[Contribution from the Chemical Laboratory of Northwestern University]

THE OZONIZATION OF TRIPLE BONDS

CHARLES D. HURD and ROBERT E. CHRIST

In 1907, Molinari[1] stated that aliphatic compounds add one molecule of ozone quantitatively for each double bond, while compounds with triple bonds in general added no ozone. This generalization was severely criticized by Harries,[2] but Molinari[3] maintained his stand. The discussion brought out the fact that ozonized air, giving rise to less than 1% of ozone in the gas stream, was important in Molinari's procedure. With ozonized oxygen, Harries was able to add ozone to the triple bonds of such compounds as stearolic or phenylpropiolic acids.

Acetylene itself reacts[4] with ozone. Formic acid is one of the products. That glyoxal is the other major product is interesting, for it demonstrates non-cleavage during ozonization, but this is apparently the only case of its kind on record. The rate of absorption of ozone by 1-heptyne has been studied,[5] but without attention to the nature of the products of ozonolysis. Recently, ozonization has been employed[6] to prove the positions of the triple bonds in 6,10-hexadecadiyne, and in 6,9-pentadecadiyne. Caproic and succinic acids were formed from the latter; caproic and malonic acids from the former.

The quantitative extent of ozonization has been practically disregarded in the above work. The present work was undertaken to obtain evidence on this point and to test the generality of ozonolysis of acetylenes. Ozone concentrations of 5% and 10% were employed. The solvent used was carbon tetrachloride. Six compounds were included: phenylpropiolic acid, 1-ethynyl-1-cyclohexanol, 1-hexyne, 1-heptyne, phenylacetylene and ethynylfenchyl alcohol. In all cases, reaction with ozone occurred. Acids were formed as predicted, in percentage yields, respectively, of 42, 52, 51,

[1] Molinari, *Ber.*, **40**, 454 (1907).

[2] Harries, *ibid.*, **40**, 4905 (1907); **41**, 1227 (1908).

[3] Molinari, *ibid.*, **41**, 585, 2782 (1908).

[4] Wohl and Braunig, *Chem.-Ztg.*, **44**, 157 (1920); Briner and Wunenburger, *Helv. Chim. Acta*, **12**, 786 (1929).

[5] Brus and Peyresblanques, *Compt. rend.*, **190**, 685 (1930).

[6] Lai, *Bull. soc. chim.*, **53**, 1537, 1543 (1933).

59, 59 and 61. It is significant that the ozonolysis never gave rise to a quantitative yield of acids even though an excess of ozone was employed.

Regarding the structures of the acetylene ozonides, formulæ I, II, III, which are analogous to formulæ IV, V, VI for olefin ozonides, should be


I   II   III
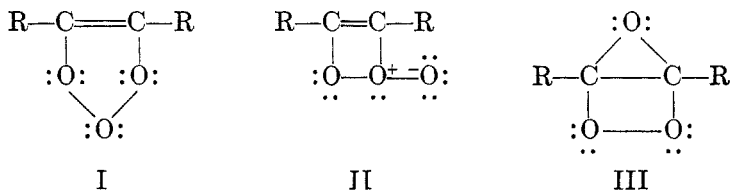
considered. Formula IV is the conventional formula of Harries, whereas V and VI are supported by Staudinger,[7] V being the unstable form which

IV   V   VI
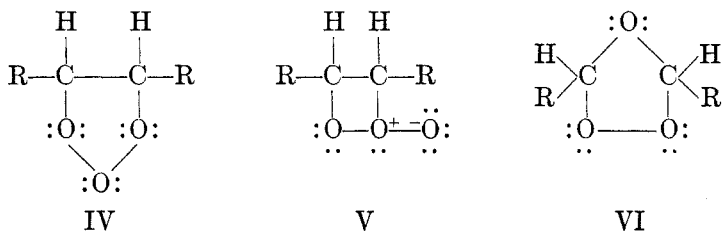
is considered to rearrange into the stable, hydrolyzable "isozonide," VI.

