[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE OXIDATION OF "DI-ISOBUTYLENE" BY OZONE

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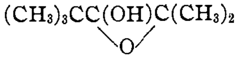
An octylene or a mixture of octylenes known as di-isobutylene was obtained by Butlerow[1] on heating equal weights of tertiary butyl alcohol, water and sulfuric acid in a water bath for twenty-four hours. Butlerow oxidized di-isobutylene with potassium dichromate and obtained carbon dioxide, acetone, acetic acid, trimethylacetic acid, a seven-carbon atom ketone (b. p. about 124°) and an eight-carbon atom acid (b. p. 205–218°). When he used a 5% solution of potassium permanganate as an oxidizing agent he obtained the three acids but neither of the ketones mentioned above. There was also produced a monohydroxy alcohol (m. p. 49–50°) to which he assigned the name of oxoctenol and the formula I and an hydroxy acid (m. p. 117°) to which he assigned the name oxoctylic acid and the formula II.

(I)



$(CH_3)_3C\underset{\diagdown O \diagup}{C(OH)C}(CH_3)_2$

(II) $(CH_3)_3CCH_2C(OH)(CH_3)COOH$

Epoxy-2,3-trimethyl-2,4,4-pentanol-3 Trimethyl-2,4,4-hydroxy-2-pentane acid-1

Prileshaiev[2] oxidized di-isobutylene with a 1% solution of magnesium permanganate and obtained almost equal quantities of oxoctenol and a glycol (formula III) and small amounts of acetone, trimethylacetic acid and oxoctylic acid. When he used a 1% solution of potassium permanganate the amount of the glycol was three and a half times the amount of oxoctenol.

(III) $(CH_3)_3CCH_2C(OH)(CH_3)CH_2OH$ (IV) $(CH_3)_3CCH{=}C(CH_3)_2$

Trimethyl-2,4,4-pentanediol-1,2 Trimethyl-2,4,4-pentene-2,3

(V) $(CH_3)_3CCH_2C(CH_3){=}CH_2$

Trimethyl-2,4,4-pentene-1,2

The above facts substantiate the view of Butlerow that di-isobutylene contains two isomers having the formulas IV and V. The present investigation was carried on for the purpose of evaluating the proportions of the isomers in the mixture and of developing practical methods for the production of such ketones, aldehydes and acids as could be obtained in good quantities from the readily available di-isobutylene. The di-isobutylene used in this investigation was prepared as by Edgar.[3] The material used had a boiling range of 101–103°. A similar product was obtained through the polymerization of isobutylene in 65% sulfuric acid, the isobutylene having been prepared by dehydrating isobutyl alcohol over alumina at 400°

[1] Butlerow, *Ann.*, **189**, 46–83 (1877).

[2] Prileshaiev, *J. Russ. Phys.-Chem. Soc.*, **39**, 769–771 (1907).

[3] Edgar, *Ind. Eng. Chem.*, **19**, 746 (1927).

This method of polymerization gave only low yields of di-isobutylene, as the principal product was tri-isobutylene.[4]

Preparation of Ozone.—Oxygen from a commercial cylinder was passed at the rate 15 liters per hour through an ozonizer consisting of three Berthelot tubes arranged essentially as described by Lee I. Smith[5] except that the inner mercury electrode was replaced by a 20% solution of sulfuric acid. The oxygen was dried over sulfuric acid and phosphorus pentoxide before passing through the ozonizer. The gas from the ozonizer contained from 3 to 4% of ozone. The ozonization was carried out in a series of three 300-ml. long-necked flasks provided with ground-glass joints. The solution of di-isobutylene was placed in the first two of the reaction flasks while the third was used as a trap. The exit gases from the third flask passed through a sulfuric acid wash bottle.

The Formation and Hydrolysis of the Ozonide of Di-isobutylene.—Preliminary experiments in which the ozonization was carried on in a chloroform solution were unsuccessful, as difficulty was encountered in decomposing the ozonide without using zinc. Acetic acid was thereafter used as a solvent. Fifty-six g. of di-isobutylene, dissolved in 100 ml. of acetic acid containing about 1% of acetic anhydride, was placed in each of the two reaction flasks and ozone passed into the flask for about twenty-four hours, at the end of which time the ozone passed through unchanged in concentration. The yield of ozonide was then determined by titrating a weighed sample of its acetic acid solution, the ozonide $C_8H_{16}O_3$ being assumed to constitute the whole of the non-acidic portion of the solution. The yield of ozonide was about 50% of the theoretical.

