pounds is greater than that of those previously reported. The observed melting points of the optically active derivatives are also somewhat higher than the literature values. A mixture of the *d*- and *l*-forms recrystallized from ethanol gave α-methylbutyraldehyde 2,4-dinitrophenylhydrazone with a melting point in good agreement with those reported for the racemic compound.

Experimental[3]

Degradation of L-Isoleucine to *d*-α-Methylbutyraldehyde 2,4-Dinitrophenylhydrazone.—In a 200-ml. steam distillation flask there was placed a solution of 0.26 g. of L-isoleucine in 20 ml. of water, and steam was introduced until boiling started. To the hot solution there was added 1.5 g. of ninhydrin in 20 ml. of water. The mixture was steam distilled and the vapor was passed into 0.36 g. of 2,4-dinitrophenylhydrazine in 300 ml. of 2 *N* hydrochloric acid. The precipitate was collected by filtration and washed well with water. There was thus obtained 0.44 g. (84%) of derivative, m.p. 132–135°, which upon recrystallization from ethanol yielded 0.35 g. (67%) of *d*-α-methylbutyraldehyde 2,4-dinitrophenylhydrazone, m.p. 135–137°, $[\alpha]_D$ +29.5°, *c* 1 in acetic acid. *Anal.*[4] Calcd. for $C_{11}H_{13}O_4N_4$; C, 49.8; H, 4.9; N, 21.1. Found: C, 49.9; H, 5.2; N, 21.0.

D-Isoleucine as well as L- and D-alloisoleucine were degraded in a similar manner.

Recrystallization of a Mixture of *d*- and *l*-α-Methylbutyraldehyde 2,4-Dinitrophenylhydrazone.—A mixture of 0.055 g. of each of the above isomers was recrystallized from ethanol to yield the racemic compound, m.p. 129–130° (lit. 128–128.5°,[5] 129–130°[6]).

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(3) All m.p.'s are corrected.

(4) Analysis by R. J. Koegel and staff of this Laboratory.

(5) J. D. Roberts and C. Green, THIS JOURNAL, **68**, 214 (1946).

(6) G. Dunn, G. T. Newbold and F. S. Spring, *J. Chem. Soc.*, S 131 (1949).

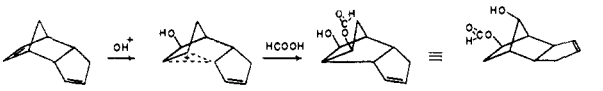
(7) U. S. Public Health Service, Department of Health, Education and Welfare.

The Action of Performic Acid on Dicyclopentadiene[1]

BY MARSHALL GATES AND S. PAUL MALCHICK

RECEIVED AUGUST 19, 1953

We have observed a rearrangement as a result of the action of performic acid[2] on *endo*-dicyclopentadiene which appears to be another example of the well-known[3] *endo–exo* rearrangement occurring in similarly constituted systems. The reaction proceeds readily to yield a glycol monoformate from which a glycol is obtainable on hydrolysis, but this glycol does not react with lead tetraacetate and is inert to periodic acid and is thus clearly not a 1,2-glycol. The following formulation,[1,4] entirely analogous to earlier suggestions,[3] appears plausible.



Cope and co-workers have observed the production of 1,4-cycloöctanediol by the action of performic acid on cycloöctene and by the action of formic acid on cycloöctene oxide,[5] although in this case the product must be produced by a hydride shift rather than by rearrangement of the carbon skeleton.

Experimental

Performic Acid Oxidation.—A well-stirred mixture of 61 g. (0.5 mole) of dicyclopentadiene and 350 cc. of 88% formic acid was cooled in an ice-bath and treated with 68 g. of 25% hydrogen peroxide (0.51 mole). The reaction was allowed to proceed until the mixture became homogeneous, and was then poured into water and extracted twice with ether. The ether layer was washed with bicarbonate, dried and concentrated to leave 58.4 g. of a yellow viscous liquid. Distillation yielded a yellow oil, b.p. 116–123° (0.7–0.8 mm.) whose infrared spectrum contained a prominent carbonyl band at 5.82 μ and a hydroxyl band at 2.92 μ. Five grams of this oil was hydrolyzed with ice-cold 5% aqueous alcoholic potassium hydroxide. After standing 1.5 hours the solution was extracted continuously for 26 hours with methylene chloride. The solvent was removed leaving 4.5 g. of a brown oil, a small amount of which was distilled in a molecular still at 0.03–0.05 mm. (block temperature 120–125°) to give the glycol as a yellow very viscous liquid whose infrared spectrum had lost all but a trace of the carbonyl band at 5.82 μ. The intensity of the hydroxyl band at 2.92 μ had increased.

