Anal. Calcd. for $C_4H_9O(OCH_3)_5$: C, 52.36; H, 9.58; OCH_3, 61.39. Found: C, 52.43; H, 9.24; OCH_3, 61.52.

2,3,4,5,6 - O - Pentamethyl - (*levo*) - sorbitol 1 - N - α-Naphthylcarbamate.—Four grams of 2,3,4,5,6-O-pentamethyl-(*levo*)-sorbitol was added to 3.5 g. of α-naphthyl isocyanate, shaken well and allowed to stand overnight. The general procedure used was that described by Bickel and French.[17] Crystals of the by-product, di-α-naphthyl urea, separated and the reaction solution set to a semisolid mass. Petroleum ether was added (b. p. 60–110°) and the mixture boiled and filtered rapidly in order to remove the di-α-naphthyl urea, which is not soluble in hot, high-boiling petroleum ether. On standing overnight at icebox temperature a waxy, white solid separated; yield 2 g. Further purification of the product with boiling petroleum ether was required to remove traces of the by-product. After four such treatments with petroleum ether the material crystallized in rose-shaped clusters; m. p. 71–72°. On recrystallization, performed by using a small quantity of ether as solvent, adding an excess of petroleum ether and seeding, long needles were obtained; m. p. 75–76°, spec. rot. −5° (22°, *c* 3, abs. $CHCl_3$).

The compound was soluble in ether, high-boiling petroleum ether, ethyl acetate, acetic acid and chloroform. It was practically insoluble in all other common solvents.

Anal. Calcd. for $C_{17}H_{16}O_2N(OCH_3)_5$: C, 62.73; H, 7.41; N, 3.32; OCH_3, 36.75. Found: C, 62.62; H, 7.43; N, 3.24; OCH_3, 36.75.

Summary

1. Gentiobiotol (6-(β-*d*-glucosido)-(*levo*)-sorbitol) has been synthesized as an amorphous material by the high pressure catalytic reduction of gentiobiose and characterized as its crystalline nonaacetate.

2. The structure of gentiobiotol was verified by its lack of Fehling reduction and by the characterization of its hydrolytic products, (*levo*)-sorbitol and *d*-glucose, as crystalline derivatives.

3. O - Nonamethyl - 4 - (β - *d* - galactosido)-(*levo*)-sorbitol and O-nonamethyl-4-(α-*d*-glucosido)-(*levo*)-sorbitol have been synthesized as distilled sirups by the methylation of lactitol and maltitol, respectively.

4. 2,3,4,5,6 - O - Pentamethyl - (*levo*) - sorbitol has been synthesized as a distilled sirup by the high pressure catalytic reduction of aldehydo-*d*-glucose pentamethyl ether and characterized as its crystalline 1-N-α-naphthylcarbamate.

COLUMBUS, OHIO   RECEIVED JANUARY 29, 1943

(17) V. T. Bickel and H. E. French, THIS JOURNAL, **48**, 747 (1926).

The Preparation of Aldehydes, Ketones, and Acids by Ozone Oxidation

BY ALBERT L. HENNE AND PHILIP HILL

Oxidation with ozone can be adapted to a practical preparation of aldehydes, ketones and acids in good yields. The results of a quantitative search for the best conditions of operation are described here. All operations were carried out on half mole quantities.

The source of ozone has been described in an earlier communication.[1]

Of the three satisfactory solvents, methylene chloride was generally preferred, since (1) it permits the carrying out of the ozonization at low temperatures (solid carbon dioxide), a procedure which lessens the loss of volatile olefins in the oxygen stream, and (2) it is easily eliminated during the hydrolysis of the ozonide. Glacial acetic acid at room temperature, and ethyl acetate were also satisfactory, the latter particularly so in the ozonization of cyclic olefins, but the use of both solvents required an efficient refluxing system.

The absorption of ozone was quantitative as

long as olefinic material was available.[2] This was repeatedly ascertained by weighing the ozonide after the removal of the solvent by suction. The end of the reaction was sensitively detected by odor, or by the break of a piece of rubber hose attached to the gas outlet tube.

