

2. The method for the determination of the structures of polymerized Schiff bases by strong reduction, first used in the case of methylene-*p*-aminophenol, was successfully extended to trimeric methylene-aniline and methylene-*p*-toluidine, whose cleavage into primary, secondary and tertiary bases indicated their cyclic structures.

3. Amorphous methylene-aniline and methylene-*p*-toluidine (the higher polymers) were examined similarly and with similar results, but their structures cannot yet be fixed because of lack of knowledge of their molecular magnitudes at lower temperatures.

4. Examination of the apparently aberrant condensation of aniline and acetaldehyde (representing the straight-chain aliphatic aldehydes) showed the products hitherto obtained to be due to secondary reactions, the primary product being the di-imine. There seems to be no satisfactory evidence for the intermediate formation of the monomeric azomethine.

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

THE ISOMERS IN "DIISOBUTYLENE." II¹

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The separation of the isomers in diisobutylene has been completed by means of two highly efficient packed columns constructed for the study of the composition of Pennsylvania petroleum.²

The diisobutylene used was prepared from tertiary butyl alcohol which had been recrystallized until its freezing point was above 23° (m. p. of pure tertiary butyl alcohol 25.5°). The diisobutylene was freed from all but traces of isobutylene and triisobutylene and higher polymers by a preliminary distillation.

The properties of the isomers are as follows

	B. p. (Cottrell), °C.		d_4^{20}	n_D^{20}	F. p., °C.
	737 mm.	760 mm. ³			
2,4,4-Trimethylpentene-1	100.1	101.2	0.7151	1.4082	— 93.6 ± 0.1
2,4,4-Trimethylpentene-2	103.4	104.5	0.7211 ⁴	1.4158	— 106.5 ± 0.1 ⁵

The high purity of the two isomers is indicated by their cooling curves.

¹ Presented by C. O. Tongberg in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College. See Whitmore and Wrenn, *THIS JOURNAL*, **53**, 3136 (1931).

² For a detailed description of these columns, their operation and this separation, see Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932).

³ The experimentally determined relation $\Delta p / \Delta \text{b. p.} = 21.8 \text{ mm./}1^\circ\text{C.}$ was used in making the correction.

⁴ The value given in the first paper is in error.

⁵ An isomorphous form was sometimes obtained with m. p. $-108.3 \pm 0.1^\circ$.

Experimental

Purification of Tertiary Butyl Alcohol.—The best grade of the commercial alcohol from the Hydrocarbon Products Company of New York showed freezing points from 15 to 20°. The chief impurity was water. This alcohol was chilled until approximately two-thirds had crystallized. The crystals were separated by suction on large Büchner funnels. They were then melted and frozen again. This process was continued until the freezing point of the melted crystals was above 23°. The mother liquors were used directly with concentrated hydrochloric acid to make tertiary butyl chloride for other researches.

Preparation of Diisobutylene.—Slight modifications of the earlier procedures were used.¹ A cooled mixture of 2500 cc. of c. p. sulfuric acid and 2500 cc. of water was used with 3500 cc. of purified tertiary butyl alcohol. The time of heating on the steam-bath was shortened to three hours. Longer heating only increased the amount of higher isomers. The hydrocarbon layer was then carefully separated and refluxed with a few grams of metallic sodium. Less than 1 g. of sodium reacted with 5 liters of the crude hydrocarbon. Suction was then applied to remove considerable quantities of dissolved isobutylene. Finally one-tenth of the hydrocarbon was distilled under diminished pressure. Then the remainder was distilled through a short column until the b. p. reached 105° (737 mm.). The yield of "diisobutylene" was about the same as under the older procedure but the labor and time involved were much less. The total amount of diisobutylene prepared in this way, from *tert.*-butyl alcohol melting above 23°, was 50 liters.

