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Acyloxonium Ion Intermediates. Oxygen-18 Studies

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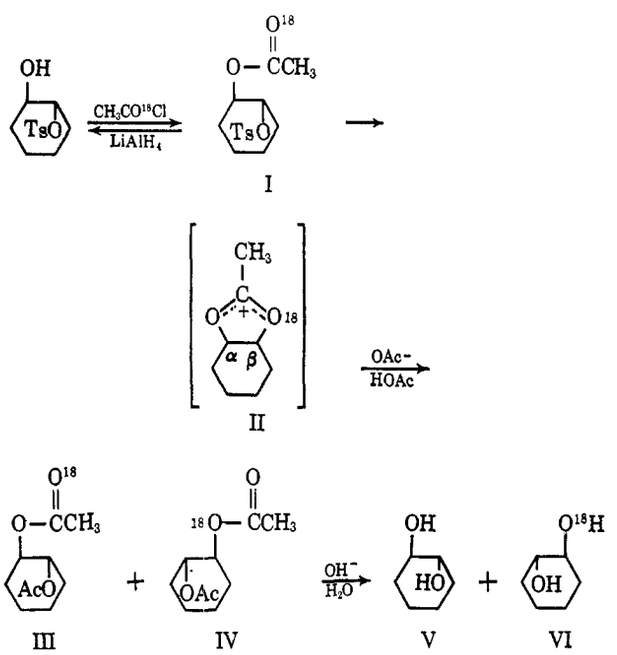
The work described herein supports the "acyloxonium ion" intermediates proposed by Winstein and Buckles[1] and further demonstrates the applicability of oxygen-18-labeling experiments in following participation by neighboring groups in solvolytic reactions as described by Dolby and Schwarz.[2]

In the course of a systematic study of polyols in our laboratory, we found it very convenient to use O^{18}-labeled acetate as a means of determining the role played by "acetoxonium ion" intermediates in reactions, such as the acetolysis of 1-O-acetyl-2-O-



p-toluenesulfonyl-*trans*-1,2-cyclohexanediol (I). The carboxyl-O^{18}-labeled compound I was prepared by acetylation of the mono-O-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediol with acetyl-O^{18} chloride in pyridine. Acetolysis of I with acetate ions in acetic acid gave a mixture of *trans*-diacetates-O^{18} (III + IV). Subsequent saponification of the diacetate-O^{18} (III + IV) afforded *trans*-1,2-cyclohexanediol-O^{18} (V + VI).

(1) S. Winstein and R. E. Buckles, *J. Am. Chem. Soc.*, **64**, 2780 (1942).
(2) L. J. Dolby and M. J. Schwarz, *J. Org. Chem.*, **30**, 3581 (1965).

Oxygen-18 analysis of the diacetate mixture (III + IV) indicated that acetolysis of I occurred with almost complete (99%) retention of O^{18}; therefore, it was apparent that loss of O^{18} *via* side reactions (*e.g.*, acetyl exchange) was not significant during this step. Most important, however, was the fact that 46% of the O^{18}, introduced into I as carboxyl-O^{18}, was found in the *trans*-1,2-cyclohexanediol-O^{18} (VI). This suggested that the "acetoxonium ion" intermediate (II) was highly symmetrical and that backside attack by an acetate ion occurred with equal ease at either the α or β carbon. For a perfectly symmetrical "acetoxonium ion" intermediate (II), a 50% incorporation of O^{18} would be expected in the final product (VI) of the reaction sequence. The experimental value of 46% approached the predicted value of 50%, if the 3% experimental error for O^{18} analysis were taken into consideration.

In the absence of potassium acetate, the acetoxonium *p*-toluenesulfonate ion pair has been known to re-form the *trans*-tosyloxyacetate (I).[3] Although in our study potassium acetate was present, which should minimize the reformation of I, it seemed important to establish clearly that the O^{18} found in *trans*-1,2-cyclohexanediol (VI) did result from the reaction sequence as outlined and not from O^{18} scrambling of the starting material (I) during the course of the reaction. From an acetolysis run of I, the starting compound was recovered from a half-completed reaction and found to contain the same O^{18} enrichment as in the original sample. Controlled hydrogenolysis of the recovered starting material (I) with lithium aluminum hydride afforded 1-O-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediol, whose O^{18} enrichment was less than 2% of that available in I. The low O^{18} enrichment suggests that there is little, if any, scrambling of the starting material during the reaction.

Although the term "acyloxonium ion" is freely used for the sake of simplicity, these results are consistent with other species, *e.g.* ion pairs, orthodiacetates, or rapidly equilibrating acetoxylcyclohexyl carbonium ions, as described by Winstein and co-workers.[3,4]

Work on other aryloxy and acyloxy arylsulfonates is in progress.