The hydrolysis of the ozonide was carried out in an apparatus adapted from the design of Whitmore and Church.[3] These authors remove the solvent before hydrolysis, at the risk of explosions; they recommend the use of zinc dust and hydroquinone in the water, and record the violence of the hydrolysis. After many trials the following modifications were adopted. (1) A solution of the ozonide in methylene chloride was dripped into the hydrolyzing medium and the solvent was allowed to distill off through the reflux

(1) Henne, THIS JOURNAL, **51**, 2676 (1929).

(2) With dienes, one molecule of ozone was rapidly fixed but the second molecule was slow to react, and systematic titration of ozone in the effluent gases was required to find the end-point of the ozonization.

(3) Whitmore and Church, THIS JOURNAL, **54**, 3710 (1932).

condenser by heat of reaction or by gentle external heating. This procedure reduced the violence of the reaction and prevented explosions. (2) In order to inhibit oxidation and polymerization, the hydrolyzing agent was made acid, with at least 25% acetic acid. The use of zinc dust was continued but hydroquinone or any other "stabilizer" was abandoned. (3) The optimum time of refluxing was set at one hour or less. Under these conditions, ketones or aldehydes were generally obtained in yields of sixty to seventy per cent.

It was found that the ozonides were most efficiently converted directly into the corresponding acid by hydrogen peroxide in acid solution. In general two moles of hydrogen peroxide for one mole of ozonide proved adequate. In carrying out this reaction it was found advantageous (though not essential) to remove the methylene chloride from the ozonide and replace it by acetic acid before hydrolysis. The acids prepared in this way were generally obtained in sixty to seventy per cent. yield.

Experimental Details

Ozonizer.—The source of ozone was a series of three Berthelot tubes modified as previously described[1] and operated at fifteen kilovolts. At an oxygen rate of twenty liters per hour, the weight concentration of ozone produced was 2 to 3% with Pyrex glass tubes. With soft glass tubes, the concentration increased to slightly over 4.5%, and it became 6% when the tubes were built of lead glass. Unfortunately the lead glass is expensive, difficult to work and impractical to repair; it cannot be recommended. On very short runs, with the ozonizer cold, the yields are about 50% higher. When running continuously, the ozonizer heats considerably. A systematic study to design a better ozonizer is under way; meanwhile, soft glass tubes will give fairly dependable service over long periods of continuous operation.

5-Methylhexanal.—A solution of one-half a mole of 6-methyl-1-heptene in 200 ml. of methylene chloride was cooled to $-78°$ and subjected overnight to a stream of 6% ozonized oxygen at 20 liters per hour, for twelve hours. It was then added in half an hour to a suspension of 32.5 g. of zinc dust in 300 ml. of 50% acetic acid, contained in a 1-liter round-bottom flask fitted with a dropping funnel, a mercury-sealed stirrer and a reflux condenser. Much heat was evolved. The methylene chloride was allowed to distil through the condenser, and caught in a cold receiver. The mixture was refluxed for one hour, stirred until cold, then extracted twice with 200 ml. of ether. The ether extract was washed with a solution of potassium iodide until all peroxides disappeared, *an essential step to avoid explosions later*. This was followed by washings with cold, diluted sodium hydroxide, hydrochloric acid and, finally, a saturated solution of sodium chloride. After drying, the ether was distilled off, then the aldehyde (b. p. 140–144°); polymers remained as a residue. After redistillation the

aldehyde had the following properties: b. p. 144° (750 mm.); $n^{20}D$ 1.4114; d^{20}_4 0.8206; 2,4-dinitrophenylhydrazone m. p. 116.6–116.8°; semicarbazone m. p. 116.0–116.7°. The alkaline wash was acidified, cooled, and extracted with ether. The ether layer was dried and distilled to obtain ether first, then the organic acid. The results averaged 62% of 5-methylhexanal, 9% of polymer, and 5% of 5-methylhexanoic acid. This accounted for 76% of the original olefin.