Fractionation of the Diisobutylene.—The details of the fractionations through the 27-ft. and the 52-ft. columns are given elsewhere.⁶ Boiling points of the fractions were taken in a Cottrell apparatus. In the case of the earlier fractions, dissolved isobutylene vitiated the boiling points.⁶ More consistent results were obtained by taking the "50 per cent. boiling point" by allowing half of each sample to boil out of the Cottrell apparatus and then reading the b. p. The boiling points were taken at pressures of 728–737 mm. and were corrected to the latter pressure. The following is a summary of the distillation of 4.5 liters of diisobutylene (n_D^{20} 1.4102) through the 52 ft. column.

Fractions	B. p. (737 mm.) (Cottrell)		n_D^{20}	Cc.
	Initial	50 Per cent.		
1–2	88.7°		1.3990–1.4063	90
3–5	95.9	100.1	1.4067–1.4076	107
6–10	99.0	100.1	1.4079–1.4081	215
11–15	99.6	100.1	1.4081	222
16–20	100.0	100.1	1.4082	223
21–65	100.1	100.1	1.4082	2303
66–75	100.1–102.9		1.4083 to 1.4147	393

⁶ Fenske and co-workers, *Ind. Eng. Chem.*, **24**, 408 (1932).

Fractions	B. p. (737 mm.) (Cottrell) Initial 50 Per cent.	n_D^{20}	Cc.
76-83	103.1-103.15	1.4150 to 1.4156	312
84-89	103.3	1.4158	264
Residue		1.4225	175
Hold-up in column			50
Loss			146

A charge of 45.5 liters of diisobutylene (n_D^{20} 1.4102) was distilled through the 27-ft. column with a take-off rate of 250-750 cc. per hour. The results obtained were essentially like those with the 52-foot column. The distillation gave 156 fractions of 250 cc. each. Fractions 6 to 97 with a volume of 23 liters boiled at 100.1 to 100.15° at 737 mm. and had n_D^{20} 1.4081-1.4083. Fractions 147 to 156 with a volume of 2360 cc. boiled at 103.25 to 103.4° at 737 mm. and had n_D^{20} 1.4158. The residue of 1900 cc. had n_D^{20} 1.4290 (value for triisobutylene is 1.4315). The hold-up and loss amounted to 1250 cc. The temperature of the still walls as taken by a thermocouple varied from 107 to 212° during the distillation.

Refractionation of the Intermediate Fractions.—A charge of 4.5 liters from fractions 122-140 from the 27-ft. column with b. p. (737 mm.) 100.7 to 103.0° and n_D^{20} 1.4098 to 1.4150 was distilled through the 52-foot column. The refractive index of the mixture was 1.4123, corresponding to a 1:1 mixture of the isomers. The take-off was at the rate of 40-50 cc. per hour. Forty-eight fractions were taken. Fractions 1 to 15 with a volume of 1400 cc. boiled at 99.7 to 100.1° at 737 mm. and had refractive indices of 1.4080 to 1.4083. Fractions 30 to 42, volume 765 cc., had b. p. (737 mm.) 102.9 to 103.1° and n_D^{20} 1.4143 to 1.4154; fractions 43 to 48, volume 558 cc., b. p. (737 mm.) 103.3 to 103.4° and indices 1.4157 to 1.4158.

Refractionation of the Higher Isomer.—A charge of 3.7 liters from fractions 141 to 156 of the distillation in the 27-ft. column, with b. p. 103.0 to 103.5° and indices 1.4150 to 1.4158 was distilled through the 52-ft. column. The start of the distillation was made with a reflux ratio of 45:1. This was decreased when the index of refraction of the distillate rose to 1.4158. The following is a summary of this distillation, which established the identity and properties of the more difficultly obtainable isomer in diisobutylene.

Fractions	B. p., (737 mm.) (Cottrell), °C.	n_D^{20}	Cc.
1-5		1.4142-1.4145	263
6-10		1.4146-1.4150	270
11-15	102.9 to 103.1	1.4150-1.4152	295
16-27	103.15 ⁷	1.4152-1.4155	647
28-35	103.2-103.4	1.4157-1.4158	570
36-53	103.4	1.4158	1600
Residue		1.4180	650

⁷ The distillation curve consistently showed a flat portion at this temperature. The nature of this material has not been determined. Its cooling curve shows it to differ decidedly from the pure 2,4,4-trimethylpentene-2. See Fig. 1, G.

