purity and surface tension were measured over a temperature range and the results compared with those given in the "International Critical Tables." A table is given in which the results for the temperatures 20, 40 and 60° are tabulated.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND FROM THE RICHARDSON MEMORIAL LABORATORY, THE TULANE UNIVERSITY OF LOUISIANA]

Ozonolysis of Pyridine Homologs, a Method of Structural Elucidation[1]

BY WILLIAM SHIVE,[2] EDWARD G. BALLWEBER[3] AND W. WILBUR ACKERMANN[2]

Utilization of ozonolysis in the degradation of certain derivatives of pyridine[4,5] and quinoline[6] has indicated that this reaction may be generally useful in the proof of structure of bases of these types. In the present work, a study of the ozonolysis products of pyridine, 2-, 3- and 4-picoline, 2,6-lutidine, 2,4,6-collidine, and 2-*s*-butyl-4,5-dimethylpyridine was made in order to determine the value of ozonolysis in structural elucidation of pyridine homologs.

Experimental

Source of Pyridine Homologs.—Commercial grades of anhydrous pyridine and 2-picoline obtained from Pittsburgh Coke and Chemical Co. were purified by redistillation through a six-foot Stedman-packed column. 3-Picoline, Eastman Kodak Co. "practical" grade, 90–95% purity, was purified by the method of Lidstone.[7] 4-Picoline and 2,6-lutidine, Eastman Kodak Co. "Eastman" grade, were also purified by the same process. 2,4,6-Collidine, Eastman Kodak Co. "Eastman" grade, was redistilled. A sample of 2-*s*-butyl-4,5-dimethylpyridine which was isolated from petroleum[5] was kindly supplied by Dr. H. L. Lochte and Dr. W. W. Crouch.

Ozonization.—The ozone used in these experiments was generated by passing dry oxygen through a silent electric discharge in a set of six Berthollet tubes connected in series by mercury-filled joints. Unless otherwise indicated, all solutions were ozonized for ten hours by passing, at a rate of 2 liters per hour, a stream of ozonized oxygen containing 5% ozone through a solution of 5 g. of the anhydrous pyridine homolog in 30 cc. of dry solvent. Ozonides as such were not detected, and these solutions of ozonized pyridine homologs consisted of relatively complex mixtures from which derivatives were isolated or in which materials were identified by specific tests. The tendency of unreacted pyridine homologs to destroy some of the more reactive compounds made the isolation of derivatives of these compounds difficult. The following experimental work is arranged according to the products of ozonolysis in order to interrelate these products and the structures of the pyridine homologs.

Formic and Acetic Acid.—An ozonized solution of each pyridine homolog was extracted with 15 cc. of water, and the aqueous layer was acidified with dilute sulfuric acid and mildly heated with 1 g. of 2,4-dinitrophenylhydrazine to convert pyruvic acid to the phenylhydrazone; otherwise, the pyruvic acid interfered with the acetate test. The mixture was cooled, filtered and distilled until 8 cc. of distillate was collected. One 3-cc. portion of the distillate was treated with magnesium, sulfuric acid and chromotropic acid as described by Eegriwe.[8] The appearance of a violet coloration indicates the presence of formic acid.

Another 3-cc. portion was treated with 2% iodine, 5% lanthanum nitrate, and ammonium hydroxide as described by Kruger and Tschirch.[9] A blue precipitate is obtained with acetic acid but not with formic acid. Other aliphatic acids also give this test.

Application of these testing procedures to ozonized solutions of pyridine, 2-, 3- and 4-picoline, and 2,6-lutidine in cyclohexane[10] and to 2,4,6-collidine in chloroform gave the results listed in Table I for formic and acetic acid.

The insoluble layer and the cyclohexane layer of an ozonized cyclohexane solution of 3-picoline were separated and tested for formic and acetic acid. A deep violet coloration was obtained only with the insoluble layer in testing for formic acid whereas neither layer gave the characteristic blue coloration in the acetate test.

