

1953

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### Recommended Citation

Raths, Fred W. and Shriner, R. L. (1953) "Synthesis of 2,4-Heptadiene," *Proceedings of the Iowa Academy of Science*: Vol. 60: No. 1 , Article 37.  
Available at: <https://scholarworks.uni.edu/pias/vol60/iss1/37>

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## Synthesis of 2,4-Heptadiene

By FRED W. RATHS<sup>1, 2</sup> AND R. L. SHRINER

2,4-Heptadiene can exist in four isomeric *cis-trans* forms; a fact which probably accounts for the different physical constants reported in the literature. The present synthesis involved a high temperature pyrolysis as the final step, in the hope that only one isomer would be formed under these conditions.

n-Propylmagnesium bromide reacted with ethyl formate to produce a 75% yield of 4-heptanol which underwent dehydration at 300° over alumina to give an 84% yield of *trans*-3-heptene. The latter was converted to a mixture of the two racemic modifications of 3,4-heptanediol (54% yield) by the action of performic acid. Acetylation gave a 75% yield of the 3,4-diacetoxyheptane which was subjected to pyrolysis at 585° in a slow stream of nitrogen. This step paralleled that previously used (1) for the preparation of 1,3-butadiene from 2,3-diacetoxybutane. The products from this vapor-phase elimination of acetic acid were condensed, washed to remove acetic acid, dried and fractionally distilled. The boiling range of 62-110° was cut into nine fractions. The 102-105° fraction was again fractionated and the largest cut which boiled at 103-104° was collected and its physical properties determined. Its u.v. absorption spectrum showed a maximum at 2280 Å which is the same maximum exhibited by other conjugated dienes such as 2,4-hexadiene (2) and 2,3-dimethyl-1,3-butadiene. Non-conjugated dienes, mono-olefins and allenes (3) do not show a maximum in this region.

Reduction of this 103-104° fraction with hydrogen and a palladium catalyst gave pure n-heptane whose physical properties checked those in the literature (4) and which differed markedly from any branched chain isomeric hexanes. Determination of unsaturation by use of iodine monochloride showed two double bonds. Thus, the 103-104° fraction is probably one of the isomeric 2,4-heptadienes.

The fractions boiling from 106-110° from the first distillation were again refractionated into seven fractions. Five of these which

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<sup>1</sup>Abstracted from the Ph.D. Thesis submitted to the Graduate School of the State University of Iowa, 1954.

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were nearly the same in amounts had the following properties.

Fraction	B.P.	$n_D^{25}$	$d_4^{20}$	Maxima in
				u.v.
3b	102-4°	1.4562	0.736	2280 Å
4b	104-5	1.4558	0.736	2280
5b	105-6	1.4548	0.736	2280
6b	106-7	1.4538	0.734	2275
7b	107-7.5	1.4562	0.734	2280

Hydrogenation of combined Fractions 6b and 7b again gave n-heptane. It is evident that a mixture of isomeric 2,4-heptadienes is present as indicated by the densities, refractive indices and u.v. maxima. None of the above fractions checked exactly the data given by Reif (5), Karasev (6), or by Henne and Turk (7); all of whom reported preparations of 2,4-heptadiene by different methods. At present there is no simple method for complete separation of the isomers or exact determination of the configuration. It is evident that the pyrolysis procedure employed in the present work gave a mixture of isomers and not just one.

#### EXPERIMENTAL PART

*4-Heptanol.* A solution of 4 moles of ethyl formate in 500 ml. of absolute ether was added with cooling to 8.1 moles of n-propylmagnesium bromide in 2.5 l. of absolute ether. The reaction mixture was worked up in the usual manner to yield 352 g. (74%) of pure 4-heptanol boiling at 57.0-57.5° at 10 mm.

*3-Heptene.* The 4-heptanol was passed over activated alumina (8) at 300-310° and the products condensed, washed with water and distilled. From 116 g. of the alcohol, there was obtained 82.5 g. (84%) of 3-heptene; b.p. 94-5°.

*3,4-Heptanediol.* To a well stirred mixture of 287 g. (2.9 moles) of 3-heptene and 885 ml. of formic acid (98-100%) at room temperature, 339 ml. of thirty per cent hydrogen peroxide (3 moles) was added in a period of five hours. The reaction mixture was washed with three 200 ml.-portions of a saturated solution of ferrous sulfate, in order to decompose the excess hydrogen peroxide. Two layers formed and the upper layer was refluxed for one hour with an excess of 3 N ethanolic potassium hydroxide. The ethanol was removed by distillation and the residue was washed with three 100 ml.-portions of water. The liquid was distilled under reduced pressure and 208 g. (53.9%) of product collected, b.p. 83-84.5°/1 mm.,  $n_D^{26}$  1.4420. The product solidified and was recrystallized three times from petroleum ether. It still melted over a range of 75-85° indicating that it is a mixture of two *dl*-isomers.