Freezing Point Data.—A chromel-copel thermocouple was used to read the temperatures. A sample of about 20 cc. was placed in a glass-jacketed test-tube, which was put in a large Dewar flask containing liquid

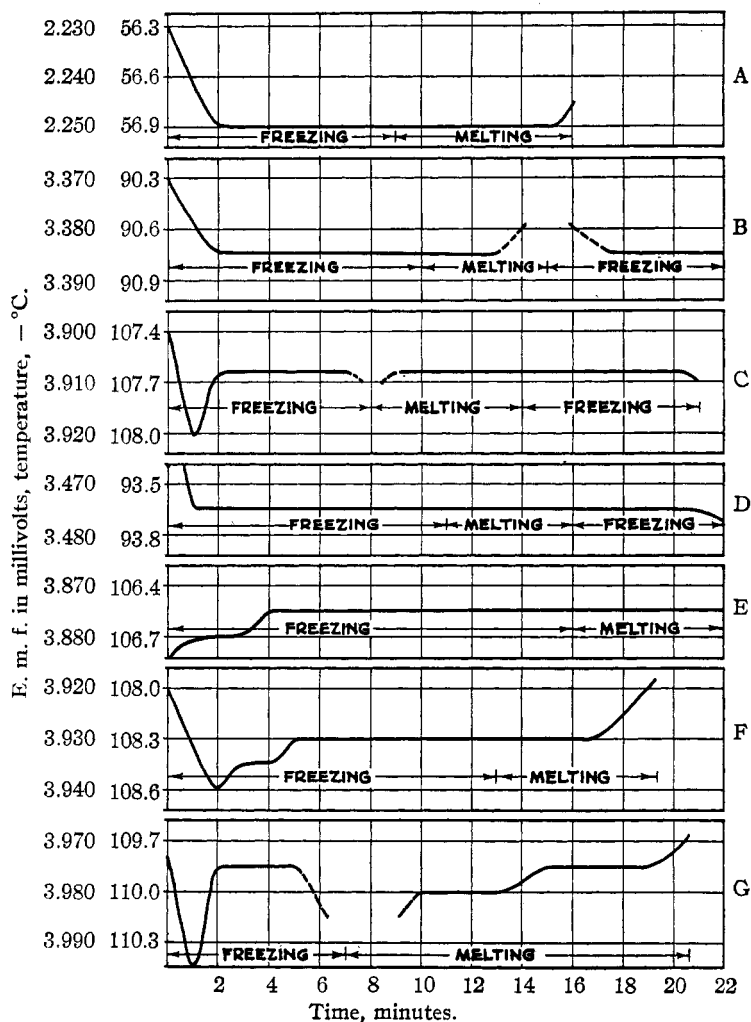


Fig. 1.—Freezing and melting curves.

	Substance	B. p. (760 mm.), °C.	n_D^{20}	F. p., m. p., °C.
A	<i>n</i> -Octane	125.4	1.3970	— 56.9
B	<i>n</i> -Heptane	98.4	1.3878	— 90.7
C	2,4,4-Trimethylpentane	99.3	1.3912	— 107.7
D	2,4,4-Trimethylpentene-1	101.2	1.4082	— 93.6
E	2,4,4-Trimethylpentene-2	104.5	1.4158	— 106.5
F	Isomorphous form of E	104.5	1.4158	— 108.3
G	"Low fraction" of E	104.2	1.4150	— 109.8 to — 110.0

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	$^{\circ}\text{C.}$
Mercury	1.568	— 38.9
<i>n</i> -Octane	2.250	— 56.9
Carbon dioxide snow	3.000	— 78.9
<i>n</i> -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.

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[CONTRIBUTION FROM THE LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF
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THE ISOMERS IN "DIISOBUTYLENE." III.¹ DETERMINATION OF THEIR STRUCTURE²

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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).