Pyruvic Acid: Isolation of Derivatives.—An ozonized solution of 2,4,6-collidine in chloroform was treated with 20 cc. of 50% acetic acid containing 4 g. of phenylhydrazine. After standing for several minutes, the mixture was diluted with water and heated to remove the chloroform. The viscous, orange liquid which separated was extracted with ether, and the portion insoluble in ether or dilute acetic acid was removed by filtration. The ether solution was evaporated to dryness, and the residue was recrystallized from benzene to obtain 0.52 g. of yellow-brown, needle crystals, m. p. 171–172° with gas evolution. This product is evidently identical with the pyruvic acid phenylhydrazone obtained by Fischer and Jourdan,[11] but not with the isomeric form, m. p. 192°, which is usually obtained.

Anal. Calcd. for $C_9H_{10}O_2N_2$: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.91; H, 5.93; N, 15.74.

With this indication of the presence of pyruvic acid in the ozonolysis products of methyl substituted pyridine homologs, the following procedure was used for the isolation of the 2,4-dinitrophenylhydrazone For example, an ozonized solution of 2,4,6-collidine in chloroform was extracted with 15 cc. of water, and the aqueous layer was treated with 1 g. of 2,4-dinitrophenylhydrazine, 10 cc. of ethanol and 10 cc. of dilute hydrochloric acid. The mixture was heated, cooled and filtered. The insoluble material was washed with hot dilute hydrochloric acid and digested with 5% sodium bicarbonate. The filtrate from the digestion was cooled and acidified with hydrochloric acid to obtain a

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(4) Shive, Roberts, Mahan and Bailey, THIS JOURNAL, **64**, 909 (1942).

(5) Lochte, Crouch and Thomas, *ibid.*, **64**, 2753 (1942).

(6) Schenck and Bailey, *ibid.*, **62**, 1967 (1940).

(7) Lidstone, *J. Chem. Soc.*, 241 (1940).

(8) Eegriwe, *Z. anal. Chem.*, **110**, 22 (1937).

(9) Kruger and Tschirch, *Ber.*, **63**, 826 (1930).

(10) Durland and Adkins, THIS JOURNAL, **61**, 429 (1939), reported the formation of cyclohexanone, formic acid and adipic acid on ozonization of cyclohexane. We have been unable to identify formic acid among the ozonolysis products of cyclohexane, and the other two products did not seriously interfere with our experiments.

(11) Fischer and Jourdan, *Ber.*, **16**, 2241 (1883).

TABLE I

COMPOUNDS[a] IDENTIFIED IN THE OZONOLYSIS PRODUCTS OF PYRIDINE HOMOLOGS

Homolog	Formic acid	Acetic acid	Pyruvic acid: Before hydrolysis (cyclohexane layer)	Pyruvic acid: After hydrolysis (insoluble cyclohexane)	Pyruvaldehyde	Glyoxal	Glyoxylic acid
Pyridine	+	−	−	−	−	+[b]	+
2-Picoline	+	+	−	+[b]	+(?)[c]	+[b]	+
3-Picoline	+	−[d]	+[b]	−	+[b]	+(?)[c]	+
4-Picoline	+	−[d]	+[b]	−	+[b]	+[b]	
2,6-Lutidine	−	+	−	+[b]	+[b]	+[b]	
2,4,6-Collidine	−	+	+[b]	+[b]	+[b]	−	

[a] Compounds not listed in table are diacetyl, a derivative of which was isolated from the ozonolysis products of 2-*s*-butyl-4,5-dimethylpyridine, oxalic acid, identified in the ozonolysis products of 2- and 3-picoline (only compounds tested), and nitric acid and carbon dioxide from the ozonolysis of all pyridine homologs. + or − indicated a positive or negative interpretation of specific test as to presence of the compound in the ozonolysis products. [b] Confirmed by isolation and identification of a derivative. [c] Attempts to isolate derivatives failed; the specificity of the test is to be questioned. [d] Separate experiments with ozonization of freshly distilled pyruvic acid in pyridine and cyclohexane gave positive tests for acetic acid; hence, the sensitivity of the test to indicate very small amounts of acetic acid in such mixtures is in doubt.

bright yellow substance which was recrystallized from ethanol, m. p. 214–216°. A mixed melting point with a known sample of pyruvic acid 2,4-dinitrophenylhydrazone also melted at 214–216°. This method applied to 2-picoline ozonized in chloroform and to 3- and 4-picoline ozonized in cyclohexane gave similar results. By a similar method, an ozonized cyclohexane solution of 2,6-lutidine was extracted with water, acidified with dilute sulfuric acid and distilled to half-volume. The distillate was treated with 2,4-dinitrophenylhydrazine to obtain pyruvic acid 2,4-dinitrophenylhydrazone.

