8. 3-Methyl-2-pentanol was the only alcohol obtained from the reaction of 2,3-epoxybutane with a dioxane precipitate from ethylmagnesium bromide.

9. Some new urethans of 3-methyl-2-pentanol, 3-methyl-3-pentanol and 3-methyl-2-butanol were described.

NEW BRUNSWICK, N. J. RECEIVED AUGUST 25, 1936

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Isolation of 1,2-Diketones from the Ozonization of Disubstituted Acetylenes

BY THOMAS L. JACOBS

In a recent paper, Hurd and Christ[1] have discussed the course of the ozonization of acetylenes. They formulate the reaction as proceeding through a 1,2-diketone which is assumed to be oxidized by the hydrogen peroxide produced from the decomposition of the ozonide. From the six acetylenes ozonized, they isolated only acids in yields of 42–61%. The isolation of glyoxal in 81% yield from the ozonization of acetylene[2] is the only instance in which a 1,2-dicarbonyl compound actually has been obtained.

I have ozonized diphenylacetylene and benzylphenylacetylene[3] under carefully controlled conditions, and have isolated benzil and benzylphenyl diketone. At −78° the action of ozone on diphenylacetylene produced an unstable ozonide which decomposed to a black tar shortly after the solvent was removed. When the ozonization was carried out in petroleum ether at 5–15°, the product was a yellow oil which on hydrolysis gave benzoic acid in 65% and benzil in 5% yield. The unstable ozonide apparently produced the same yellow oil as an intermediate when treated with water. When benzylphenylacetylene ozonide, prepared at −30 to −40°, was decomposed with water, the sole products were a mixture of acids and tar. From the acid mixture were isolated benzoic acid in 60% and phenylacetic acid in 10% of the theoretical yield.

$$C_6H_5C{\equiv}CCH_2C_6H_5 \xrightarrow[H_2O]{O_3} C_6H_5COOH + C_6H_5CH_2COOH$$

When the product of ozonization was decomposed with neutral potassium iodide solution, benzylphenyl diketone was isolated in 25% yield. In addition, a small amount of acidic material and much tar were obtained. One attempt was also made to decompose the ozonide by distillation under reduced pressure. A mixture of acid and neutral material resulted, from which a low yield of a mixture of acids was obtained. The neutral portion was accidentally lost.

Ozone was never absorbed completely by any of the acetylenes investigated. The rate of absorption was nearly constant until one mole of ozone had been taken up for each mole of acetylene treated, and then began to fall off rapidly. In one experiment in which the ozonization was continued beyond this point, the initial absorption was 83% and dropped to 25%, but decreased only slowly from this point. The residual absorption probably represents attack of the benzene rings.

The isolation of 1,2-diketones does not prove that such compounds are always intermediates in the production of acids by the ozonization of acetylenes, but the brilliant yellow color of the oil which appears during the preparation or decomposition of the ozonides does suggest that this is the case. In this connection it should be noted that benzil is not attacked by ozone under the conditions of the experiments. The detailed mechanism postulated for the reaction by Hurd and Christ[1] assumes the formation of only monomolecular species, and this appears subject to some question. The amorphous character of the unstable product of ozonization at low temperatures indicates that it is probably polymeric.

An extension of the investigation has been temporarily interrupted, and a report of experiments already completed is made at this time in consideration of the publication of Hurd and Christ.[1]

Experimental

An ozonizer of the Henne[4] type yielding 6.5 to 8% of ozone when oxygen was supplied at 18 to 14 liters per hour was used. Ozone concentrations were determined by the

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[1] Hurd and Christ, *J. Org. Chem.*, **1**, 141 (1936).

[2] Briner and Wunenburger, *Helv. Chim. Acta*, **12**, 786 (1929).

[3] The synthesis, properties and reactions of this compound and related acetylenes will be described in a paper by Johnson, Schwartz and Jacobs. See also Schwartz, Cornell Thesis, 1931; Jacobs, Cornell Thesis, 1935.

[4] Henne, THIS JOURNAL, **51**, 2676 (1929).

potassium iodide method of Smith.[5] The amount of ozone used was easily found by successive determinations on the oxygen stream first as it came from the ozonizer and second after it had passed through the solution of the acetylene. Dry oxygen was used. In experiments below 0°, the stream of ozonized oxygen was passed through a glass coil immersed in solid carbon dioxide–acetone before entering the reaction flask.

The Ozonization of Diphenylacetylene

Diphenylacetylene was prepared from benzil by the method of Schlenk, Bergmann and Rodloff[6] or by the action of alcoholic potassium hydroxide on stilbene dibromide.