Anal.[6] Calcd. for $C_{10}H_{14}O_2$: C, 72.31; H, 8.42. Found: C, 71.97; H, 8.01.

Lead Tetraacetate Oxidation.—A solution of 6.45 g. (0.039 mole) of the above glycol and 17.3 g. (0.039 mole) of lead tetraacetate in 35 ml. of glacial acetic acid and 200 ml. of methanol was shaken mechanically until no test could be obtained with starch–potassium iodide indicator. The methanol was removed under reduced pressure and the remaining solution was diluted with bicarbonate solution. The precipitated lead salts were removed and the filtrate was extracted three times with ether. Concentration of the dried extracts yielded 2.3 g. of a yellow liquid which was distilled in a molecular still at 0.03 mm. (block temperature 110°) to give a very viscous yellow oil whose infrared spectrum was identical with that of the starting material.

Periodic Acid Oxidation.—An excess of the above glycol in alcohol was treated with 25 ml. of 0.1532 *N* periodic acid[7] and allowed to stand for 11 hours. The solution was then neutralized with bicarbonate and a borax buffer and excess potassium iodide were added. The liberated iodine required 33.0 cc. of 0.1053 *N* thiosulfate, corresponding to 22.7 cc. (91%) of unused periodic acid.

(1) Taken from a dissertation presented to the faculty of Arts and Sciences of the University of Rochester in partial fulfillment of the requirements for the degree Doctor of Philosophy.

(2) D. Swern, G. N. Billen, T. W. Findley and J. T. Scanlan, THIS JOURNAL, **67**, 1786 (1945).

(3) P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946); R. B. Woodward and H. Baer, *ibid.*, **70**, 1161 (1948); see also S. Winstein, *et al.*, *ibid.*, **74**, 1127 (1952), and P. D. Bartlett, Abstracts, Twelfth National Organic Chemistry Symposium, Denver, Colorado, 1951, p. 1.

(4) The stereochemistry illustrated for the two substituents follows from the initially preferred *exo* addition of the OH+ entity after which the reaction of the ion with formate ion or formic acid at the side opposite the unsaturated five-membered rings yields the configuration given.

(5) A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5884 (1952).

(6) Analysis by Mme. Odette Sauvage.

(7) Prepared according to H. H. Willard and C. H. Greathouse, THIS JOURNAL, **60**, 2869 (1938).

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The β-Nitration of 2-Thenaldehyde

BY WILLIAM O. FOYE, JOHN J. HEFFERREN AND EDWARD G. FELDMANN

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Recent activity in the preparation and biologic testing of nitroaldehyde derivatives has provided a number of compounds that have anti-viral activity, such as 5-nitro-2-furaldehyde semicarbazone[1]

(1) M. D. Eaton, M. E. Perry and I. M. Gocke, *Proc. Soc. Exptl. Biol. Med.*, **77**, 422 (1951).

and 5-nitro-2-thenaldehyde thiosemicarbazone.[2] Since no derivatives of 4-nitro-2-thenaldehyde or 4-nitro-2-furaldehyde have been reported, a synthesis of these compounds was attempted by direct nitration of the unprotected aldehydes, in analogy to the formation of *m*-nitrobenzaldehyde[3] by nitration. Furthermore, no methods of synthesis of these compounds have been described previously, although Gever[4] recently isolated 4-nitro-2-thenaldehyde as a by-product in the preparation of 5-nitro-2-thenaldehyde diacetate.

The nitration was carried out in a somewhat different fashion from that described for *m*-nitrobenzaldehyde[3] by dissolving the aldehyde in concentrated sulfuric acid, cooling to −10° by the addition of carbon dioxide snow, and adding the nitrating solution slowly at the stated temperature. A yield of 64.5% of pure 4-nitro-2-thenaldehyde was obtained after fractionation of the product, but no aldehyde could be detected in the dark solution resulting from the nitration of 2-furaldehyde, either by reaction with 2,4-dinitrophenylhydrazine or by distillation. When this procedure was carried out with benzaldehyde, however, a yield of 90% of purified *m*-nitrobenzaldehyde, was obtained—an improvement over the 75–84% yields which have been reported.[3]

The nitration of a 2-substituted thiophene in the 4-position is an exception to the previous findings that substitution predominates in the 5-position regardless of the type of director present in the 2-position.[5] In addition no evidence of 5-nitro-2-thenaldehyde could be detected in the product.