5-Methylhexanoic Acid.—The ozonide was obtained as above. Its solvent was removed by suction and replaced by 100 ml. of acetic acid. The solution was dripped into a mixture of 114 g. of 30% hydrogen peroxide, 5 ml. of concentrated sulfuric acid and 200 ml. of water in the flask described. Cautious heating was applied progressively. This phase needed careful watching because the reaction became vigorous and required intermittent cooling. Refluxing was continued for two hours. After cooling to ice temperature, extraction with ether was performed. The ether layer was then extracted with a solution of sodium hydroxide. The latter was acidified, extracted with ether. This was dried, then distilled. The acid was collected at 200–210°. On redistillation it had the following characteristics: b. p. 204–207° (752 mm.); $n^{20}D$ 1.4220; d^{20}_4 0.9163; amide m. p. 99.5–100°; p-bromophenacyl ester m. p. 72.5–73.0°. The yields averaged 67%.

2-Hexanone.—The ozonide of 2-methyl-1-hexene was obtained and hydrolyzed as indicated in the first preparation. The ketone had the following characteristics: b. p. 124.0–124.5° (738 mm.); $n^{20}D$ 1.4002; d^{20}_4 0.8118; 2,4-dinitrophenylhydrazone m. p. 107.0–107.2°; semicarbazone m. p. 122.2–122.5°. The yields averaged 60%.

Adipic Acid.—A solution of 20.5 g. of cyclohexene in 100 ml. of ethyl acetate was cooled to $-78°$ and ozonized. (Note: in acetic anhydride, explosion occurred.) A portion of 150 ml. of acetic acid was added, and the mixture of ethyl acetate and acetic acid was partly evaporated by suction. More acetic acid was added and the treatment repeated. A suspension was obtained, which was treated as in the second preparation. The aqueous solution was evaporated to dryness, recrystallized from water, washed with petroleum ether, then recrystallized from water. The adipic acid melted at 150–151°, and its p-bromophenacyl ester at 153–154°. The yields averaged 60%.

Phenylacetic Acid:—The ozonide of allylbenzene was obtained and hydrolyzed as shown in the second preparation. The ether solution was evaporated to dryness and the residue recrystallized from petroleum ether. Phenylacetic acid was obtained in 50% yield. It melted at 74–75° and its p-bromophenacyl ester at 88.7–89.0°.

Phenylacetic Aldehyde.—All attempts from allylbenzene failed.

7-Methyloctanal.—The ozonization and hydrolysis of 8-methyl-1-nonene (44 g. or 0.314 mole) were performed as shown in the first preparation. On distillation 29.3 g. (0.209 mole) of the aldehyde, b. p. 98–103° (140 mm.) was collected, corresponding to a yield of 66.6% of the theoretical. Refractionation gave a center fraction, b. p. 92–94° (120 mm.); 2,4-dinitrophenylhydrazone, m. p. 99–99.5°; semicarbazone, m. p. 79–80°.

4-Methyl-2-octanone.—2,4-Dimethyl-1-octene (26.7 g., 0.19 mole) was treated in the manner employed to prepare 2-hexanone. On distillation, fractions b. p. 90–94° (40 mm.), were collected, amounting to 18.6 g. (0.131 mole) or 68.9% of the theoretical yield. Refractionation gave a center cut, b. p. 92–94° (40 mm.); 2,4-dinitrophenyl-hydrazone, oil; semicarbazone. m. p. 69–70°.

Summary

Practical directions are given to obtain 60 to 70% of aldehydes, ketones or acids by oxidation of olefins with ozone.

