air. The sample was stirred very vigorously and the e. m. f. taken every twenty seconds with a Leeds and Northrup No. 8662 Portable, Double Range, Precision Potentiometer. The sample was cooled slowly until it was practically impossible to move the stirrer, then the glass-jacketed test-tube was transferred to an empty Dewar flask and the sample allowed to melt slowly. In this way freezing and melting curves were obtained, Fig. 1.

With the exception of 2,4,4-trimethylpentene-2, the substances did not supercool more than 0.3°, if at all. 2,4,4-Trimethylpentene-2, however, sometimes supercooled as much as 10°, despite the most vigorous stirring used. Ordinarily this isomer had a freezing point of 106.55°, but sometimes a value of 108.3° was obtained. Both were definite fixed points.

The thermocouple was calibrated at the following points

	E. m. f., millivolts	°C.
Mercury	1.568	− 38.9
n-Octane	2.250	− 56.9
Carbon dioxide snow	3.000	− 78.9
n-Heptane	3.385	− 90.7
2,4,4-Trimethylpentane, "iso-octane"	3.908	−107.7

Summary

1. The separation of diisobutylene into 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2 has been accomplished by single distillations through the highly effective columns constructed for the separation of Pennsylvania petroleum into its constituents.
2. The purity of the isomers has been established by accurate determinations of their cooling curves.

State College, Pennsylvania

[Contribution from the Laboratory of the School of Chemistry and Physics of the Pennsylvania State College]

THE ISOMERS IN "DIISOBUTYLENE." III.[1] DETERMINATION OF THEIR STRUCTURE[2]

By Frank C. Whitmore and James M. Church

Received May 17, 1932 Published September 5, 1932

Butlerow, the discoverer of diisobutylene, recognized it as a mixture of two isomeric octylenes, 2,4,4-trimethylpentene-1 (I) and 2,4,4-trimethylpentene-2 (II).[3] The oxidation products upon which this conclusion was based included acetone, acetic acid, formic acid, trimethylacetic acid, tertiary-butylacetic acid and methyl neopentyl ketone. Recently the

---

[1] See preceding article.

[2] Presented by James M. Church in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College.

[3] Butlerow, *Ann.*, **189**, 46–83 (1877); *J. Russ. Phys.-Chem. Soc.*, **14**, 201 (1882); Wagner, *Ber.*, **21**, 1230 (1888); Prileshajew, *J. Russ. Phys.-Chem. Soc.*, **39**, 769 (1907).

presence of the two isomers has been established definitely by ozonolysis experiments.[4] These indicated (I) and (II) to be present in a ratio of approximately 4:1. The separation of the isomers in this Laboratory showed the lower-boiling isomer to be present in four times the amount of the higher-boiling product. This, taken in conjunction with the work of McCubbin and Adkins, indicated that the lower boiling isomer was (I). This would also agree with the generalizations of Boord and his co-workers[5] on the influence of the position of the double bond on the boiling points of isomeric olefins. Since some of the work on rearrangements in this Laboratory[6] necessitated a definite knowledge of the structure of the higher-boiling diisobutylene, the pure isomers were ozonized. The result was a complete confirmation of the conclusions drawn from the results of McCubbin and Adkins and from the separation of the isomers in this Laboratory.

The lower boiling isomer (b. p. 101.2° (760 mm.)) gave formaldehyde, methyl neopentyl ketone and a trace of tertiary-butylacetic acid but no acetone. It was thus proved to be 2,4,4-trimethylpentene-1.

The higher boiling isomer (b. p. 104.5° (760 mm.)) gave acetone, trimethylacetaldehyde and trimethylacetic acid but no formaldehyde. It was thus 2,4,4-trimethylpentene-2.

The absence of acetone and of formaldehyde in the ozonization of the samples of the lower and the higher boiling isomers, respectively, indicated the completeness of the separation of the two isomers by the special columns used.[7]

Since the literature contains almost no detailed directions for the ozonolysis of relatively simple olefins and no quantitative data on such processes, the present experiments are given in full detail.

Experimental

1. General Method of Ozonization and Hydrolysis of Ozonides.—An ozonizer similar to that of L. I. Smith[8] was used. Two sets of three Berthelot Pyrex ozonizer tubes were connected in parallel. The inner portion of each tube was filled with dilute copper sulfate solution. Into this dipped the inner electrodes each consisting of two heavy copper wires twisted together. The outer electrodes were two large strips of copper in the water-bath containing the ozonizer tubes. The current was supplied by a 10,000 volt "Neon sign" transformer. Oxygen from a cylinder was bubbled through concd. sulfuric acid, over activated alumina, and through a spray and dust tower full of glass wool. A flowmeter was used. When the rate was 15 liters per hour the exit gas from three tubes of the ozonizer contained 6 to 8% ozone. All connections were made by means of mercury-sealed cup joints. The olefins were dissolved in a low-boiling saturated hydrocarbon (b. p. 0–35°) supplied by the Viking Corporation of Charleston,

---

[4] McCubbin and Adkins, THIS JOURNAL, **52**, 2547 (1930).