An amount of water approximately equal to the weight of acetic acid present (as determined by the above titration) was added to the ozonide solution. The mixture was placed in a 2-liter, three-necked flask in which was fitted a mechanical stirrer and a long reflux condenser. The amount and temperature of the water in the condenser were regulated to control the amount of refluxing. This condenser was connected at the upper end to a well-cooled condenser by means of a piece of 1-cm. glass tubing. The condensate was collected in a flask cooled in ice water. About 20 g. of zinc (30-mesh) was added to the solution in 2- or 3-gram portions over a period of one and one-half to two hours. The reaction proceeded with the evolution of a good deal of heat and it was necessary to cool the reaction flask with ice water. The mixture was stirred rapidly so that there was practically an emulsion of the ozonide and its decomposition products in the dilute acid. When the reaction had moderated somewhat (about one and one-half hours), the cooling bath was removed from around the flask and it was warmed with a small free flame.

When most of the zinc had gone into solution, the flask was heated sufficiently to cause gentle refluxing. By keeping the temperature of the water in the reflux condenser at about 70° the more volatile aldehydes and ketones distilled over with water and were accompanied by only a relatively small amount of acetic acid. The heating and stirring were continued until no more insoluble oil distilled, water being added to the distilling flask in such amounts that the volume remained nearly constant. The oily layer of the distillate was separated and dried over calcium chloride. The aqueous layer was dis-

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[4] Mr. Walter Arthur, at the suggestion of Dr. James F. Norris, began in the fall of 1926 at the Massachusetts Institute of Technology an investigation of the oxidation of di-isobutylene. Simultaneously and independently the authors began a similar study. A year later Mr. Arthur came to Wisconsin to continue his graduate work and the duplication of work was discovered. Mr. Arthur with the approval of Dr. Norris continued his study of the permanganate oxidation of di-isobutylene and expects to report on this independently.

[5] Lee I. Smith, THIS JOURNAL, **47**, 1844 (1925).

tilled several times over calcium chloride and the oily layer obtained in this way was added to the first portion. The oil was dried over calcium chloride and fractionated through a 20-cm. Widmer column. The results from a typical fractionation are shown in Table I. They were duplicated in six experiments.

TABLE I

FRACTIONATION OF THE HYDROLYSIS PRODUCTS OF THE OZONIDE OF DI-ISOBUTYLENE

Fraction	Boiling range	Weight, g.	Fraction	Boiling range	Weight, g.
A	to 65°	4.8	E	100–110	1.1
B	65– 77	7.7	F	110–120	14.4
C	77– 90	0.8	G	120–130	38.1
D	90–100	0.2	H	Residue	10.3

The fraction boiling up to 65° was identified as acetone by means of the dibenzal derivative, m. p. 111°; and as the *p*-nitrophenylhydrazone, m. p. 148°. Fraction B formed a semicarbazone melting at 190.7° (corr.), which corresponds with the melting point of trimethylacetaldehyde semicarbazone (191°). This fraction was also oxidized to an acid boiling at 162–165° which formed an amide melting at 153° (corr.). Trimethylacetic acid boils at 163.7° and its amide melts at 153–154°. The fractions boiling between 100 and 130° were washed with water and sodium carbonate solution for the removal of acetic and formic acids. The resulting oil after drying over calcium chloride or sodium sulfate weighed 40 g., distilled between 123–126° and gave a semicarbazone melting at 176° (corr.).

Anal. Calcd. for $C_7H_{14}O$: C, 73.62; H, 12.36. Found: C, 73.33; H, 12.51.

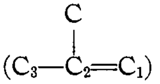
Anal. Calcd. for $C_8H_{17}N_3O$: N, 24.54. Found: N, 24.65.

