for carbon. The results show that a diketone is formed which boils at the same temperature as the diketone from levo-laurolene.

Several determinations of the optical activity of the diketone from dextro-laurolene, as above prepared, showed it to be optically inactive. Experiments were performed with the diketone in the pure form as well as in 20.5 per cent. ethereal and alcoholic solutions.

As in the case with diketone from levo-laurolene, the diketone from dextro-laurolene gave an oily oxime and phenylhydrazone.

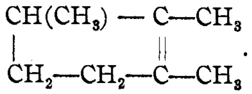
The semicarbazone was a white crystalline product which separated from water after long standing. It melted fairly sharply at 192° (cor.) and appeared to resolidify and again melt at 225° (cor.). A very recent preparation gave a semicarbazone which melted at 228° (cor.) with no evidence of a preliminary melting. The analysis of the product melting first at 192° gave:

Calculated for $C_{10}H_{20}O_2N_6$: N, 32.81. Found: N, 33.25

It is evident that the oxidation product of dextro-laurolene is a diketone identical with the diketone obtained from levo-laurolene. Therefore dextro- and levo-laurolene are mixtures of optical isomers, but the *d*- and *l*-forms occur in different proportions. In the levo-laurolene the *l*-form predominates while in the dextro-laurolene the *d*-form is in excess.

Structure of Laurolene.

The experiments described in this paper give further confirmation of the structure of laurolene first proposed by Eijkman[1] on the basis of refractometric studies and advocated by us in our previous paper.[2] They have shown, also, that both *d*- and *l*-laurolene give a diketone by oxidation and that the semicarbazones of the ketones from the two hydrocarbons are, apparently, identical, indicating that the two hydrocarbons differ only in configuration and are otherwise identical in structure. The formula established for laurolene is,



URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. IV. SYNTHESIS OF LAUROLENE.

BY WILLIAM A. NOYES AND L. P. KYRIAKIDES.

Received June 24, 1910.

Of the two hydrocarbons having the formula C_8H_{14}, the structure of isolaurolene has been established synthetically by Blanc.[3] Eijkman,[4]

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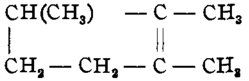
[1] *Chem. Weekblad*, 1906, No. 45; 1907, No. 4; *Chem. Zentr.*, 1907, II, 1208.

[2] THIS JOURNAL, 31, 671.

[3] *Bull. soc. chim.*, (3) 19, 703; *Compt. rend.*, 142, 1084.

[4] *Chem. weekblad.*, 1906, No. 45; 1907, No. 4; *Chem. Zentralbl.*, 1907, II, 1208.

having studied the optical properties of laurolene, has proposed the structure



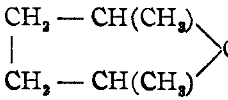
$$\begin{array}{l} CH(CH_3) \quad -C-CH_3 \\ | \qquad\qquad\quad \| \\ CH_2-CH_2-C-CH_3 \end{array}$$

for this hydrocarbon.

Noyes and Derick[1] have given experimental evidence in favor of the formula proposed by Eijkman. They oxidized laurolene, and obtained an active diketone. The only formula for laurolene—an active body itself—consistent with this behavior on oxidation is that proposed by Eijkman.

The object of the present investigation has been to establish the constitution of laurolene by synthesis. As will be seen, we have verified experimentally the constitution of laurolene, as given above.

Preparation of 2,5-dimethylcyclopentanone



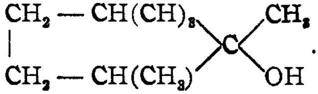
$$\left.\begin{array}{l} CH_2-CH(CH_3) \\ | \\ CH_2-CH(CH_3) \end{array}\right\rangle CO.$$

—The separation of *dl,α,α′*-dimethyladipic acid into its optically active components[2] was undertaken in the hope that this might be the starting point for the preparation, synthetically, of an optically active laurolene. When the dextro-*α,α′*-dimethyladipic acid was mixed with lime and distilled, the resulting dimethylcyclopentanone proved to be optically inactive.

Having failed to secure an optically active ketone, in our further experiments the mixture of "meso" and racemic *α,α′*-dimethyladipic acids obtained by the saponification of dimethyl ketonetetracarboxylic ester (see preceding paper) was used. Portions of 12 to 13 grams of these acids were mixed with about 25 grams of calcium oxide and the mixture placed in a small distilling bulb, of such size that it was nearly filled. The bulb was placed in a bath of Wood's metal and heated until the ketone was formed and distilled away.