COLUMBUS, OHIO   RECEIVED NOVEMBER 27, 1941

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Action of Acids on 2,3-Diphenyl-2,3-epoxyindanone

BY C. F. KOELSCH AND C. D. LE CLAIRE

By the action of sulfuric acid on 2,3-diphenyl-2,3-epoxyindanone (I) in acetic acid solution, Weitz and Scheffer[1] obtained a straw yellow compound which they formulated as a lactone (II). When hydrochloric acid was used in place of sulfuric acid, there was obtained a colorless substance formulated as a hydroxy lactone (IV). Acidification of a solution of II in sodium hydroxide yielded an acid (III), but when a similar solution of IV was acidified, IV was precipitated unchanged. When an alkaline solution of IV was warmed, a neutral yellow compound (m. p. 127–129°) isomeric with II precipitated. It was suggested that this yellow compound might be 3,3-diphenylindandione (VI), although not much weight was attached to this suggestion because the compound gave no quinoxaline.

The sulfuric acid product is II, as previously formulated, for on hydrolysis with alcoholic alkali it yields the acid III, and this acid must be o-desylbenzoic acid since on treatment with stronger alkali it yields benzoic acid and o-benzylbenzoic acid. When III is dehydrated, it yields a white substance which despite its lack of color, is identical with II. The yellow color of II, a former basis for criticism of the structure assigned, is thus caused by adsorbed impurities.
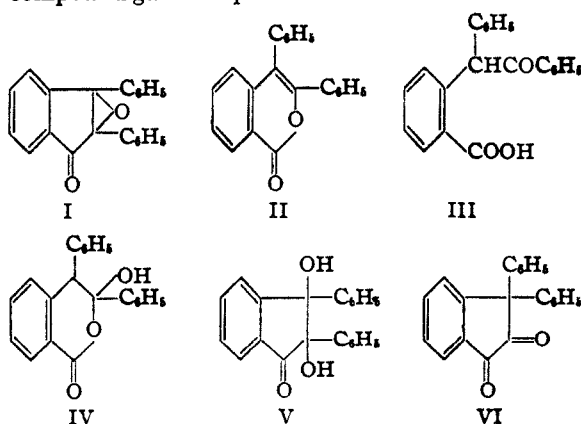
In view of the behavior of II toward alkali, the compound obtained from the oxide and hydrochloric acid cannot have structure IV, for a substance having this structure should likewise be hydrolyzed to the acid III. The compound reacts with lead tetraacetate yielding o-benzoylbenzil, and, therefore, it must be the glycol V.

The reported conversion of the glycol (V) into a yellow compound of m. p. 127–129° could not be repeated. Boiled for a short time with alkali, the glycol was unchanged, and when the boiling was prolonged, the compound yielded benzoic acid, o-benzoylbenzoic acid, and o-benzoylbenzil.

Consideration of the structure now established for II renders it likely that the substance obtained by the action of acids on 3-(p-dimethylamino-phenyl)-2,3-epoxy-2-(o-formylphenyl)-indanone[3] is 4 - (p - dimethylaminophenyl) - 3 - (o - formyl-phenyl)-isocoumarin rather than 3-(p-dimethyl-aminophenyl) - spiro - [indan - 2,1'(3') - isobenzo-furan]-dione-1,3'; the new formulation accounts for the aldehydic properties reported for the substance.

A synthesis of VI was of considerable interest,[2] and a detailed investigation of the compounds of Weitz and Scheffer was, therefore, undertaken in the hope that one of their yellow compounds might actually be a diketone. The results of this investigation are reported in the present paper.

Experimental

3,4-Diphenylisocoumarin (II).—A suspension of 5 g. of the oxide (I) in 25 ml. of acetic acid containing one drop of sulfuric acid was warmed gently for a few minutes. The solid dissolved, and the yellow lactone (5 g.) rapidly separated. Recrystallized from acetic acid several times,

(1) Weitz and Scheffer, *Ber.*, **54**, 2344 (1921).

(2) The desired synthesis has been carried out using 3,3-diphenyl-indanone-1 as the starting material: Koelsch and Le Claire, *J. Org. Chem.*, **6**, 516 (1941).

(3) Weitz, *Ann.*, **418**, 1 (1918).