[5] C. E. Boord, "Some Generalizations on the Physical Properties of Olefins," Buffalo Meeting, American Chemical Society, Sept. 2, 1931.

[6] See the following article.

[7] Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932).

[8] Smith, THIS JOURNAL, **47**, 1844 (1925).

West Virginia. The solution was contained in a special tall 500-cc. ozonizing bottle with a sealed-in bubble tube. The exit tube was supplied with a rubber tube leading to a hood. As soon as ozone ceased to be absorbed by the olefin, the excess caused the rubber tube to crack off. This indication was as sensitive as the usual starch–potassium iodide test. The ozonizations were conducted at −10°.

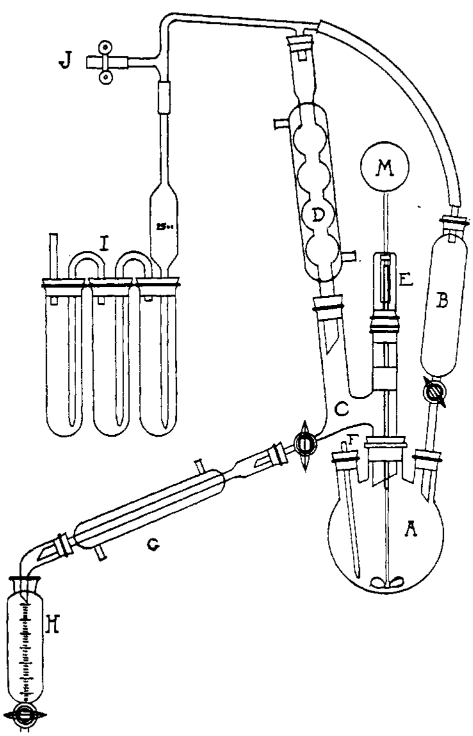

Fig. 1.—A, a 1000-cc. three-necked flask containing water, zinc and catalysts; B, dropping funnel containing liquid ozonide; C, special distilling adapter; D, reflux condenser held at desired temperature; E, mercury seal stirrer; F, entrance for nitrogen gas; G, water-cooled condenser; H, graduated receiver; I, absorption apparatus for volatile materials; J, emergency valve; M, motor.

The solvent was removed from the ozonide solution under reduced pressure at 35°. The clear, slightly yellow or colorless liquid ozonide was weighed. In a few isolated cases the ozonides decomposed violently. Consequently the containers were always kept in wire gauze holders. The hydrolysis of the ozonides was done in a special apparatus developed with P. A. Krueger of this Laboratory (Fig. 1). The liquid ozonide was added from a dropping funnel to a stirred boiling mixture of 300–500 cc. of water and an amount of zinc dust equivalent to the ozonide together with traces of hydroquinone and silver nitrate. A stream of nitrogen was used to carry the volatile products to a suitable condensing and scrubbing system. The aqueous layer of the distillate was added to the main flask and distilled through the system again until no more oily products formed. The final aqueous distillate was saved for testing for water-soluble products.

Separation, Identification and Estimation of the Ozonolysis Products.—The aqueous distillate was tested for formaldehyde, formic acid and acetone by standard methods.

The oily layer was fractionally distilled through a 70 × 1 cm. glass, indented, adiabatic (electrically heated and insulated with two glass jackets), total condensation, variable take-off column.[9]

Ozonolysis of the Lower-boiling Diisobutylene.—This is typical of many experiments with this substance. One-half mole (56 g.) of a sample of b. p. 100.1° (737 mm.), n_D^{20} 1.4082 and d_4^{20} 0.715 was dissolved in 300 cc. of the low-boiling hydrocarbon and ozonized at −10°; time, sixteen hours. Removal of the solvent at 35° gave 75.5 g. of a slightly greenish yellow liquid ozonide with a little solid product; yield, 94.5%. The ozonide was decomposed as outlined above. The process was very violent. The distillate contained 57 cc. of oil and 200 cc. of a water layer. The nitrogen gas was washed at 0° with 50 cc. of ether which was then used to extract the aqueous layer after the de-

---

[9] See THIS JOURNAL, p. 3451.

termination of formaldehyde in it. The total crude products obtained amounted to a yield of 93% based on the ozonide. Qualitative tests for formaldehyde with fuchsin reägent, Tollens' reagent and 1% aqueous resorcinol were obtained. Iodimetric titration showed 13.4 g. of formaldehyde or a yield of 94.6%. Three distillations of the oily product through the 70 × 1 cm. column gave the following fractions at 738 mm.

Fraction	B. p., °C.	Wt., g.	n_D^{20}
A 1	36–120	2.7	1.3994
2	120–123	2.9	1.4018
3	123–124.5	36.8	1.4030
4	124.5–180	3.6	1.4067
5	180–190	1.2	1.4116
6	Residue	3.7	1.4355

Fraction A 3 gave a semicarbazone which after two crystallizations from petroleum ether (b. p. 70–90°) melted at 176° (corr.), corresponding to the m. p. of the semicarbazone of methyl neopentyl ketone as obtained by McCubbin and Adkins.[4] Fraction A 5 gave an acid amide which was difficultly purified by crystallization from ethyl acetate and petroleum ether to give m. p. 130–131°. This was not lowered by mixing with the known amide of tertiary-butylacetic acid, m. p. 132°.