By this method 73 grams of the *α,α′*-dimethyladipic acids gave 33 grams of the purified ketone boiling at 146–149°, the main portion at 147–148°. This is about 70 per cent. of the theoretical yield. Zelinsky and Rudski[3] give the boiling point as 145–147°. Better yields of the cyclopentanone are obtained by distilling the acid in portions of 6 grams each.

1,2,5-Trimethylcyclopentanol-1.



$$\left.\begin{array}{l} CH_2-CH(CH)_3 \\ | \\ CH_2-CH(CH_3) \end{array}\right\rangle C \left\langle\begin{array}{l} CH_3 \\ \\ OH \end{array}\right.$$

. — This compound was prepared from the dimethylcyclopentanone by means of the Barbier–Grignard reaction. Eight grams of clean magnesium

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[1] THIS JOURNAL, 31, 669.

[2] *Ibid.*, 32, 1057.

[3] *Ber.*, 29, 304.

ribbon were put in a flask, with 25–30 cc. absolute ether and 50 grams of methyl iodide were added, the flask being provided with a protected reflux condenser. As soon as the reaction became vigorous, the reaction mixture was cooled. Towards the end, it was heated gently on the steam bath. When the solution of the magnesium was complete, the solution was cooled in ice water, and shaken continuously, while 30 grams of the cyclopentanone were added drop by drop, on account of the violence of the reaction. The mixture was left in the cold for about a quarter of an hour and then warmed on the steam bath for an hour. The reaction product soon separated out as a solid.

The ether was then mostly evaporated off, and the product added slowly to crushed ice, while the latter was being stirred. Local heating is to be avoided, as the alcohol has a strong tendency to decompose.

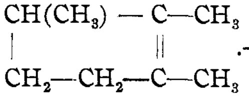
Ice-cold acetic acid was slowly added until the liquid separated into two clear layers. The upper layer was separated, washed once with dilute acetic acid, twice with dilute potassium hydroxide, and dried quickly over sodium sulphate. The cyclopentanol was then fractionated under a very low pressure.

The substance boils at 56–60° in the neighborhood of 8 mm. Yield about 65 per cent.

Analysis:			
	Calculated for $C_8H_{16}O$:	C, 74.98	H, 12.68
	Found:	C, 74.44	H, 12.74

The specific gravity was $d_{4°}^{15°} = 0.9121$.

The refractive index as read on the Abbé refractometer and corrected was $n = 1.4554$ at 16.7°.

Synthetic laurolene, C_8H_{14} or 

$$\begin{array}{lcl} CH(CH_3) & — & C—CH_3 \\ | & & \| \\ CH_2—CH_2 & — & C—CH_3 \end{array}$$

.—Simply heating the cyclopentanol at ordinary pressure induces the breaking off of a molecule of water. However, complete dehydration in this way is a tedious process. In order to obtain the pure unsaturated hydrocarbon, we have usually used Zelinsky's method.[1]

Eleven grams of the cyclic alcohol, which had lost most of its water by two distillations at ordinary pressures, were mixed with 10 grams of powdered anhydrous oxalic acid, heated at 100–110°, and distilled. Repeating the heating with oxalic once more, and subjecting the distillate to steam distillation, drying the product over calcium chloride, and fractionating, we obtained the hydrocarbon boiling at 119–122°. The specific gravity was $d_{4°}^{15°} = 0.8039$.

Analysis of the hydrocarbon after it had stood a month:

Calculated for C_8H_{14}:	C, 87.27 ;	H, 12.72
Found:	C, 87.06, 87.16;	H, 13.15, 13.03.

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[1] *Ber.*, 34, 3249.

In the last preparation of the hydrocarbon we used phosphorus pentoxide as a dehydrating agent. It was necessary to dry the cyclopentanol over phosphorus pentoxide and distil several times before the dehydration was complete. The final fractional distillation gave a product that distilled mostly at 121.6°. The hydrocarbon prepared in this way was found to oxidize rapidly in the air, so that the substance two weeks after its preparation gave 73.86 per cent. carbon instead of the theoretical 87.72 per cent.