Tests.—The insoluble layer from an ozonized cyclohexane solution of each pyridine homolog was separated, washed with cyclohexane, and dissolved in 15 cc. of water. After treating 2 cc. of this solution with a few drops of 10% sodium nitroprusside and 3 cc. of concentrated ammonium hydroxide, only yellow colorations developed. A green to blue-green coloration is obtained with pyruvic acid,[12] depending on the concentration. On addition of 5 drops of concentrated sulfuric acid and heating to 60° for ten minutes before testing with nitroprusside and ammonia, the results listed in Table I were obtained. Glyoxal in concentrations greater than 1 drop of 30% glyoxal in 2 cc. of 0.25 *N* pyruvic acid inhibited completely the pyruvic acid test; only a deep red color was obtained. Thus the results obtained above were checked by distilling to half-volume an aqueous extract of ozonolysis products acidified with dilute sulfuric acid and testing the distillate for pyruvate. Deep blue-violet colorations were obtained with 2-picoline, 2,6-lutidine and 2,4,6-collidine, but not with other homologs.

The cyclohexane layer from the ozonolysis of each pyridine homolog was extracted with 10 cc. of 5% sodium hydroxide. The extract was acidified with sulfuric acid, and the test for pyruvic acid applied to 2 cc. of this acidified extract. The results are listed in Table I.

Pyruvaldehyde: Isolation of Derivatives.—An ozonized chloroform solution of 2,4,6-collidine was treated with 20 cc. of water, and the solvent was removed under reduced pressure. The aqueous layer was treated with 1 g. of 2,4-dinitrophenylhydrazine, 10 cc. of ethanol and 10 cc. of dilute hydrochloric acid. The mixture was heated to boiling, cooled and filtered. The insoluble material was washed with hot dilute hydrochloric acid and then with 5% sodium bicarbonate solution to remove the pyruvic acid derivative. The insoluble residue was again washed with dilute hydrochloric acid and then with ethanol. The portion soluble in nitrobenzene was recrystallized from that solvent to form red-orange crystals which became discolored on heating to 290° and melted with decomposition at 299–300°. A mixed melting point with a known sample of pyruvaldehyde 2,4-dinitrophenylosazone showed no depression.

The same derivative was isolated and identified in a similar manner from ozonized cyclohexane solutions of 3-picoline and 2,6-lutidine. 4-Picoline gave similar results, but the procedure was altered in that the aqueous solution prepared from the ozonized cyclohexane solution of the base was distilled under reduced pressure in the presence of sulfuric acid, and the distillate was treated with 2,4-dinitrophenylhydrazine as described above.

Tests.—All attempts to obtain pyruvaldehyde as the 2,4-dinitrophenylosazone or the *m*-nitrobenzoylosazone from an ozonized solution of 2-picoline in chloroform failed. However, the following test indicated that pyruvaldehyde was present: Addition of 1 cc. of 20% sodium bisulfite to 0.5 cc. of an ozonized chloroform solution of 2-picoline was followed by solvent removal on the steam cone. The mixture was acidified with 3 cc. of concentrated hydrochloric acid, heated on the steam cone to remove the sulfur dioxide and then cooled. After adding 0.5 cc. of freshly prepared 0.1% α-methylindole, the test solution was then allowed to stand for two hours at room temperature. A violet coloration developed which has been described as a test for pyruvaldehyde.[13] Application of this test to other pyridine homologs gave the results listed in Table I. However, pyruvic acid interferes to some extent with this test so that the presence of pyruvaldehyde in the products from 2-picoline was doubtful.

Glyoxal: Isolation of Derivatives.—Ozonization of pyridine in cyclohexane gave an insoluble layer which was treated with 4 g. of phenylhydrazine in 25 cc. of ethanol. On warming the mixture for a few minutes and cooling, light yellow crystals, m. p. 176–178° with decomposition, were obtained. A mixed melting point with an authentic sample of glyoxal phenylosazone showed no depression.

