One-tenth mole of α-alkylcinnamic acid dibromide (or the crude product obtained by adding one-tenth mole of bromine to one-tenth mole of α-alkylcinnamic acid in carbon tetrachloride and then evaporating the carbon tetrachloride with a current of air) was gradually added to a solution of 0.7 mole of potassium hydroxide in 100 cc. of alcohol. Sufficient heat was evolved to cause the mixture to boil. Most of the alcohol was then removed with the aid of a column. Water was added to the residue and the product steam distilled, the water in the distillate being returned to the boiler. The oil was separated and dried; yield of crude, about 70%. These acetylenes are colorless oils, lighter than water, with a "green-leaf" odor resembling methyl heptine carbonate.

**Acknowledgments.**—The authors are indebted to Mr. Richard O. Roblin, Jr., for the synthesis of butyl acetone, to the Florasynth Laboratories for a gift of benzaldehyde, to the Sharples Solvents Corp. for a gift of methyl propyl carbinol and especially to the American Manufacturers of Toilet Articles and the National Academy of Sciences for financial aid.

## Summary

Condensation of benzaldehyde with ethyl, *n*-propyl, *n*-butyl and *n*-amyl acetone yielded the corresponding methyl (α-alkyl-)-styryl ketones, which were converted into the α-alkylcinnamic acids by means of sodium hypochlorite. These acids, through their dibromides, were converted into the β-alkyl-β-bromostyrenes and the alkylphenylacetylenes.

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# THE OZONIDES OF ORTHO-XYLENE AND THE STRUCTURE OF THE BENZENE RING[1]

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RECEIVED SEPTEMBER 10, 1931 PUBLISHED JANUARY 7, 1932

## Introduction

The problem of the existence and the position of ethylenic linkages in benzene with the possibility of the existence of isomeric ortho-disubstitution products has been the subject of many interesting speculations ever since Kekulé[3] advanced his theory of the structure of the benzene nucleus. Some results have been published[4] which indicate the occurrence of such isomers.

Harries and his co-workers[5] have described osazone derivatives of the decomposition products of ozonides of benzene and mesitylene. It seemed

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[1] Presented before the Organic Division of the American Chemical Society at its 80th meeting in Cincinnati, 1930.

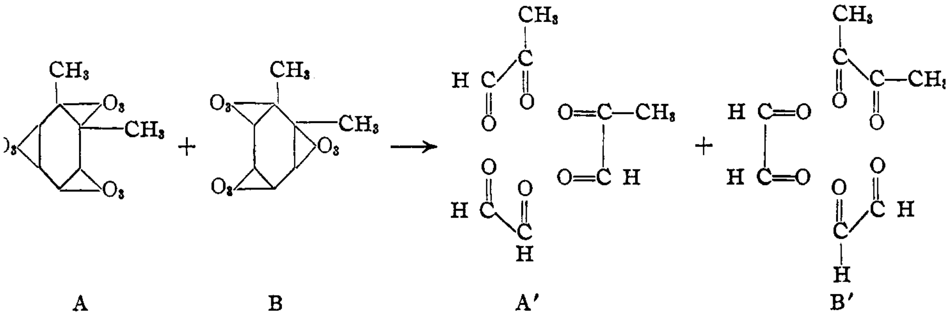
[2] Abstract of a thesis presented to the Graduate Faculty by A. G. Cole in partial fulfilment of the requirements for the degree of Master of Science.

[3] Kekulé, *Ann.*, **137**, 158 (1866).

[4] Borsche and Bahr, *ibid.*, **402**, 81 (1913); Hodgson, *Chem. Abstracts*, **21**, 572 (1927).

[5] Harries, "Ozone and seine Einwirkung," Julius Springer, Berlin, **1916**.

evident that similar results could be obtained by ozonizing *o*-xylene and obtaining derivatives of the decomposition products. Assuming that a conjugated arrangement of the double bonds in its nucleus does occur, *o*-xylene should, theoretically, be convertible into two ozonides because of the position of its two methyl groups. These two ozonides should produce three products upon decomposition with water, whereas, in the cases of benzene and mesitylene, only one decomposition product is possible in each case. The following scheme shows the two possible ozonides and their three decomposition products.



The same decomposition products would be possible if the two structures of *o*-xylene pictured above merely represented phases of some complex dynamic structure which may actually exist, since the process of ozonization would tend to stabilize these two phases. Accordingly *o*-xylene was subjected to the action of 15% ozone and a product obtained which when decomposed with water yielded derivatives of the above three decomposition products: glyoxal, methylglyoxal and dimethylglyoxal or diacetyl. Since these decomposition products are possible only in the event that two ozonides were previously formed, it follows that there were present in *o*-xylene, the above two structures or their equivalents.

The osazones and *p*-nitrophenylosazone derivatives of the above three decomposition products were all isolated, with the exception of methylglyoxal osazone, and identified by their melting points and mixed melting point determinations with authentic specimens. A small quantity of material which was apparently diacetyl was also isolated.

Various solvents for *o*-xylene were tried during ozonization. With petroleum ether, an insoluble product in the form of small transparent crystals was obtained. These were very explosive when removed from the ether. With acetic acid and acetic anhydride, a clear yellow solution was obtained which was decomposed by pouring onto cracked ice. Acetic anhydride was found to be the best solvent since it ensures an anhydrous medium and both itself and its hydrolysis product, acetic acid, are not acted upon by ozone.