In order to free the hydrocarbon from the oxidation product, the mixture was fractionated, and the fraction boiling up to 125° collected. This was then subjected to steam distillation, until the volume of the distillate was about 10 cc. This was dried, and fractionated, when about 5 grams of the hydrocarbon boiling at 120–122° was obtained.

Analysis of the product immediately after distillation:

Calculated: C, 87.27; H, 12.72. Found: C, 86.90; H, 12.94.

The refractive index of the hydrocarbon was = 1.4464 at 16.5°.

In the purification of the alcohol and hydrocarbon we observed the same characteristic green coloration which was observed by Walker and Henderson[1] and which we have often noticed in working with lauronolic acid and laurolene.

The hydrocarbon was oxidized with the theoretical amount of a 2 per cent. solution of potassium permanganate in the cold. The oxidation product was extracted several times with ether, directly from the oxidation mixture. On fractionating the product, about 0.6 gram of substance was obtained boiling at about 75° in the neighborhood of 5 mm.

Analysis: Calculated for $C_8H_{14}O_2$: C, 67.60; H, 9.86
Found: C, 69.79, 70.09; H, 10.42, 10.36.

The substance that was obtained as oxidized in the air, was treated with a little 2 per cent. solution of potassium permanganate and purified. It was analyzed, and gave: C, 71.93; H, 10.59. Working with about 5 grams of the hydrocarbon and the yield in the oxidation product being so poor, we could not expect a very pure product. However, comparison of this oxidation product, with that obtained by Noyes and Derick[2] by the oxidation of the laurolene from the decomposition of aminolauronic acid, shows that they are the same. Noyes and Derick give as the boiling point of their diketone 203.6°. (See the preceding paper). Two samples of our oxidation product, prepared from two distinct preparations of the hydrocarbon, gave 203° and 204° as the boiling points of the oxidation products, respectively.

Noyes and Derick give 0.9844 as the specific gravity of their pure diketone. The one last prepared by us gave 0.9733 at 20°. Both the

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[1] *J. Chem. Soc.*, **49**, 749.

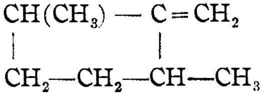
[2] THIS JOURNAL, **31**, 669.

lower specific gravity and the analyses indicate that the diketone retained a small amount of the hydrocarbon from which it was impossible to separate it owing to the small amount available.

Comparison of constants of the hydrocarbons:

	Boiling point.	Sp. gr. at 15°.	n at 16.5°.
C_8H_{14} from aminolauronic acid..........	120–122°	0.8030	1.4471
C_8H_{14} synthetic........................	120–122°	0.8039	1.4464

The structure of laurolene as Δ'-1,2,3-trimethylcyclopentone must therefore be considered as fully established.

Professor Eijkman has kindly determined the refractometric constants of our synthetic laurolene. He finds the refractive index slightly less than that of the laurolene from camphor, as we have done. He also finds the dispersion somewhat less and suggests that the synthetic laurolene may contain some *pseudolaurolene*,  , which would account for the difference. We hope to publish Professor Eijkman's results with laurolene and with some of the other compounds later.

URBANA, ILL., August, 1910.

[CONTRIBUTION FROM THE LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

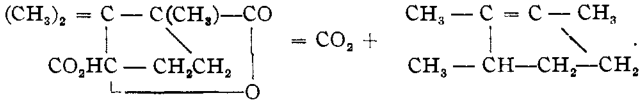
MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. V. MECHANISM OF THE REACTIONS BY WHICH LAUROLENE IS FORMED.

BY WILLIAM A. NOYES.

Received June 24, 1910.

Having established the structure of laurolene (see the preceding papers) it is now possible to discuss intelligently the reactions by which it is formed. The most important of these are the following:

1. By the slow distillation of camphanic acid[1] or by distilling calcium camphanate[2]



The yield is 53 per cent. of the theoretical (Aschan) and the hydrocarbon is sometimes levorotatory and at other times dextrorotatory.

2. By the distillation of lauronolic acid[3] (allocampholytic acid):

$$C_8H_{13}CO_2H = C_8H_{14} + CO_2.$$

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[1] Wreden, *Ann.*, 163, 336; Aschan, *Ann.*, 290, 187; Zelinsky, *Ann.*, 319, 311; Crossley and Renouf, *J. Chem. Soc.*, 89, 27.

[2] Rupe and Maull, *Ber.*, 26, 1202.

[3] Walker and Henderson, *J. Chem. Soc.*, 69, 749.