All of the various formulæ lend themselves satisfactorily to the interpretation of the evidence of hydrolysis. All three forms (I, II, III) would give rise to acids (RCOOH) on hydrolysis, *via* α-diketones (RCOCOR, or glyoxals if R = H) and hydrogen peroxide. The following equations may be used to illustrate the formation of glyoxal from acetylene ozonide by each of the formulæ in question.
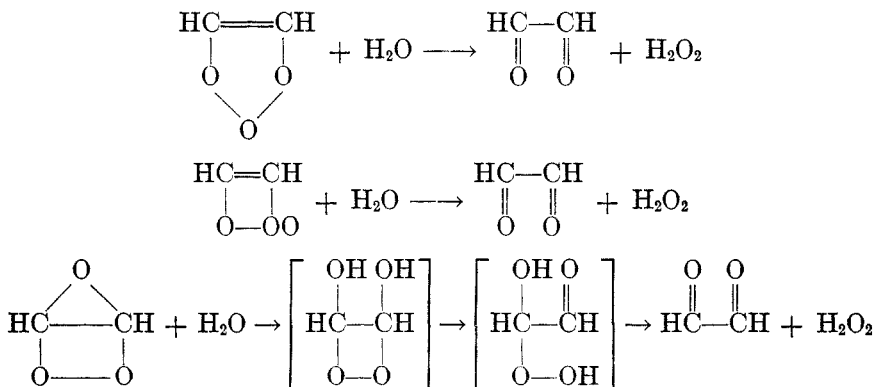
[7] STAUDINGER, *Ber.*, **58**, 1088 (1925); RIECHE, "Alkylperoxide und Ozonide." Theo. Steinkopff, Dresden and Leipzig, **1931**, pp. 133, 155.

In all cases, the subsequent reaction is: $HCOCHO + HOOH \rightarrow 2HCOOH$. Hence the present evidence cannot be used to decide between the various possibilities. As Rieche points out, however, the evidence for V is better than that for IV. On this basis, II is preferred as the structure for the initial addition product of ozone to the acetylene.

EXPERIMENTAL

Materials.—1-Ethynyl-1-cyclohexanol was prepared according to the directions of Rupe, Messner and Kambli, as modified by Hurd and Jones.[8] The directions for the synthesis of ethynylfenchyl alcohol will be presented in another paper. The phenylacetylene was redistilled before use; b.p., 139°. The phenylpropiolic acid (m.p., 136°) was synthesized from pure phenylacetylene. Modifications of the method of Lebeau and Picon[9] were adopted for the preparation of 1-hexyne and 1-heptyne. Alkyl bromides were used instead of alkyl iodides. After considerable preliminary experimentation, the following conditions were developed for a large-scale run, and for hexyne of high purity.

1-Hexyne.—A 5-l. three-necked, round-bottomed flask, fitted with a mercury-sealed stirrer, an inlet tube reaching to the bottom of the flask, and an exit tube of large bore leading into a hood, was immersed in a crock wrapped with one layer of 6-mm. asbestos paper and cooled with a mixture of "dry ice" (1.4 kg.) and acetone. The air in the flask was replaced by hydrogen, after which 161 g. (7 moles) of sliced sodium was inserted. Ammonia was then condensed in the flask with constant stirring until it was three-fourths full. A current of acetylene was then passed in until the blue color (sodium) had disappeared. A dropping funnel was inserted in place of the inlet tube and 959 g. (7 moles) of *n*-butyl bromide was run in slowly.

The flask was then allowed to warm up to room temperature over a period of six hours, to permit the ammonia to distill off slowly. Enough water was then added to dissolve the sodium bromide, with care to allow for the heating effect caused by any unused sodamide. The insoluble layer was separated, washed with dilute sulfuric acid and dried over calcium chloride. After this, it was carefully fractionated through a Davis column. A 406-g. fraction boiling at 71–72° was collected. Analysis of this material by the method of Hill and Tyson[10] gave corrected values for 1-hexyne of 93.4 and 94.2%. This corresponds to a 64% yield of pure 1-hexyne.