Isolation of derivatives of glyoxal from the corresponding derivatives of other carbonyl compounds formed during the ozonolysis of pyridine homologs was facilitated by the low solubility of some glyoxal derivatives in nitrobenzene. For example, after addition of 20 cc. of water to an ozonized solution of 2-picoline in chloroform, the chloroform was removed under reduced pressure. The aqueous solution was heated with 1 g. of 2,4-dinitrophenylhydrazine and 5 cc. of concentrated hydrochloric acid. The precipitate, obtained on cooling, was digested with hot nitrobenzene to obtain red crystals, m. p. 329–331° with decomposition. A mixed melting point with a known sample of glyoxal 2,4-dinitrophenylosazone showed no depression.

Also, an aqueous extract of an ozonized solution of 4-picoline in cyclohexane was acidified with dilute sulfuric acid and warmed with 0.5 g. of *m*-nitrobenzhydrazide. A precipitate, obtained on cooling, was washed with hot ethanol, cold dilute sodium bicarbonate, and again with ethanol, and then digested with nitrobenzene to obtain a colorless, insoluble substance, m. p. 339–341° with de-

(12) Simon, *Compt. rend.*, **125**, 534 (1897).

(13) Dische and Robbins, *Biochem. Z.*, **271**, 304 (1934).

composition. A mixed melting point with glyoxal *m*-nitrobenzoylosazone showed no depression.

Similarly, an ozonized solution of 2,6-lutidine in chloroform was treated with 15 cc. of water, and the chloroform was then removed under reduced pressure. Treatment of the aqueous solution in the manner described above resulted in the isolation of glyoxal *m*-nitrobenzoylosazone.

Attempts to isolate either the *m*-nitrobenzoylosazone or the 2,4-dinitrophenylosazone of glyoxal from an ozonized cyclohexane solution of 3-picoline by the procedures employed above were not successful. However, the following test indicated the presence of glyoxal in the ozonolysis products of 3-picoline.

Tests.—3-Picoline was ozonized in chloroform. After removal of the solvent by heating 0.5 cc. of the ozonized solution with 0.5 cc. of water on the steam cone, the mixture was treated with 3 cc. of concentrated hydrochloric acid and 1 mg. of resorcinol, heated for several minutes on the steam cone, cooled, and made alkaline with sodium hydroxide. The blue color which was formed in the acidic solution and the intense blue-violet in alkaline solution has been described as a test for glyoxal.[14] Application of this test to other homologs gave the results listed in Table I. However, it is possible that other products interfere with this test as consistent results were difficult to obtain; hence, the presence of glyoxal in the products of hydrolysis of the ozonized solution of 3-picoline was doubtful.

Glyoxylic Acid.—Pyridine hydrochloride, prepared by passing dry hydrogen chloride through pyridine, was ozonized in chloroform. After the chloroform was removed under reduced pressure, the residue was dissolved in 15 cc. of water. A few drops of the aqueous solution were added to 1 cc. of 1% pyrogallol in concentrated sulfuric acid. On heating to 80° on a water-bath, the blue coloration which developed has been described as indicating the presence of glyoxylic acid.[15] The same results were obtained with 2- and 3-picoline, the only other bases treated in this way.

All attempts to isolate glyoxylic acid as the phenylhydrazone from the ozonolysis products of pyridine hydrochloride failed. However, a small amount of a barium salt was isolated by treating the ozonolysis products prepared as described above with barium hydroxide and pyridine. The precipitated salts were recrystallized from dilute ethanol. The second crop of crystals gave the test for glyoxylic acid as described above whereas the first crop did not. The barium glyoxylate crystals were treated with phenylhydrazine in dilute acetic acid to obtain light yellow crystals in amounts insufficient for purification and identification.

Oxalic Acid.—An ozonized chloroform solution of 2-picoline was extracted with 10 cc. of 2% sodium hydroxide. The alkaline extract was acidified with acetic acid and treated with 10 cc. of 20% calcium chloride. On standing and centrifuging, a small amount of a colorless precipitate was obtained which was then washed with ethanol. This dried material was heated with 0.5 cc. of 85% phosphoric acid containing a little diphenylamine and added to alcohol as described by Feigl and Frehden.[16] A brilliant blue color appeared and after extracting with ether and allowing the mixture to stand, a blue-violet layer separated. This has been described as a specific test for oxalic acid. This procedure applied to 3-picoline, the only other homolog tested in this manner, gave identical results.