The low-boiling diisobutylene thus gave yields of formaldehyde and methyl neopentyl ketone of 94.6 and 67.8%, respectively, as well as a small amount of tertiary-butylacetic acid, thus proving it to be 2,4,4-trimethylpentene-1. The iodimetric titration of the aqueous solution gave no iodoform, proving the absence of acetone and consequently the absence of the high-boiling isomer in the material ozonized.

Ozonolysis of the Higher-boiling Diisobutylene.—A typical run was as follows. One-half mole (56 g.) of a sample of b. p. 103.4° (737 mm.), n_D^{20} 1.4158 and d_4^{20} 0.721 was ozonized as above. Considerable amounts of white solid separated in the apparatus, clogging the delivery tube at times. The crude ozonide weighed 69 g., a yield of 86.2%. It was a colorless oil containing a small amount of a white solid. This solid exploded when heated on a spatula. The ozonide was decomposed in the usual way. The reaction was even more violent than with the isomeric ozonide. The addition to the boiling decomposition mixture required three hours. The products were 37 cc. of oil and 150 cc. of aqueous distillate. The mixture in the decomposition flask was a thick grayish-white mass. Treatment with 100 cc. of 25% sulfuric acid and distillation gave an additional 14 cc. of oil. The total weight of oil was 41 g. This, with 13.9 g. of acetone found in the water layer, represented a yield of 88.8% based on the ozonide.

The aqueous layer gave no test for formaldehyde. The dibenzal derivative of acetone was obtained, m. p. 110°. Iodimetric titration showed the presence of 13.9 g. of acetone in the aqueous layer. Iodoform was formed.

The oily layer was separated by six distillations through the 70 × 1 cm. column. The final fractions obtained at 733 mm. were:

Fraction	B. p., °C.	Wt., g.	n_D^{20}
B 1	53–58	6.3	1.3652
2	58–72	1.4	1.3741
3	72–77	4.9	1.3808
4	77–121	2.5	1.3945
5	121–124	1.5	1.4028
6	124–158	3.8	1.4073
7	158–162	8.6	1.4107
8	Residue	2.4	1.4409

Fraction B 1 gave dibenzalacetone, m. p. 110°. The m. p. of a mixture with the known substance was 109°. Fraction B 3 gave the 2,4-dinitrophenylhydrazone of trimethylacetaldehyde, m. p. 210°, mixed m. p. 210°. Fraction B 7 gave the amide of trimethylacetic acid, m. p. 153°, mixed m. p. 151°. Most of this acid product was obtained from the acidification of the decomposition mixture. No semicarbazone could be obtained from Fraction B 5.

The high-boiling diisobutylene thus gave yields of acetone, trimethylacetaldehyde and trimethylacetic acid of 81.3, 13.2 and 21.5%, respectively, thus proving it to be 2,4,4-trimethylpentene-2. The absence of formaldehyde and methyl neopentyl ketone among the ozonolysis products showed the completeness of the separation from the low-boiling isomer.

Summary

1. The low-boiling and high-boiling isomers of diisobutylene have been proved to be 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2, respectively.

2. The completeness of the separation of these isomers is confirmed by the fact that neither gives ozonolysis products which would be expected from the other.

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

THE DEHYDRATION OF SECONDARY CARBINOLS CONTAINING A NEOPENTYL SYSTEM. I.

ISOPROPYL-*TERT.*-BUTYLCARBINOL. PRELIMINARY PAPER[1]

BY FRANK C. WHITMORE AND A. L. HOUK

RECEIVED MAY 17, 1932 PUBLISHED SEPTEMBER 5, 1932

The dehydration of this carbinol was studied because it presents three possibilities.[2] (1) Normal dehydration by the removal of the secondary hydroxyl and the tertiary hydrogen, similar to the dehydration of methylisopropylcarbinol to give trimethylethylene, would produce the higher boiling di-isobutylene, 2,4,4-trimethylpentene-2, which has been thoroughly characterized in this Laboratory.[3] (2) A shift of the tertiary hydrogen would given an organic "ion"[4] related to the two di-isobutylenes. This would be expected to lose a proton to give these two substances in the ratio of 4:1, the lower boiling isomer, 2,4,4-trimethylpentene-1, predominat-

---

[1] Presented by A. L. Houk in partial fulfilment of the requirements for the degree of Ph.D. at the Pennsylvania State College.

[2] This carbinol was prepared and dehydrated at Northwestern University in 1928 by H. C. Benedict, Jr. No definite knowledge of the resulting olefins was then obtained because of the inadequacy of the distillation equipment available; *cf.* Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932).

[3] See preceding article.

[4] See *ibid.*, p. 3274.