X ultimately obtained. This is shown by its refractive index and the indices of the mixed nitroisobutylene fractions (e and f) obtained from it. Second, even though all of the intermediate fractions gave high boiling residues upon redistillation, the original distillations of the 295.9 g. of crude product converted all but 5.5 g. to materials b. <100° (1 mm.). This indicates that there was very little or no formation of stable telomeric or condensed products in the original reaction.

The one point left in doubt concerns the origin of the acetone (V) which could have come either from the dealdolization of XIII or the dealdolization of II, followed by reaction of the resulting acetoxime with water and/or nitrous acid. We have arbitrarily selected the latter route in our calculation because of the greater instability of II.

Thus, the initial contents of XIII, XIV and XV were assumed to be the same as the corrected values for those in the final products. The content of XII was taken as the final amount less that formed in the distillation of fraction (j) and the initial content of XI taken as the final content less the 10% formed during the distillation which gave fractions (u-w). The resulting estimate of the initial product composition is shown in Table I.

This estimate means that in our reaction, which consumed 2.85 moles of isobutylene, the initial product mixture should have contained ($^1/_4$ × 1.89) moles of I, 0.62 mole of XI, 0.06 mole of XII, 0.25 mole of XIII, 0.02 mole of XIV and 0.01 mole of XV. The formation of such a mixture would require the consumption of 7.195 moles of NO and would produce at the same time 1.66 moles of N_2 and 0.18 mole of water. These are within experimental error of the observed values, namely, 7.13 moles of NO consumed, 1.72 moles of N_2 produced and 0.183 mole of H_2O (3.0 g. × 325.7/295.9) removed from the first falling film distillate.

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Rates of Acetolysis of *cis*- and *trans*-2-Nitroxycyclohexyl *p*-Bromobenzenesulfonates and *p*-Toluenesulfonates

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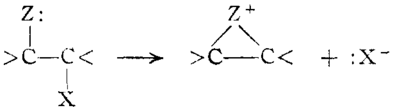
The rates of solvolysis of *cis*- and *trans*-2-nitroxycyclohexyl *p*-bromobenzenesulfonates and *p*-toluenesulfonates in acetic acid at 87.9° have been measured. Solvolyses with the *trans* isomers proceed at a rate less than twice that of the *cis* isomers, indicating that the nitroxy group is not an effective anchimeric group. The preparations of these arenesulfonates and of *cis*- and *trans*-1,2-cyclohexanediol mononitrates are described.

Winstein and his co-workers[1] have shown that rate enhancement occurs when a group on a β-carbon atom participates in solvolysis of another group on the α-carbon atom, *viz*.



(1)

For example, the *p*-bromobenzenesulfonate (brosylate) of *trans*-2-acetoxycyclohexanol—where the acetoxy group is sterically situated so as to permit participation as in (1)—solvolyzes in acetic acid 630 times as rapidly as the *cis* isomer (where participation is sterically impossible). In similar fashion *trans*-2-bromocyclohexyl brosylate reacts 800 times as rapidly as the *cis* isomer. These groups therefore are effective participants. However, both *cis* and *trans*-cyclohexanediol dibrosylate react at about the same rate. Thus arenesulfonoxy groups are ineffective in this participation.

The rates of solvolysis of *cis*- and *trans*-2-nitroxycyclohexyl *p*-bromobenzenesulfonate and *p*-toluenesulfonate were determined in acetic acid at 87.9°, substantially as described by Winstein and co-workers.[1] The rate constants are given in Table I (average of two runs), along with data of Winstein for 2-acetoxycyclohexyl and 2-*p*-bromobenzenesulfonoxycyclohexyl brosylates and/or tosylates.