Markownikoff[6] claimed that the semicarbazone of ethyl tertiary butyl ketone melted at 174–175°. Favorski[7] reported that the melting point of this semicarbazone was 144°. Ethyl tertiary butyl ketone was synthesized and the melting point of its semicarbazone found to be 144°. An attempt to synthesize the isomeric neopentyl methyl ketone from acetoacetic ester and tertiary butyl bromide resulted in a failure.

The ketone boiling at 123–126° upon oxidation with dichromate was converted into two acids, one of them boiling mainly at 164–165° and the other at 175–180°. The acids formed amides melting at 153.5 and 126°, respectively. The amide of trimethylacetic acid melts at 153–154° and that of tertiary butyl acetic acid at 132°. All of the above facts point to a ketone having the structure $(CH_3)_3CCH_2COCH_3$, *i.e.*, methyl neopentyl ketone or dimethyl-4,4-pentanone-2.

In addition to the products referred to above, *i.e.*, acetone, trimethylacetaldehyde and methyl neopentyl ketone, there were also formed during the hydrolysis of the ozonide considerable quantities of formaldehyde and carbon dioxide.

Acetone and trimethylacetaldehyde were formed in approximately equal amounts (0.082 and 0.089 moles, respectively) and are presumably oxidation products of an octene of formula IV. The amount of methyl neopentyl ketone produced was approximately 3.7 times the amounts of acetone and trimethylacetaldehyde and indicates a corresponding predominance of an octene of formula V. This is in good agreement with Prileshaiev's conclusions as to the ratio of the isomers as determined by oxidation of the mixture of isomers using a 1% solution of potassium permanganate.



Isobutylene ($C_3\text{—}\overset{\overset{\displaystyle C}{|}}{C_2}\text{=}C_1$) may add to isobutylene in at least four ways.

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[6] Markownikoff, *Ber.*, **33**, 1906 (1900).

[7] Favorski, *J. Russ. Phys.-Chem. Soc.*, **44**, 1339–1395 (1912).

(1) The hydrogen of the methylene group of one molecule may add: (a) to the number 1 carbon atom or (b) to the 2 carbon of the second molecule. (2) The hydrogen of one of the methyl groups in the first molecule may add (a) to the number 1 carbon atom or (b) to the number 2 carbon atom of the second molecule. The predominance of the octene of formula V indicates that in the polymerization of isobutylene the reaction proceeds predominantly according to 2a, *i. e.*, the labile hydrogen for addition is in the methyl rather than in the methylene group, and the preferred direction of addition involves the addition of hydrogen to the more hydrogenated carbon atom. It should be noted that the presence of an octene of formula IV in the mixture does not necessarily indicate that addition took place according to scheme 1a since sulfuric acid would be expected to cause the rearrangement of an octene of formula V to one of formula IV.

Summary

Methyl neopentyl ketone, $(CH_3)_3CCH_2COCH_3$, and trimethylacetaldehyde were produced in the ratio of approximately 3.7 to 1 when di-isobutylene was ozonized and the ozonide hydrolyzed. This indicates that di-isobutylene contains two isomeric octylenes, *i. e.*, trimethyl-2,4,4-pentene-1,2 and trimethyl-2,4,4-pentene-2,3, with the former in considerable excess. It appears then that when isobutylene undergoes polymerization the labile hydrogen for addition is in the methyl rather than in the methylene group, and that the predominant direction of additions involves the addition of hydrogen to the more hydrogenated carbon atom.

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NITROFURFURAL AND NITROFURYLACRYLIC ACID

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Introduction

In connection with the preparation of aminofurans and their diazo compounds, it was necessary to have a series of readily accessible nitrofurans and their derivatives. We turned to the nitration of furfural because this aldehyde is available in large quantities and at a low price. Apparently, the literature contains no description of the preparation of a nitrofurfural. However, attempts have been made to nitrate furfural.[1]

By means of the technique of Gilman and Wright[2] for introducing substituents in furfural, we have succeeded in preparing the first nitrofurfural. As might have been predicted, the nitro group markedly increases

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[1] Marquis, *Compt. rend.*, **135**, 505 (1902).

[2] Gilman and Wright, THIS JOURNAL, **52**, 1170 (1930).