Experimental Section

Preparation of Acetic Acid-O^{18}.—Water containing 10.78% O^{18} enrichment was used. One-half gram of H_2O^{18} (0.0274 mole) was placed in a 20-ml, round-bottom flask and was frozen by immersion of the flask and content into a Dry Ice–acetone bath. After addition of a small Teflon-coated stirring bar to the flask, it was affixed with a reflux condenser, through which 2.86 g (0.0364 mole) of freshly distilled acetyl chloride was added. The reaction mixture was permitted to warm up to room temperature with constant stirring by a magnetic stirrer. As soon as evidence for reaction was noted (formation of gas bubbles), the reaction flask was cooled immediately in a Dry Ice–acetone bath. This cooling procedure was repeated as often as necessary to maintain control over the rate of reaction. After the reaction was finished, the product was refluxed for 4 hr to expel most of

(3) R. M. Roberts, J. Corse, R. Boschan, D. Seymour, and S. Winstein, *J. Am. Chem. Soc.*, **80**, 1247 (1958).
(4) S. Winstein, C. Hanson, and E. Grunwald, *ibid.*, **70**, 812 (1948).
(5) Melting points are uncorrected. Oxygen-18 analyses were performed by Analytical Corporation, New York, N. Y., and the Department of Chemistry, Arizona State University, using the procedure of D. Rittenburg and L. Ponticorvo [*Intern. J. Appl. Radiation Isotopes*, **1**, 208 (1956–1957)]. Possible error in O^{18} analysis was estimated as ±3%. Elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

the HCl. The acetic acid produced was not purified, but was used directly for the preparation of acetyl chloride-O^{18}.

Preparation of Acetyl Chloride-O^{18}.—Phosphorus trichloride (1.24 g, 0.009 mole) was added to the cooled reaction product from the previous step and the resultant solution was stirred at room temperature for 30 min. To one end of an U-shaped connecting tube with a stopcock attached for evacuation, the reaction flask was affixed and a receiving flask was attached to the other end. After the reactants were frozen in the reaction flask by immersion into liquid nitrogen, the system was throughly outgassed at *ca.* 0.5 mm. After 2 hr, the stopcock to the system was closed and the liquid nitrogen bath was transferred from the reaction flask to the receiving flask. As the reaction mixture warmed to room temperature, the labeled acetyl chloride distilled into the receiving flask, yielding 2.0 g (70%).

Preparation of Mono-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediol.—This compound was prepared according to a known procedure.[6] Recrystallization from Skellysolve C–benzene gave a pure sample of the compound with the correct melting point and elemental analysis.

Preparation of 1-O-acetyl-2-O-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediolcarboxyl-O^{18} (I).—The monotosyl ester (6.3 g, 0.023 mole) was dissolved in 15 ml of dry dichloromethane containing 2.0 ml dry pyridine. The flask was cooled in an ice bath and a solution of 2.0 g of acetyl chloride-O^{18} in 5.0 ml of dry dichloromethane was added dropwise, while the reaction was stirred by means of a magnetic stirrer. After addition of the acetyl chloride-O^{18}, the reaction was left at room temperature for 14 hr. The contents of the flask were poured into 100 ml of 0.5 *M* HCl and the desired product was extracted with 200 ml of diethyl ether. The ethereal solution was washed with 50 ml 10% $NaHCO_3$ solution, then with two 50-ml portions of distilled water, and dried with anhydrous sodium sulfate. Evaporation of the solvent yielded white, granular crystals which were recrystallized from aqueous methanol, yielding 3.8 g (53%), mp 77–78°.

Anal. Calcd for $C_{15}H_{20}O_5S$: C, 57.67; H, 6.45. Found: C, 57.57; H, 6.59; O^{18}, 0.987 atom % excess.

***trans*-1,2-Diacetoxylcyclohexanecarboxyl-O^{18} (III + IV).**—Acetolysis of I (3.0 g) according to procedure of Winstein, *et al.*,[6] yielded 1.5 g (73%) of *trans*-1,2-diacetoxycyclohexanecarboxyl-O^{18}, bp 119–119.5° (12 mm) [lit.[6] bp 120° (11 mm)].

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.96; H, 8.06. Found: C, 59.92; H, 8.16; O^{18}, 1.230 atom % excess (1.238 = 100% retention of O^{18} from I).

***trans*-1,2-Cyclohexanediol-O^{18} (V + VI).**—Saponification of a mixture of diactates (III + IV) by a known procedure[6] yielded *trans*-1,2-cyclohexanediol-O^{18}, which was purified by two recrystallizations from carbon tetrachloride and followed by sublimation, mp 102.8–103.1°.

Anal. Calcd for $C_6H_{12}O_2$: C, 62.04; H, 10.42. Found. C, 62.18; H, 10.42; O^{18}, 1.22 atom % excess (1.230 = 50% incorporation of O^{18} from III + IV).