Purification.—Some of the hexyne was treated with alcoholic silver nitrate. The precipitate was collected, washed with alcohol, and dried. Thirty-nine grams of this salt ($C_4H_9C \equiv CAg \cdot AgNO_3$) was mixed in a distilling flask with 39 g. of ammonium thiocyanate and 200 cc. of water. 1-Hexyne was liberated on distillation. This was separated, washed with dilute sulfuric acid, dried over calcium chloride, and distilled. The yield was 3.9 g. (40%) but the loss was largely mechanical. In larger duplicate runs, a total of 60 g. of pure 1-hexyne was collected; b.p., 71°; n_D^{19}, 1.400. Analysis as before gave uncorrected values of 97.0 and 97.4%. Since this was pure 1-hexyne, a correction factor of 2.8% was placed on the analytical method, this factor being applied on the first analysis of the crude hexyne. The pure hexyne was taken for ozonolysis.

1-Heptyne.—The general procedure was the same as that given for hexyne, except that a mixture of about equal parts of *n*-pentyl bromide and *n*-pentyl chloride was

[8] HURD AND JONES, *J. Am. Chem. Soc.*, **56**, 1924 (1934).

[9] LEBEAU AND PICON, *Compt. rend.*, **156**, 1077 (1913); PICON, *ibid.*, **169**, 32 (1919).

[10] HILL AND TYSON, *J. Am. Chem. Soc.*, **50**, 172 (1928).

used, rather than the bromide alone. The crude heptyne fraction contained only 33% of 1-heptyne by analysis. The purification by silver nitrate gave pure 1-heptyne which, as with the pure hexyne, required the correction factor in the analysis. The uncorrected analytical value was 98%. A total of 82 g. of this pure 1-heptyne was obtained; b.p., 98.5°; n_D^{20} 1.417.

General Method of Ozonization.—An ozonizer of the Henne[11] type was used. A stream of dry oxygen was employed. The ozone concentration in the ozonized gas was determined by the potassium iodide method of Smith[12]; *e.g.*, with a rate of flow of 4.7 l. per hour, the O_3-concentration was 8–10%. In general, from 1 to 4 g. of the acetylene to be ozonized was dissolved in dry carbon tetrachloride (50–80 cc.) and the solution was kept ice-cold during the ozonization. A considerable excess of ozone was employed in all cases. The excess became apparent when the solution assumed a faint blue color.

To hydrolyze the ozonides, it was only necessary to add water (75–100 cc.) and distill from a steam bath. The distillate (of carbon tetrachloride) was shaken with water and titrated with standard alkali to determine the small amount of acids which distilled also. In most cases this figure was almost negligible, but it was

TABLE I

DATA CONCERNING OZONIZATIONS

SUBSTANCE		CCl₄ cc.	OZONE		NaOH CONSUMED BY ACIDS FORMED		YIELD OF ACIDS, %
Name	g.		Vol., l.	Concn. %	cc.	Normality	
Phenylpropiolic Acid	4.00	80	223	5	85.30	0.4096	42.4
Phenylacetylene	2.00	80	95.2	5	56.40	0.4096	59.1
1-Hexyne	1.07	60	67.6	5	32.20	0.4170	51.1
1-Heptyne	1.84	100	31.8	5	207.5	0.1089	59.4
Ethynylcyclohexanol	2.00	85	93.5	9	41.00	0.4096	52.2
Ethynylfenchyl alcohol	3.00	75	113	9	50.20	0.4096	61.3

included in the total amount of acids formed. In the cases of the ozonides of hexyne and heptyne the solvent was distilled off before adding the water. In all cases, the aqueous solutions were titrated to determine the acid content. The details of characteristic experiments are collected in Table I.