Two methods for isolating the osazone derivatives of the decomposition products were employed. The first method was to treat the decomposition mixture with a solution of phenylhydrazine acetate or *p*-nitrophenylhydrazine hydrochloride and isolate the individual derivatives by a process of fractional crystallization. The second and most satisfactory method was roughly to separate the three decomposition products by steam distillation before the conversion into the above derivatives.

When the decomposition mixture of the ozonides was distilled and the first fourth of the distillate repeatedly distilled in the presence of 15% sulfuric acid, a small amount of a liquid was finally obtained which was apparently diacetyl.

## Experimental

All melting points given herein are uncorrected.

The ozonizing apparatus used for all experiments was essentially that described by Levine.[6] This apparatus gave a 15% concentration of ozone when oxygen was used.

The *o*-xylene used in the experiments was obtained from the Eastman Kodak Company. Its melting point was −28° and its boiling point 142 ± 0.1°.

**Ozonization of *o*-Xylene in Various Solvents.**—A solution of 3 g. of *o*-xylene in 15 g. of petroleum ether was cooled to −25 to −30° and ozone passed through for twenty-four hours. A transparent precipitate of fine crystals separated from the solution. It was explosive when removed from the solvent.

When acetic anhydride was used in place of petroleum ether, 3 g. of *o*-xylene was dissolved in 15 cc. of acetic anhydride, cooled to −30° and ozonized with 15% ozone for three to four hours. The acetic anhydride dissolves the ozonides of *o*-xylene and hence no precipitate was formed.

**Isolation of Glyoxal and Diacetyl Osazones.**—An acetic anhydride solution of *o*-xylene was ozonized as described above and the resulting product was decomposed by stirring it with crushed ice. The three decomposition products were roughly separated from each other by a process of fractional steam distillation. Upon distilling the water solution of these products, the first fraction, about one-fourth of the original volume, contained most of the diacetyl since this substance is very volatile with steam. Methylglyoxal, which is considerably less volatile with steam, was obtained in the second fraction, one-half the original volume. The non-volatile glyoxal remained in the residue.

When the first fraction was treated with phenylhydrazine acetate, a flocculent precipitate formed. By recrystallizing this material several times from benzene (or alcohol), clear yellow flakes were obtained which melted at 238–239°. The substance was identified as diacetyl osazone by a mixed melting point determination.

By treating the second fraction with phenylhydrazine acetate, a dark oil was formed from which it was impossible to isolate a crystalline product.

The residue upon similar treatment, gave a precipitate which recrystallized from benzene or alcohol in the form of yellow flaky crystals; m. p. 167–168°. The substance was identified by a mixed melting point determination.

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[6] Levine, *Northwest Science*, **3**, 19 (1929).

**Isolation of *p*-Nitrophenylosazones of Glyoxal, Methylglyoxal and Diacetyl.**—Two methods were employed in isolating these products. One method was to first roughly to separate the decomposition products of the ozonides by fractionally distilling the decomposition mixture as described above and then treating each of the three fractions obtained with *p*-nitrophenylhydrazine hydrochloride. The first portion of the distillate gave a substance which after recrystallization from nitrobenzene as fine red needle-shaped crystals, melted at 313°. Small dull red crystals purified by recrystallization from dimethylaniline and which melted at 284–285° were obtained from the second fraction. The residue which contained glyoxal in the polymerized form gave a precipitate with *p*-nitrophenylhydrazine hydrochloride which melted at 309–310° after the material was recrystallized from nitrobenzene as fine, red needle-shaped crystals. The first product was identified as diacetyl-*p*-nitrophenylosazone, the second as methylglyoxal-*p*-nitrophenylosazone and the last as glyoxal-*p*-nitrophenylosazone by mixed melting point determinations with authentic compounds.

A second method of isolation used was to treat the mixture of decomposition products with *p*-nitrophenylhydrazine hydrochloride directly and then to selectively dissolve from the dried precipitated material, one product at a time by the use of suitable solvents. By extracting the mixture of products with pyridine, diacetyl-*p*-nitrophenylosazone was roughly isolated since the other two products are comparatively insoluble in this solvent. It was purified by repeated crystallizations. The residue after this extraction was then extracted with dimethylaniline. From the dimethylaniline portion methylglyoxal-*p*-nitrophenylosazone was isolated. By recrystallizing the material remaining after these two extractions several times from benzene, the *p*-nitrophenylosazone of glyoxal was obtained. In each of these cases the substance was identified by the method used above.

**Isolation of Diacetyl as a Decomposition Product of the Ozonides.**—Distillation of the mixture obtained by decomposing the ozonized product with ice, then repeatedly distilling the first one-fourth of the distillate in the presence of 15% sulfuric acid, gave a small quantity of liquid which was apparently diacetyl. Although there was not sufficient material to permit of proper purification, its boiling point was within the range of that for diacetyl. .Its color, odor, miscibility with water and behavior during distillation from a water solution checked well with the corresponding properties of diacetyl.

## Summary

1. *o*-Xylene was ozonized in various solvents, acetic anhydride being found the most suitable.

From the mixture obtained by decomposing the ozonization products with ice, phenylhydrazine derivatives of glyoxal and diacetyl and *p*-nitrophenylhydrazine derivatives of glyoxal, methylglyoxal and diacetyl were isolated. A small quantity of a substance which was apparently diacetyl was likewise isolated.

2. Since three decomposition products were obtained it appears as if *o*-xylene exists in two isomeric configurations.

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