Partial Acetolysis of 1-O-Acetyl-2-O-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediolcarbonyl-O^{18}.—The approximate half-life of the reaction was determined by quenching, every 5 min, 1-ml aliquots of the reaction solution. In this experiment, unlabeled 1-O-acetyl-2-O-toluenesulfonyl-*trans*-cyclohexanediol was solvolyzed, according to the procedure of Winstein, *et al.*[6] Each aliquot was shaken in a separatory funnel, along with 5 ml of benzene and 10 ml of 5% aqueous sodium bicarbonate solution. The organic layer was washed twice with 10 ml of water and then dried over anhydrous sodium sulfate. Each benzene solution was spotted consecutively on an 8 × 8 in. thin layer chromatographic plate, which was coated with a 100-μ layer of Absorbosil-3.[7] When all the samples were spotted, the plate was developed twice in ethyl ether–Skellysolve B (2:3, v/v). The spotted materials were located by spraying the plate with 0.5% methanolic iodine solution. Half-life for this reaction was estimated to be *ca.* 12 min by this technique.

Acetolysis of 1-O-acetyl-2-O-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediolcarbonyl-O^{18} (4.8 g; O^{18}, 1.05 atom % excess) was carried out as previously described, except that the reaction was quenched after 10 min in 150 ml of ice–water. Twenty-five grams of solid sodium bicarbonate was added to neutralize the acetic acid. The organic components were extracted with four 50-ml portions of benzene. The combined benzene extracts were washed with three 50-ml portions of water and dried over anhydrous sodium sulfate. Solvent removal left an oily residue, which crystallized upon addition of aqueous methanol and chilling the solution. After separation of the crystalline material, the mother liquor was subjected to silicic acid column chromatography (¾ × 9 in.), using Skellysolve B–ethyl ether (2:1, v/v) as the eluent. The combined yield of recovered starting materials by fractional crystallization and chromatography after two crystallizations from aqueous methanol was 1.05 g, mp 78.2–78.8°. It had the proper C–H analysis and the O^{18} enrichment was 1.09 atom %.

Hydrogenolysis of the Recovered 1-O-Acetyl-2-O-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediol-O^{18}.—The recovered O^{18} ester (900 mg, 2.9 mmole; O^{18}, 1.09 atom % excess) from the previous experiment and 25 ml of anhydrous ether were placed in a 100-ml, three-necked flask, affixed with a reflux condenser, an addition funnel, and a magnetic stirrer. Lithium aluminum hydride (120 mg, 3.1 mmoles), dissolved in 25 ml of anhydrous ether and cooled to 0°, was added through the addition funnel at a rate sufficient to maintain gentle reflux; addition time about 1 min. After a total reaction time of 3.5 min, 1 ml of ethanol and 1 ml of water were added to the reaction mixture and heated to reflux for 10 min. The solids were filtered and washed with two 30-ml portions of chloroform. From the combined filtrates, a granular, white solid was obtained, upon solvent removal under reduced pressure. After two recrystallizations from Skellysolve B, 150 mg of pure monotoluenesulfonyl-*trans*-1,2-cyclohexanediol was obtained, mp 97.0–97.8°. This material gave the correct elemental analysis and O^{18} enrichment was 0.28 atom %.

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(7) A product of Applied Science Laboratories, Inc., State College, Pa.

Nitrile Oxides. VIII. Cyanogen N-Oxide[1]

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The remarkable stability of cyanogen bis-N-oxide (I), O←N≡C—C≡N→O, at least in dilute solutions, compared with other simple aliphatic nitrile oxides, *e.g.*, acetonitrile oxide,[2] has been attributed to the unusually large number of resonance-hybrid structures which are possible for I.[3] To support this assumption, the investigation of cyanogen N-oxide (II), NC—C≡N→O, seemed of interest, since II, although closely related to I, cannot achieve so high a degree of resonance stabilization as I. For the preparation of II we started with the known cyanoformhydroximic chloride (III),[4] from which we tried to liberate II by reaction with aqueous bases under the various conditions described for the generation of I from oxalobishydroximic chloride (dichloroglyoxime).[3b] Ether extracts obtained from the above reaction at 0° had an intense, aggressive odor, different from III and presumably attributable to II, which, however, disappeared within 1 min. As expected, immediate infrared spectroscopy of these ether solutions did not

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(3) (a) C. Grundmann, *Angew. Chem. Intern. Ed. Engl.*, **2**, 260 (1963); (b) C. Grundmann, V. Mini, J. M. Dean, and H.-D. Frommeld, *Ann.*, **687**, 191 (1965).

(4) H. Houben and H. Kauffmann, *Ber.*, **46**, 3821 (1913).