TABLE I

REACTION RATE CONSTANTS FOR ACETOLYSIS OF 2-SUBSTITUTED CYCLOHEXYL *p*-TOLUENESULFONATES AND *p*-BROMOBENZENESULFONATES

2-Substituent	Temp., °C.	10^8k, sec.$^{-1}$
p-Toluenesulfonates		
trans-Acetoxy	99.7	20,000[a]
cis-Acetoxy	99.7	53[a]
	88	*ca.* 18[b]
trans-Nitroxy[c]	87.88	5.6
cis-Nitroxy[c]	87.88	3.9
p-Bromobenzenesulfonates		
Hydrogen	74.95	15,000[d]
trans-Acetoxy	74.95	3750[d]
cis-Acetoxy	74.95	5.9[d]
trans-Bromobenzenesulfonoxy	74.95	8.5[d]
	88	*ca.* 30[e]
cis-Bromobenzenesulfonoxy	74.95	9.5[d]
	88	*ca.* 30[e]
trans-Nitroxy[c]	87.88	13
cis-Nitroxy[c]	87.88	7.1

[a] Data of Winstein, Grunwald, Buckles and Hansen.[1a] [b] Estimated from data at 100° by assuming rate constant is one-third of value at 100°. [c] Present work; solution contained 0.05*M* sodium acetate and 0.36*M* water. [d] Data of Winstein, Grunwald and Ingraham.[1b] [e] Estimated from data at 75° by assuming rate constant is thrice that at 75°.

It will be noted that the *trans*-nitroxy compounds are less than twice as reactive as the corresponding *cis* compounds and that their rate constants for solvolysis are of the same order of magnitude as the *cis*-2-acetoxy compounds or the 2-arenesulfonoxy compounds. The results indicate clearly that effective participation of nitroxy does not obtain and that an intermediate such as I is not being formed in the rate-determining step in solvolysis. The effect of the nitroxy group appears limited to its inductive effect (similar to the *cis*-acetoxy and the arenesulfonoxy group), which thus slows down the rate significantly with respect to cyclohexyl

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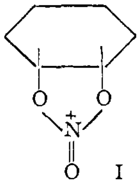
[1] (a) S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, THIS JOURNAL, **70**, 816 (1948); (b) S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

arenesulfonates, but it would be of interest to determine the stereochemistry of the solvolysis to see whether compound I may be still involved in stereochemical control.


I

Many of the compounds for this study were prepared for the first time. The *trans* compounds were prepared by the reaction sequence: cyclohexene oxide plus nitric acid to *trans*-1,2-cyclohexanediol mononitrate; mononitrate plus arenesulfonyl chloride to nitroxycyclohexyl arenesulfonate. The *cis* compounds were prepared from *cis*-1,2-cyclohexanediol monoacetate.[2] This was nitrated, and the nitroxy acetate was hydrolyzed selectively with dilute base to remove the acetoxy group and retain the nitrate group. The resulting *cis*-diol mononitrate was then arenesulfonated. The structure of each of the mononitrates was established by hydrogenolysis.

Acknowledgments.—The authors are indebted to the Office of Ordnance Research, U. S. Army, for support of this research under a contract between that Office and the University of Colorado. The analyses were performed by Galbraith Microanalytical Laboratories.

Experimental

Determination of Rate Constants.—The rate constants were determined substantially as described by Winstein, Hanson and Grunwald.[3] The solvent was acetic acid containing excess sodium acetate, 0.05 *M*, and water, 0.36 *M*, and the solutions were titrated with standard perchloric acid in acetic acid, using either brom phenol blue or methyl violet as indicator.

***trans*-2-Nitroxycyclohexyl *p*-Toluenesulfonate.**—A solution of 0.50 g. (3 mmoles) of *trans*-cyclohexanediol mononitrate[4] and 0.6 g. of *p*-toluenesulfonyl chloride in enough pyridine to dissolve the reagents was kept in a refrigerator for 3.5 days. The reaction mixture was poured into water, the solid removed by filtration and recrystallized once from benzene–petroleum ether and twice from cyclohexane. It then melted at 84.0–84.3°.

Anal. Calcd. for $C_{13}H_{17}O_6NS$: C, 49.51; H, 5.43. Found: C, 49.71; H, 5.57.

trans-2-Nitroxycyclohexyl *p*-bromobenzenesulfonate was prepared in the same fashion (time 1.5 days) with *p*-bromobenzenesulfonyl chloride. After three recrystallizations, it melted at 89.6–90.3°.

Anal. Calcd. for $C_{12}H_{14}O_6BrNS$: C, 37.90; H, 3.71. Found: C, 37.81; H, 3.82.