Diacetyl.—An ozonized solution of 3 g. of 2-*s*-butyl-4,5-dimethylpyridine in 20 cc. of chloroform was distilled to approximately one-third of the original volume. The distillate was treated with 2 cc. of 50% acetic acid and 1 g. of phenylhydrazine, heated on a steam cone to remove the chloroform, diluted with water and filtered to obtain yellow crystals which melted at 239–241° after recrystallization from alcohol. A mixed melting point with an authentic sample of diacetyl phenylosazone showed no depression.

Nitric Acid.—The insoluble layer of an ozonized cyclohexane solution of 2,4,6-collidine was removed, and the crystalline portion was separated from the oily material. Recrystallization of the solid substance from a mixture of ethyl acetate and acetone gave white needles (15 mg.) of 2,4,6-collidine nitrate which sublimed with decomposition at 197–198.5°.

Anal. Calcd. for $C_8H_{12}N_2O_3$: N, 15.21; mol. wt., 184. Found: N, 15.00; neut. equiv., 189.

The product was further identified by conversion to the picrate, m. p. 157–157.5°, in the usual manner. A mixed melting point with an authentic sample of 2,4,6-collidine picrate showed no depression.

In order to determine if nitrogen as an impurity caused the formation of nitrate, 2,4,6-collidine was ozonized in cyclohexane with electrolytic oxygen. The insoluble layer resulting from the ozonolysis was dissolved in water. A few drops of this solution was treated with a drop of a solution of 1 mg. of diphenylamine in 10 cc. of concentrated sulfuric acid. A deep blue color developed indicating the presence of nitrate.[17] Ozonized water or cyclohexane did not give this nitrate test.

All the pyridine homologs gave similar results, a deep blue coloration indicating the presence of nitrates.

Hydrochlorides from Ozonization in Chloroform.—An ozonized chloroform solution of 2,4,6-collidine was distilled to half volume, and 15 cc. of benzene was added. On evaporation of the mixture to 15 cc. and cooling, colorless needles separated which, on recrystallization from a mixture of chloroform and benzene, sublimed without melting above 225°. This material apparently was 2,4,6-collidine hydrochloride as the material gave a positive test for chloride.

Anal. Calcd. for $C_8H_{12}NCl$: C, 60.95; H, 7.67. Found: C, 60.57; H, 7.49.

Similarly, hygroscopic white crystals which gave a chloride test were isolated from an ozonized chloroform solution of 2,6-lutidine. The 2,6-lutidine hydrochloride thus isolated was identified by conversion to the picrate, m. p. 164.0–165.5°, in the usual manner. A mixed melting point with a known sample showed no depression.

Carbon Dioxide.—The gases from the ozonization of each base were passed through a saturated solution of barium hydroxide. A white precipitate, insoluble in water, was formed. Solution of the material was effected in dilute hydrochloric acid with effervescence of a gas which, on passing through a saturated solution of barium hydroxide, caused again the precipitation of barium carbonate. Larger amounts of barium carbonate were obtained with pyridine and 2-, 3- and 4-picoline than with either 2,6-lutidine or 2,4,6-collidine.

Discussion

In view of these results, we propose the following generalizations concerning the ozonolysis of pyridine homologs. On ozonization, pyridine homologs form mainly diozonides as would be expected since the rate of reaction of ozone is much greater with a carbon to carbon than with a carbon to nitrogen double bond.[18] Asymmetrically substituted pyridines because of resonance give rise to two different diozonides. However, these diozonides of pyridine homologs decompose during the ozonization forming the products of ozonolysis and precluding the possibility of isolating the diozonides as such.

For simplification in discussing the fate of pyridine homologs on ozonolysis, the molecule can be considered in two parts, one containing the

(14) Tommile, *Acta Chem. Fennica*, **7B**, 85 (1934); *C. A.*, **28**, 4008 (1934).

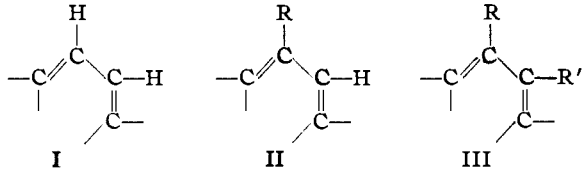
(15) Fearon, *Biochem. J.*, **14**, 548 (1920).