Anal. Calcd. for  $C_7H_{10}O_2$ : C, 63.63; H, 12.12

Found: C, 64.05; H, 12.44

*3,4-Diacetoxyheptane.* A mixture of 45 g. (0.34 mole) of 3,4-heptanediol, 208.7 g. (2.05 moles) of acetic anhydride, and 1 ml. of pyridine was heated on a steam bath for twelve hours. The products were poured into water, separated, and washed with a saturated sodium carbonate solution. The organic layer was dried over anhydrous sodium sulfate, distilled through a 40 cm., column packed with glass helices. The ester amounted to 55.0 g. (74.9%) and had the following constants: b.p. 91-98°/1-1.5 mm.;  $n_D^{26}$  1.4239;  $d_4^{32}$  0.983.

Anal. Calcd. for  $C_{11}H_{20}O_4$ : C, 61.11; H, 9.26

Found: C, 61.04; H, 9.31

*Pyrolysis of 3,4-Diacetoxyheptane.* The pyrolysis reaction was carried out in a stream of nitrogen equal to 6 ml. per second. The 3,4-diacetoxyheptane, 264 g. (1.22 moles) was passed into a vaporizer kept at 270° at a flow rate of 1 ml. per 33 seconds and then into a Vycor tube heated to 585°. Three traps cooled by a dry ice-acetone mixture were used to condense the reaction products. The contact time for the reaction was 7.1 seconds which was defined as the volume of the reaction zone divided by the volume of the incoming stream per unit time. After the receivers containing the condensed products were allowed to come to room temperature, the product was washed four times with 50 ml. of water, separated and dried over anhydrous sodium sulfate. Two grams of hydroquinone was added and the organic liquid was fractionally distilled through a 40 cm. glass helices packed column. In one run, titration of the aqueous wash liquid showed 90% of the theoretical amount of acetic acid.

*Run I.* From 54 g. of the ester, there resulted 26.2 g. of pyrolysis products which gave 14.2 g. of hydrocarbon fractions. Fractionation of these gave a sample of a 2,4-heptadiene showing u.v. absorption maximum at 2280 Å. Its constants were: b.p. 102-103;  $n_D^{20}$  1.4498  $d_4^{20}$  0.731. Unsaturation by iodine monochloride showed 99.1% diene.

Anal. Calcd. for  $C_7H_{12}$ : C, 87.50; H, 12.50

Found: C, 86.97; H, 12.49

*Run II.* From 264 g. of ester there was obtained 109 g. of condensed products of which 75 g. consisted of hydrocarbons boiling from 62 to 110°. This was separated into nine fractions and the cuts boiling 102-105° refractionated through a Vigreux column. The chief fraction (11 g.) boiled at 103-4° and showed u.v. maximum at 2280 Å. It had  $n_D^{20}$  1.4532 and  $d_4^{22}$  0.728. A solution of 10 g. of this fraction in ethanol was reduced with hydrogen and

palladium black. The catalyst was removed by filtration and the filtrate diluted with water. The hydrocarbon layer was washed with concentrated sulfuric acid, then with water, dried, and distilled. The fraction boiling 97-98° with  $n_D^{20}$  1.3887 and  $d_4^{27}$  0.682 corresponded to n-heptane (4).

The fractions boiling from 106-110° from the first fractional distillation above were refractionated to give the following:

Fraction	b.p. 749 mm	$n_D^{20}$	$d_4^{20}$	Wt(g)	U.V.
1b	96-99°	1.4421	0.761	1.5	.....
2b	99-102°	1.4476	0.755	2.0	.....
3b	102-104°	1.4562	0.736	5.0	2280 Å
4b	104-105°	1.4558	0.736	5.5	2280 Å
5b	105-106°	1.4548	0.736	6.0	2280 Å
6b	106-107°	1.4538	0.734	5.6	2275 Å
7b	107-107.5°	1.4566	0.734	4.6	2285 Å

Literature Values

Reif (5)	104-106°	1.4486	0.733	....	.....
Karasev (6)	103-104	1.4456	0.738	....	.....
Henne & Turk (7)	109.6	1.4578	0.738	....	.....

None of the previous workers reported the u.v. data on their compounds. In the present work, a sample of 2,3-dimethyl-1,3-butadiene was prepared (9) and its u.v. absorption spectrum determined. It had a sharp maximum at 2280 Å.

Hydrogenation of the combined fractions 6b and 7b again gave n-heptane. The refractive indices, densities and u.v. maxima for fractions 3b through 7b indicate that these are mixtures of isomers of 2,4-heptadiene since the boiling points slowly rise from 102° to 107.5° with about equal amounts for each degree rise.

Anal. of Combined Fractions 6b and 7b.

Calcd. for  $C_7H_{12}$ : C, 87.50; H, 12.50

Found: C, 86.63; H, 12.64

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