Indentification of acids from phenylpropiolic acid (A), phenylacetylene (B), ethynylcyclohexanol (C), and ethynylfenchyl alcohol (D).—After titration of the acids, the neutral solutions of the sodium salts were evaporated to small volume, treated with decolorizing charcoal, and extracted with ether to remove any organic impurities. Traces of ether were removed by further evaporation. Oxalic acid (from A) and formic acid (from B, C, D) were indicated by the decolorization of potassium permanganate solution by test portions. The remainder of the solution was acidified with sulfuric acid. Benzoic acid (from A) separated as a heavy white precipitate; m.p. and mixture m.p., 120°. The benzoic acid from B melted at 121° and weighed 1.22 g. When mixed with authentic benzoic acid, it melted also at 121°. After

[11] HENNE, *ibid.*, **51**, 2676 (1929).

[12] SMITH, *ibid.*, **47**, 1844 (1925).

acidification, the solution from C gradually yielded a small quantity of 1-hydroxy-1-cyclohexanecarboxylic acid. This, after recrystallization from alcohol, gave the correct[13] melting point of 106–107°. The acid produced from D, after two crystallizations from alcohol, appeared as white flakes which melted at 92°. That this was dl-α-fenchocarboxylic acid,[14] m.p. 92°, was confirmed by its neutralization equivalent of 195: 0.0840 g. required 3.80 cc. of 0.1132 N alkali for neutralization (calc'd neutral. equ., 198).

Identification of acids from 1-hexyne.—After hydrolysis of the ozonide, the volume of the aqueous solution was made up to 110 cc. and analyzed by the Duclaux method.[15] Exactly 10.0 cc. of the solution required 23.6 cc. of the alkali used. Of the remaining 100 cc., 30.0 cc. was distilled. It required 90.17 cc. of the same alkali. From these data, the percentage ratio of formic to valeric acids was 48.5:51.5, or about 1:1.

Identification of acids from 1-heptyne.—In this case, the solution of acids was neutralized and evaporated to dryness. One g. of the salts was dissolved in water and the formate content determined by permanganate titration. A total of 0.0048 equivalent, or 0.326 g. of sodium formate, was found. By difference, the weight of sodium caproate must have been 0.674 g. or 0.0049 equivalent. Here again, the ratio of 1:1 (0.0048:0.0049) was found.

The caproic acid was identified by treating the solution from the permanganate titration with sulfuric acid and distilling. The distillate, made up to 110 cc., was analyzed by the Duclaux method. The 10.0 cc. portion required 7.31 cc. of alkali. The first, second, and third 10-cc. portions of distillate (from the 100 cc., which represented 73.10 cc. of alkali) required 23.90, 16.80 and 13.20 cc. of the same alkali. Thus, the Duclaux values were 32.6, 23.0 and 18.2, which are those for caproic acid. Confirmatory evidence was obtained by evaporating this solution of sodium caproate to dryness and treating it with p-bromophenacyl bromide. The m.p. (and mixture m.p.) of the p-bromophenacyl caproate thus obtained was 71°.

SUMMARY

The ozonolysis of triple bonds has been studied with these six acetylene representatives: phenylpropiolic acid, phenylacetylene, 1-hexyne, 1-heptyne, ethynylcyclohexanol, ethynylfenchyl alcohol. With the ozone concentrations used, namely, 5 or 10%, ozonization was satisfactory in all cases. The acids which resulted from cleavage of the triple bonds were formed in 42–61% yields. Methods for the identification of these acids are given. Details are included for the synthesis of pure 1-hexyne in quantity.

[13] BUCHERER, *Ber.*, **27**, 1231 (1894).

[14] WALLACH, *Ann.*, **259**, 326 (1890).

[15] Calculated by method of VIRTANEN AND PULKKI, *J. Am. Chem. Soc.*, **50**, 3138 (1928).