(16) Feigl and Frehden, *Microchemie*, **18**, 272 (1935).

(17) Feigl, "Qualitative Analysis by Spot Tests," Nordemann Publishing Co., Inc., New York, 1937, p. 199.

(18) Meisenheimer, *Ber.*, **54**, 3206 (1921).

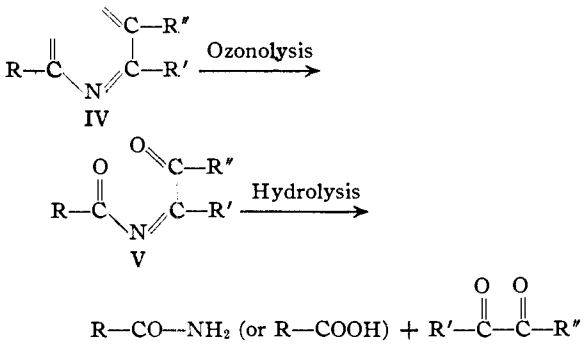
nitrogen atom and the other which is cleaved from it by the decomposition of the unstable diozonide. For the latter part of the molecule, there are three possible types of groupings as follows



I II III

The decomposition of unstable ozonides of pyridine homologs results in the formation of glyoxal, oxalic acid, and probably glyoxylic acid from compounds containing the structural unit I, R—CO—CHO and R—CO—COOH from compounds with II, and R—CO—CO—R′ from those containing III. The formation of product of the type R—CO—COOH could be explained by the decomposition of unstable ozonides directly from the "molozonide" as suggested by Staudinger[19]; however, another mechanism equally effective in explaining the results must be considered in which the nitrogen atom, an electron donor, may accept an oxygen atom, thus decomposing the ozonide and serving as an oxygen carrier in that this complex may then be the oxidizing agent.

The nitrogen containing portion of pyridine homologs can be represented as undergoing the following conversion during ozonolysis and hydrolysis



$$R—CO—NH_2 \text{ (or } R—COOH) + R'—\overset{O}{\overset{\|}{C}}—\overset{O}{\overset{\|}{C}}—R''$$

When R″ is a hydrogen atom, ozonolysis forms two compounds of type V where R″—CO— is replaced by —CHO and —COOH groups. This appears to be true also when R is a hydrogen atom, but whether R′ is hydrogen or alkyl does not appear to alter the reaction.

The nitrogen containing complex V which was formed during ozonization of lower pyridine homologs was usually a relatively stable complex, insoluble in cyclohexane but somewhat soluble in chloroform, which hydrolyzed slowly on standing in dilute acid or alkali. Although ozonization in cyclohexane formed an insoluble layer of complex composition in all cases, the nitrogen containing cleavage product separated practically completely in this layer; hence, cleavage products somewhat soluble in cyclohexane, such as pyruvic acid, can be separated in this manner from the nitrogen containing moiety. All attempts to isolate a nitrogen containing cleavage product failed but resulted in the isolation of such compounds as the nitrate and hydrochloride of the pyridine homolog.

The insoluble layer formed in cyclohexane by ozonization of 2-picoline, 2,6-lutidine and 2,4,6-collidine gave a test for pyruvic acid on hydrolysis whereas that of pyridine and 3- and 4-picoline did not form this acid on hydrolysis; however, the cyclohexane layer from ozonization of 3- and 4-picoline and 2,4,6-collidine contained pyruvic acid whereas that of pyridine, 2-picoline, and 2,6-lutidine did not give a test for that acid. Thus, the complex, $CH_3—C(COOH)=N—C=O$, formed on ozonolysis of α-methyl-β-unsubstituted pyridine homologs was insoluble in cyclohexane and gave the pyruvic acid test only after hydrolysis. On the other hand, the group, $—C=CH—C(CH_3)=C—$, was cleaved during ozonization forming pyruvic acid which appeared in the cyclohexane layer.

Treatment of ozonolysis products of 3- and 4-picoline, 2,6-lutidine and 2,4,6-collidine with 2,4-dinitrophenylhydrazine gave in all cases pyruvaldehyde 2,4-dinitrophenylosazone. The amount of this material obtained from 4-picoline was very small. Pyruvaldehyde was not isolated from the ozonolysis products of 2-picoline; however, a test indicated that it might have been present at least in small amounts.