The Isolation of Benzil.—A solution of 35.6 g. (0.2 mole) of diphenylacetylene in 350 cc. of purified petroleum ether was ozonized at 5–15°. The solvent was attacked almost as rapidly as the compound, but impurities thus introduced were volatile with steam. The ozonized solution, which contained a heavy, yellow, insoluble oil, was steam distilled, and the residue extracted with hot water. The oil remaining was dissolved in ether and extracted with 2% sodium hydroxide. The total benzoic acid obtained was 31.9 g. (65.5% yield). The ether solution gave 8.4 g. of neutral material from which 2.3 g. (5.5% yield) of benzil was obtained, m. p. 94–95°, mixed m. p. the same. The quinoxaline derivative was prepared, m. p. and mixed m. p. 124.5–125°. The residual neutral material was a mixture from which a very little more benzil was obtained by distillation.

Ozonization at −78°.—A solution of 5.2 g. of diphenylacetylene in 100 g. of methyl chloride was ozonized at −78°. The resulting mixture was opaque, and contained an amorphous white precipitate. The solvent was allowed to evaporate and the product was a pasty, yellowish, almost odorless mass, which after remaining at room temperature for about fifteen minutes decomposed suddenly with a considerable heat effect and the evolution of acrid white fumes. Benzoic acid was isolated in poor yield from the black tar remaining. The unstable ozonide was found to ignite with a puff and much liberation of carbon when heated on a platinum foil; it liberated iodine from neutral potassium iodide solution, reacted violently with concentrated sulfuric acid, and on heating in water was converted into a brilliant yellow oil, apparently the same as that obtained directly by ozonization at the higher temperature.

The Ozonization of Benzylphenylacetylene

All experiments with this compound were carried out in purified ethyl chloride at −30 to −40°.

Decomposition of the Ozonide with Potassium Iodide.—By ozonization of 5 g. (0.027 mole) of benzylphenylacetylene and evaporation of the solvent was obtained 5 cc. of a yellow oil containing considerable solid material. This product was decomposed by standing for fifteen hours with dilute, slightly acid potassium iodide solution; titration with thiosulfate (19.2 cc. of 0.4177 *N* required) gave the iodine liberated as 0.004 mole, equivalent to about one-seventh of the acetylene taken. The solution was extracted with ether and this extract washed with water and 10% sodium carbonate solution and dried over anhydrous potassium carbonate. Distillation gave 1.5 g. of a yellow oil, b. p. 161° (4 mm.). The product gave a quinoxaline derivative, m. p. 97–98°. Kohler and Barnes[7] report the boiling point of benzylphenyl diketone as 175° (8 mm.), and the melting point of the quinoxaline derivative as 97–98°. A mixed melting point of the quinoxaline derivative with that prepared by Kohler and Barnes showed no depression.

Decomposition of the Ozonide with Water.—The material from the ozonization of 19.2 g. (0.1 mole) of benzylphenylacetylene was extracted several times with hot water. Impure benzoic acid resulted on cooling and the acid was purified by crystallization from water. All aqueous residues were then extracted with ether in a continuous extractor for two hours. A total of 3.13 g. of mixed acids resulted; in order to effect a separation, the mixture was esterified in ether with diazomethane, and the mixture of esters distilled through a small, simplified Podbielniak-type column[8] (35 cm. long, 3 mm. internal diameter, containing a spiral of No. 28 platinum wire). This gave 0.94 g. of methyl benzoate, b. p. 72–73° (8 mm.), and 1.57 g. of methyl phenylacetate, b. p. 90–90.5° (8 mm.). Known methyl phenylacetate distilled through the same column at 89–90° (7.5 mm.). The recovery of pure, separated esters from the mixture of acids was 90%. The methyl phenylacetate from the ozonization had a refractive index of $n^{16}\mathrm{D}$ 1.5102, compared with $n^{16}\mathrm{D}$ 1.5100 for the sample prepared by standard methods (lit., $n^{16}\mathrm{D}$ 1.5091). Both of these samples were converted to phenylacetamide by reaction with concentrated ammonium hydroxide. The melting point and mixed melting point was 159–160°. The total benzoic acid (including methyl benzoate) isolated from this ozonization was 7.3 g. (0.06 mole), a yield of 60%, assuming complete conversion of the acetylene to one mole of each acid. The phenylacetic acid recovered amounted to 0.01 mole (10% yield). The oily residue from the water extraction was not further examined.

Summary

From the decomposition of the products of ozonization of diphenylacetylene and benzylphenylacetylene, the corresponding 1,2-diketones have been isolated, as well as the expected acids.

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(5) Smith, THIS JOURNAL, **47**, 1844 (1925).

(6) Schlenk, Bergmann and Rodloff, *Ann.*, **463**, 76 (1928).

(7) Kohler and Barnes, THIS JOURNAL, **56**, 211 (1934).

(8) Podbielniak, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 177 (1931); **5**, 119 (1933).