$. In the ultraviolet the compound showed maxima at 279 mμ (log ϵ 3.22) and 285 mμ (log ϵ 3.20). Alkaline hydrolysis of the adduct yielded *exo*-2-*syn*-7-bicyclo[2,2,1]heptanediol in 73% yield, identified by direct comparison with authentic material. On the basis of this evidence, adduct II is assigned the structure of the cyclic phthalate of the 2,7-diol.



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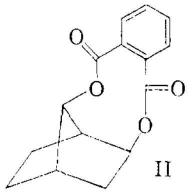

Examination of the infrared absorption spectrum of the original product mixture showed absorption in the carbonyl region at 1855 and 1790 cm.$^{-1}$, attributed to phthalic anhydride, and at 1780 cm.$^{-1}$ (in addition to the phthalate bands described above). The phthalic anhydride was isolated in 10% yield. The material absorbing at 1780 cm.$^{-1}$ was not isolated but is presumed to be lactonic *ortho*-ester, compounds of type III. In the reaction of phthaloyl peroxide with *cis*- and *trans*-stilbene compounds of type III are major products,[4] showing strong absorption at 1778 cm.$^{-1}$ in the infrared.

The fourth product isolated from the reaction was a liquid of analysis corresponding to a one-to-one adduct of norbornylene and carbon tetra-

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[1] Part IV, F. D. Greene, THIS JOURNAL, **81**, 1503 (1959).

[2] General Electric Fellow 1957–1958. This article is based upon a portion of the Ph.D. thesis of W. W. Rees, 1958.

[3] F. D. Greene and W. W. Rees, THIS JOURNAL, **80**, 3432 (1958).

[4] F. D. Greene, *ibid.*, **78**, 2250 (1956).