By formation and isolation of derivatives in a similar manner, glyoxal was obtained from the ozonolysis products of pyridine, 2- and 4-picoline, and 2,6-lutidine. The amount of glyoxal derivative isolated from the products of 2,6-lutidine was very small, and no glyoxal derivative was isolated from ozonolysis products of 3-picoline; the major portion of the glyoxal forming groups in 3-picoline was probably converted into glyoxylic acid and oxalic acid since tests indicated the presence of these compounds in the ozonolysis products. However, spot tests indicated the presence of traces of glyoxal. Ozonolysis products of both 2-picoline and pyridine gave spot tests for glyoxylic acid. The products of the former compound were tested for oxalic acid which was present in appreciable amounts.

The ozonization of *dl*-2-*s*-butyl-4,5-dimethylpyridine in chloroform, distillation of two-thirds of the solvent, and isolation of diacetyl as the phenylosazone from the distillate revealed that the products of ozonolysis were formed from an unstable ozonide and that 3,4- or 4,5-disubstituted pyridine homologs may be expected to form compounds of the type R—CO—CO—R′.

Formic acid was identified among the com-

(19) Staudinger, *Ber.*, **58**, 1088 (1925); Long, *Chem. Rev.*, **27**, 437 (1940).

pounds formed on hydrolysis of the ozonolysis products of pyridine, 2-, 3- and 4-picoline, but it was not identified among the compounds similarly obtained from 2,6-lutidine and 2,4,6-collidine; hence, formic acid arises only from pyridine homologs with unsubstituted α-positions. Acetic acid was identified among the substances formed by hydrolysis of the materials produced on ozonization of 2-picoline, 2,6-lutidine and 2,4,6-collidine but was not identified among the products obtained in a similar manner from pyridine and 3- and 4-picoline. Since pyruvic acid was found to be a product of ozonolysis of 3- and 4-picoline and since a freshly distilled sample of pyruvic acid was found to form on ozonization in cyclohexane and pyridine sufficient acetic acid for identification, it is possible that small amounts of acetic acid insufficient for identification by the testing procedure may have formed. However, in general it may be said that relatively large yields of acetic acid may arise from only α-methyl substituted pyridine homologs.

The formation of nitric acid and carbon dioxide during ozonization of pyridine homologs indicated that the degradation proceeded further than indicated by the equations given above. The nitric acid could have been formed by ozonolysis of the carbon to nitrogen double bond, and since evolution of carbon dioxide from the reaction mixture during ozonization was greater when pyridine homologs containing unsubstituted α-positions were employed, the formation of the type of grouping, H—O—CO—N=C=, might have accounted through decarboxylation for the abundance of carbon dioxide which was formed.

As a method of structural elucidation, the usefulness of ozonolysis is shown by Table II which lists products which indicate certain structural groupings in pyridine homologs.

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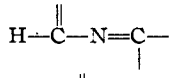
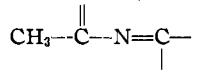
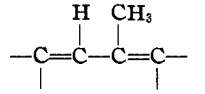
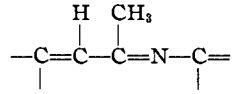
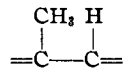
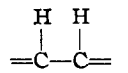
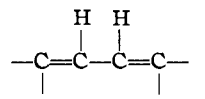
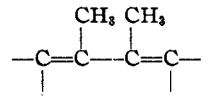
TABLE II

CORRELATION OF OZONOLYSIS PRODUCTS WITH STRUCTURAL UNITS

Product	Treatment of ozonolysis mixture to form products	Structural unit indicated
Formic acid	Hydrolysis	
Acetic acid	Hydrolysis	
Pyruvic acid	Before hydrolysis (in cyclohexane layer)	
	After hydrolysis (usually cyclohexane insoluble layer)	
Pyruvaldehyde	Treated with derivative reagent	
Glyoxal	Treated with derivative reagent	
Oxalic acid	None	
Diacetyl	Solvent distilled and tested	

Summary

1. Seven pyridine homologs have been ozonized, and products formed by ozonolysis followed in some cases by hydrolysis have been identified either by means of spot tests or by actual isolation of the product or a derivative.

2. Some proposals concerning the mechanism of ozonolysis of pyridine homologs have been made.

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