***cis*-1,2-Cyclohexanediol Mononitrate.**—A solution containing[2] 13.0 g. (0.082 mole) of 1,2-cyclohexanediol monoacetate and 6.43 g. of diacetate (estimated by saponification equivalent) in 40 ml. of chloroform was added dropwise over a period of 2 hr. to a solution of 10.7 ml. of nitric acid (d. 1.50, 98% nitric acid) in 50 ml. of 96% sulfuric acid. A temperature between −25 and −7° was maintained during the addition. The reaction mixture was poured into ice-water, and the chloroform layer was separated. The water layer was extracted once with 50 ml. of chloroform. The combined chloroform extracts were washed with water, saturated sodium bicarbonate and water. The chloroform solution was dried over anhydrous magnesium sulfate, and the material was distilled. The product, which was a mixture of *cis*-2-acetoxycyclohexyl nitrate and *cis*-1,2-cyclohexanediol diacetate, boiled at 68–73° (0.5 mm.) and weighed 16.7 g. The product was estimated to contain 9.4 g. (58% of mixture, 56% yield) of 2-acetoxycyclohexyl nitrate by quantitative hydrogenolysis over platinum oxide catalyst.

Sixteen grams of this mixture was treated with 100 ml. of 1.4 *M* sodium hydroxide solution in 75 vol. % ethanol at room temperature for 50 minutes. The extent of reaction was followed by titration of aliquots with standard hydrochloric acid, and it was apparent that hydrolysis of the acetate ester groups from the diacetate and nitrate–acetate was substantially complete at the end of this time. This method takes advantage of the relative inertness of nitrate esters to hydrolysis with alkali.[5-7] The solution was then neutralized with dilute acid, saturated with sodium chloride and extracted with three 100-ml. portions of ether. The ether extracts were combined and washed with 400 ml. of saturated salt solution. The ethereal solution was dried overnight over anhydrous magnesium sulfate, and the ether was distilled. The product, *cis*-1,2-cyclohexanediol mononitrate, boiled at 63–63.2° (0.3 mm.), $n^{20}\text{D}$ 1.4787, and weighed 3.81 g. (54% yield).

Anal. Calcd. for $C_6H_{11}NO_4$: C, 44.71; H, 6.88; N, 8.69. Found: C, 44.62; H, 6.72; N, 8.55.

Hydrogenolysis of this nitrate over platinum oxide at atmospheric pressure gave crude *cis*-diol, m.p. 89–96°, mixed m.p. with *cis*-diol,[2] 89–96°, mixed m.p. with *trans*-diol,[2] 66–80°.

cis-2-Nitroxycyclohexyl *p*-toluenesulfonate was prepared as described above for the *trans* isomer, m.p. after recrystallization from cyclohexane, 74.5–75.2°.

Anal. Calcd. for $C_{13}H_{17}O_6NS$: C, 49.51; H, 5.43. Found: C, 49.50; H, 5.52.

cis-2-Nitroxy *p*-bromobenzenesulfonate was prepared as described above for the *trans* isomer, m.p. after recrystallization from cyclohexane, 94–94.5°.

Anal. Calcd. for $C_{12}H_{14}O_6BrNS$: C, 37.90; H, 3.71. Found: C, 37.97; H, 3.72.

BOULDER, COLORADO

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[2] S. Winstein and R. E. Buckles, THIS JOURNAL, **64**, 2787 (1942); S. Winstein, H. V. Hess and R. E. Buckles, *ibid.*, **64**, 2796 (1942); D. Ginsberg, *ibid.*, **75**, 5746 (1953).

[3] S. Winstein, C. Hanson and E. Grunwald, *ibid.*, **70**, 812 (1948).

[4] A. G. Brook and G. F. Wright, *Can. J. Chem.*, **29**, 308 (1951).

[5] J. W. Baker and D. M. Easty, *Nature*, **166**, 156 (1950); *J. Chem. Soc.*, 1193, 1208 (1953).

[6] S. J. Cristol, B. Franzus and A. Shadan, THIS JOURNAL, **77**, 2512 (1955).

[7] B. Franzus, Ph.D. thesis, University of Colorado, 1954.