Experimental

4-Nitro-2-thenaldehyde.—To a beaker containing 21.2 g. (0.22 mole) of concentrated sulfuric acid cooled to −10° by means of carbon dioxide snow and surrounded by an ice-bath was added slowly 8.7 g. (0.08 mole) of 2-thenaldehyde (prepared by the Sommelet method[6]). Stirring was employed throughout the reaction, and the temperature was held at −10° by the addition of more Dry Ice as needed. After complete addition of the aldehyde, a nitrating solution of previously cooled fuming nitric acid (18.9 g., 0.30 mole) and concentrated sulfuric acid (14.1 g., 0.14 mole) was likewise slowly introduced. The addition consumed two hours, and the reaction mixture was stirred for another half-hour at the same temperature, after which it was allowed to warm gradually to 0°. The reaction mixture was then poured into 300 g. of a cracked ice-water mixture, stirred for several minutes, and extracted with two 200-cc. portions of diethyl ether. The ether solution was dried over sodium sulfate and evaporated to approximately 30 cc. over a steam-bath, after which it was fractionally distilled under reduced pressure. The fraction boiling at 126–131° at 3 mm. was collected, and 7.9 g. (64.5%) of yellow crystals, m.p. 35–37°, solidified in the receiver.

The semicarbazone, a yellow solid, melted[7] at 234–236°; Gever[4] reported melting points of 36–37° for the nitroaldehyde and 234–235° for the semicarbazone.

The 2,4-dinitrophenylhydrazone, an orange solid, melted at 290–294°.

Anal.[8] Calcd. for $C_{11}H_7N_5O_6S$: C, 39.16; H, 2.09. Found: C, 38.61; H, 2.24.

The phenylhydrazone, golden platelets, melted at 192–194°.

Anal. Calcd. for $C_{11}H_9N_3O_2S$: C, 53.42; H, 3.67. Found: C, 53.76; H, 3.79.

(2) S. A. Minton, J. E. Officer and R. L. Thompson, *J. Immunol.*, **70**, 222 (1953).

(3) C. Bertagnini, *Ann.*, **79**, 260 (1851); O. Widman, *Ber.*, **13**, 678 (1880); D. W. Bissell, U. S. Patent 1,509,412 (1924); R. N. Icke, C. E. Redemann, B. B. Wisegarver and G. E. Alles, *Org. Syntheses*, **29**, 72 (1949).

(4) G. Gever, THIS JOURNAL, **75**, 4585 (1953).

(5) H. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, pp. 147, 225.

(6) F. W. Dunn, T. D. Waugh and K. Dittmer, THIS JOURNAL, **68**, 2118 (1946).

(7) The melting points are uncorrected.

(8) The analyses were carried out by the Clark Microanalytical Laboratory, Urbana, Ill.

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The Stereochemistry of Ether Cleavage

BY HAROLD HART AND HERBERT S. ELEUTERIO

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The steric consequences of suggested mechanisms[1] for the cleavage of ethers by acidic reagents are clear, but were not studied systematically until recently.[2] The first step in these mechanisms is the formation of an oxonium salt, or something akin to one. This may then dissociate to a carbonium ion and an alcohol (or phenol) molecule, resulting in much racemization but some inversion at the carbon undergoing C–O fission. Alternatively, the second step may be a bimolecular nucleophilic displacement of an alcohol (or phenol) molecule, again resulting in inversion. Evidence for each of these mechanisms was obtained by Burwell.[2]

We have found that a third alternative is necessary to account for the configurational changes which occur when α-phenethyl aryl ethers are cleaved by hydrogen chloride. α-Phenethyl chloride and the corresponding phenol resulted in a few minutes when hydrogen chloride was bubbled at room temperature or 50°, into these ethers, either pure or in a solvent (benzene, acetone, di-*n*-butyl ether, methanol). The configurations of some optically active α-phenethyl aryl ethers with respect to α-phenethyl chloride recently have been established.[3] When these optically active ethers were cleaved, α-phenethyl chloride was formed *with retention of configuration*, and with a minimum of 38% retention of optical purity. The same stereochemical results were obtained whether the aryl portion of the ether was phenyl, *p*-tolyl or mesityl, without a solvent, in benzene or in acetone (the extent of racemization was greater in the latter solvent).

No previously proposed mechanism for ether cleavage predicts retention of configuration at the carbon atom undergoing C–O fission. Retention has been observed, however, in the C–O fission of certain alcohols, particularly when arylalkylcarbinols react at low temperatures with hydrogen halides. Retention in the case of alcohols has been explained as an internal displacement (S_Ni).[4] We suggest that when an ether is cleaved by a

(1) See, for example, well known texts by Hammett, Remick, Alexander and others.

(2) R. L. Burwell, Jr., L. M. Elkin and L. G. Maury, THIS JOURNAL, **73**, 2428 (1951).

(3) H. Hart and H. S. Eleuterio, *ibid.*, **76**, 519 (1953).

(4) For a brief discussion and leading references, see E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 92–94.