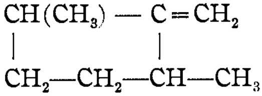
lower specific gravity and the analyses indicate that the diketone retained a small amount of the hydrocarbon from which it was impossible to separate it owing to the small amount available.

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.]

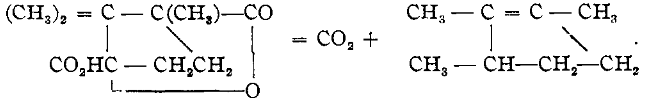
MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. V. MECHANISM OF THE REACTIONS BY WHICH LAUROLENE IS FORMED.

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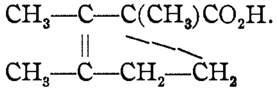
[1] Wreden, *Ann.*, 163, 336; Aschan, *Ann.*, 290, 187; Zelinsky, *Ann.*, 319, 311; Crossley and Renouf, *J. Chem. Soc.*, 89, 27.

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

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

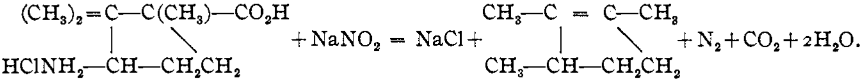
The yield is not given and there is some indication that the allocampholytic acid used was a mixture. The hydrocarbon obtained was levorotatory. The shifting of the methyl group in this case may have occurred either during the formation of the lauronolic acid or during its decomposition to form laurolene. On the basis of refractometric measurements Eijkman concludes that the former is the case[1] and that the structure of lauronolic acid is



$$\begin{array}{l} CH_3—C—C(CH_3)CO_2H \\ \quad\;\; \| \qquad \searrow \\ CH_3—C—CH_2—CH_2 \end{array}$$

It is our intention to study this question further from the chemical side.

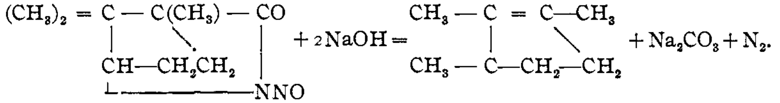
3. By the interaction of sodium nitrite and the hydrochloride of aminolauronic acid.[2]



$$\begin{array}{l} (CH_3)_2{=}C—C(CH_3)—CO_2H \\ \qquad\quad | \qquad \diagdown \\ HClNH_2—CH—CH_2CH_2 \end{array} + NaNO_2 = NaCl + \begin{array}{l} CH_3—C = C—CH_3 \\ \qquad\; | \qquad \diagdown \\ CH_3—CH—CH_2CH_2 \end{array} + N_2 + CO_2 + 2H_2O.$$

The yield is 19 per cent. of the theoretical[3] and the hydrocarbon is dextrorotatory.

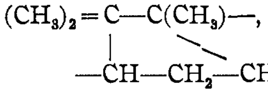
4. By heating the nitroso derivative of aminolauronic anhydride with sodium hydroxide.[4]



$$\begin{array}{l} (CH_3)_2 = C — C(CH_3) — CO \\ \qquad\quad | \qquad \diagdown \qquad\;\; | \\ \qquad CH—CH_2CH_2 \quad | \\ \qquad \llcorner\!——————NNO \end{array} + 2NaOH = \begin{array}{l} CH_3 — C = C—CH_3 \\ \qquad\quad | \qquad \diagdown \\ CH_3 — C—CH_2—CH_2 \end{array} + Na_2CO_3 + N_2.$$

The yield is 53 per cent. of the theory and the hydrocarbon is levorotatory.

A consideration of these reactions leads us to the conclusion that the decompositions which take place lead to the formation of the complex



$$\begin{array}{l} (CH_3)_2{=}C—C(CH_3)— \\ \qquad\quad | \qquad \searrow \\ \quad —CH—CH_2—CH_2 \end{array}$$

which is, of course, incapable of an independent existence. Under these conditions one of the "gem" methyl groups shifts to the lower carbon atom giving an opportunity for the formation of a double union between the two upper carbon atoms of the ring. Erlenmeyer[5] suggested the intermediate formation of a trimethylene ring in such cases but the fact that phenyl groups may shift their places as easily as methyl and that atoms in the para position in such phenyl groups remain para,[6] has rendered this explanation almost untenable. It seems much simpler to assume that one of the methyl groups is momentarily detached only to combine at once with the adjacent carbon atom.

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[1] Private communication.

[2] Noyes, *Am. Chem. J.*, 17, 432.

[3] Noyes and Derick, THIS JOURNAL, 31, 671.

[4] Noyes and Taveau, *Am. Chem. J.*, 35, 379. See also THIS JOURNAL, 31, 671.

[5] *Ber.*, 14, 322.

[6] Montague, *Rec. trav. chim.*, 24, 105; 25, 413.

The loosening of the affinity of the "gem" methyl groups for the carbon atom to which they are attached through the free valences of the two carbon atoms to which that carbon atom is attached is probably an important factor in the reaction.[1] About the only apparent objection to the view here expressed is the ordinary experience with carbon compounds that carbon atoms do not readily separate from each other. But we know that at higher temperatures or in the presence of negative groups such separations do frequently occur. That the parts which separate may recombine to a more stable grouping is to be expected. For the pinacone-pinacolin rearrangement and also for the α- and β-campholytic acids it has been shown that the shifting of the methyl group may be reversible, which points strongly to the probability that separation between carbon atoms may be much more frequent than we have supposed. Only in those cases where an opportunity is presented for a more stable grouping will the separation result in a rearrangement. The fact that laurolene has a higher specific gravity and boiling point than isolaurolene makes it extremely probable that its heat of combustion is also higher and that the shifting of the methyl group is accompanied by a dissipation of energy. Isolaurolene, of course, more nearly retains the structure of camphor. It is, perhaps, worth while to call attention to the fact that in the decompositions of camphanic acid and of the nitroso compound, in both of which cases the two carbon atoms of the ring are associated by a cyclic grouping, the loss of carbon dioxide and formation of laurolene occurs in much larger amount than it does in case 3 where the primary decomposition affects the amino group only.

It may also be remarked that if we assume that these reactions are ionic in character the free valences in the intermediate product will be positive and negative respectively and that the methyl group which shifts its place would be negative as it does so. This is in accord with the hypothesis first proposed by the writer in 1901[2] that atoms of the same element may in different cases assume either positive or negative charges. Essentially the same fundamental idea has been proposed quite independently by Abegg[3] and, from a wholly different point of view, by J. J. Thompson.[4]

The loss of carbon dioxide in these reactions is probably closely related to the loss of carbon dioxide by any ion of an organic acid when it loses its negative charge at the anode in electrolysis.

URBANA, ILL.

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[1] THIS JOURNAL, **31**, 1373.

[2] *Ibid.*, **23**, 463 (1901).

[3] *Z. anorg. Chem.*, **39**, 343 (1904).

[4] "The Corpuscular Theory of Matter," p. 130 (1907).