

PRIMARY DOCUMENTS

27. ON THE CATALYTIC DECOMPOSITION OF ALKYLIDENEHYDRAZINES. (SECOND PART) (UNABRIDGED)

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Translated by Vladislav Suntsov and David E. Lewis

In the previous article, a method for obtaining hydrocarbons based on the catalytic decomposition of alkylidenehydrazines of the type $R:N-NH_2$ in the presence of potassium hydroxide, was described.

In this direction, so far only alkylidenehydrazines originating from ketones (cyclic and bicyclic series) have been studied. In terms of the generalization of the method, it was interesting to explore the decomposition of alkylidenehydrazines of the aldehyde type, as well as to extend it to hydrazine derivatives with the character of an unsaturated ketone.

In this paper, the extension of our method to two series of unsaturated cyclic ketones, dihydrocarvone and carvenone, and the two unsaturated fatty aldehydes, citronellal and citral, is described.

$\Delta^{8(9)}$ -Menthene from Dihydrocarvone

Dihydrocarvone was obtained by Wallach (1) by direct reduction of dextrorotatory carvone (from Schimmel: $[\alpha]_D = +61.58^\circ$) with zinc dust and caustic potash in aqueous alcohol solution; the properties of dihydrocarvone (from the bisulfite compound): boiling point 222.5° at 752 mm.; $[\alpha]_D = -18.36^\circ$.

The compound of dihydrocarvone with hydrazine, $C_{10}H_{16}:NNH_2$, was obtained as follows: a solution of 17 g. of dihydrocarvone and 25 g. 50% hydrazine hydrate in alcohol was boiled under reflux for 5 hours, after which the alcohol and part of the hydrazine hydrate were distilled from an oil bath (bath temperature 140°). The base was dried by warming with fused potash on a water bath.

The decomposition of the base when heated with potassium hydroxide is very easy. The hydrogen [*hydrocarbon?* —translators] was distilled with steam, washed with 50% acetic acid, then with water, and dried with calcium chloride. Yield: 8 g. of hydrocarbon. Purified by boiling over sodium, the hydrocarbon boils at 170° at 750 mm. The smell of the hydrocarbon is very weak, only slightly reminiscent of menthene.

Analysis:

Weighed	0.1900 g;	CO ₂ – 0.6062 g;	H ₂ O – 0.2222 g
C ₁₀ H ₁₈	Calculated	% C –	86.87
		" H –	13.13
	Found	% C –	87.02
		" H –	13.08

Specific gravity

Weight of the compound at 20° – 1.9876 g.

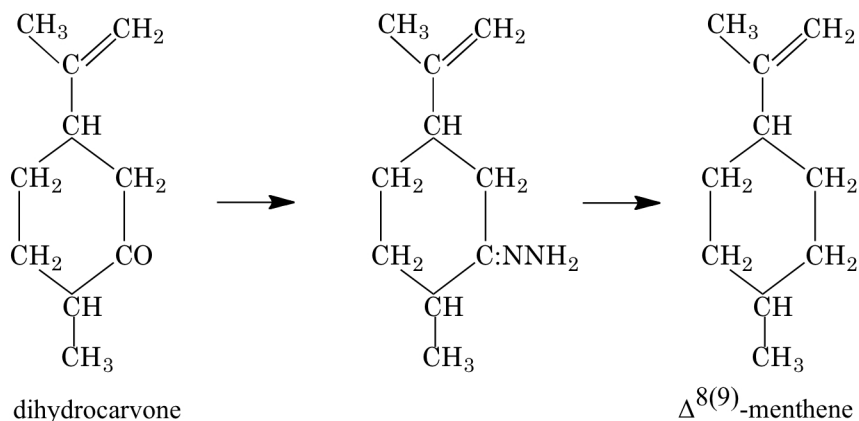
Weight of water at 0° = 2.4300 g.

$$d_{0}^{20} = 0.8142$$

Refractive index $n_D = 1.4523$. Mol. ref. $R^2 = 45.76$. Calculated for C₁₀H₁₈ $R^2 = 45.63$.

Rotation: $[\alpha]_D = -0.79^\circ$

Since it is derived from dihydrocarvone, the hydrocarbon should have the structure of $\Delta^{8(9)}$ -menthene:



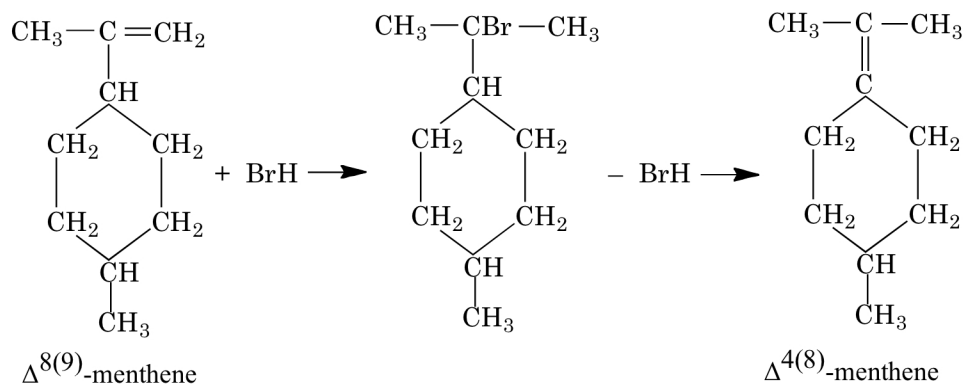
The $\Delta^{8(9)}$ -menthene obtained by Perkin (2) from *n*-menthanol(8) [*i.e.* 8-hydroxy-*p*-menthane —translators] boils at 170-170.5° at 746 mm.

Isomerization of the Hydrocarbon

6 cc of the hydrocarbon were converted into the bromide C₁₀H₁₉Br by first shaking with 20 cc of fuming hydrobromic acid, cooling in ice water, and subsequently at room temperature. Yield: 8 g of the bromide (in place of 7.75 g). On distillation with aniline, the bromide was converted to a hydrocarbon. After washing to remove aniline, and boiling over sodium, the

hydrocarbon had the following properties: boiling temperature: 170.5-172.5° at 752 mm; $d_{20}^{20} = 0.8182$; $n_D = 1.4560$; mol. ref. (3) $R^2 = 45.85$. Calc. for $C_{10}H_{18}$ $R^2 = 45.63$. Optically inactive.

The increase in the weight of the fraction boiling higher than the starting hydrocarbon is due to the partial isomerization of $\Delta^{8(9)}$ -menthene to $\Delta^{4(8)}$ -menthene:



$\Delta^{4(8)}$ -Menthene, obtained by Wallach (4) by the slow distillation of 4-methylcyclohexene-isobutyric acid boils at 172-174°; $d_{21} = 0.831$; $n_D = 1.4647$; when boiled with dilute sulfuric acid, $\Delta^{4(8)}$ -menthene is isomerized to Δ^8 -menthene (5). With this purpose, the hydrocarbon described above was heated under reflux for 8 hours with 20% sulfuric acid. After that, the hydrocarbon boiled at 170-171.5° at 766 mm.; $d_{20}^{20} = 0.8156$; $n_D = 1.4540$.

A mixture of 2 cc. of the hydrocarbon and 2 cc. of amyl nitrite was dissolved in 4 cc. of anhydrous acetic treated at 0° with 1.5 cc. of fuming hydrochloric acid. After the addition of methyl alcohol, a crystalline nitrosochloride deposited; recrystallized from benzene, the nitrosochloride melted at 129°. The melting point of the nitrosochloride corresponds to that of the nitrosochloride of inactive Δ^3 -menthene. The conversion of $\Delta^{4(8)}$ -menthene into Δ^3 -menthene is reflected in the physical properties of the hydrocarbon: the boiling point is lowered to 170-171.5° at 766 mm (instead of 170.5-172.5° at 752 mm) and the specific gravity to 0.8156 (instead of 0.8182 at 20°).

1. Inactive Δ^3 -menthene from carvenone.

Carvenone was prepared as follows: 1 vol. dihydrocarvone was dissolved in 1½ vol. of fuming hydrobromic acid under cooling in ice-water; when diluted with water a dense bromide precipitated, from which carvenone with the following properties was obtained by decomposition with alcoholic alkali by heating on a water bath: b.p. 233.5-234.5° at 750 mm.; $d_{20}^{20} = 0.9263$; $n_D = 1.4828$; optically inactive; semicarbazone melts at 201°.

The compound of carvenone with hydrazine $C_{10}H_{16}:NNH_2$ was obtained by refluxing an alcoholic solution of 8 g. of carvenone and 8 g. of 50% hydrazine hydrate. After distilling off ethanol in an oil bath at 140°, the base was dried with fused potash by heating on a water bath, and then decomposed by distillation in the presence of fused potassium hydroxide. The distillate

was redistilled with steam, washed with 50% acetic acid and water and dried over calcium chloride. The yield was 4 g. of hydrocarbon. After boiling over sodium, the hydrocarbon boiled at 168.7° at 750 mm.

Specific gravity.

Weight of the substance at 20° = 1.9757 g;

The weight of water at 0° = 2.4300

$$d_{0}^{20} = 0.8130.$$

$n_D = 1.4523$; $R^2 = 45.71$; Calc. for $C_{10}H_{18}$ $R^2 = 45.63$.

Optically inactive.

A solution of 3 cc. of the hydrocarbon and 3 cc. of amyl nitrite in 6 cc of anhydrous acetic acid was treated with 2 cc of fuming hydrochloric acid. After the addition of alcohol, the nitrosochloride separates as a white crystalline solid. Recrystallized from benzene, it melts at 128°.

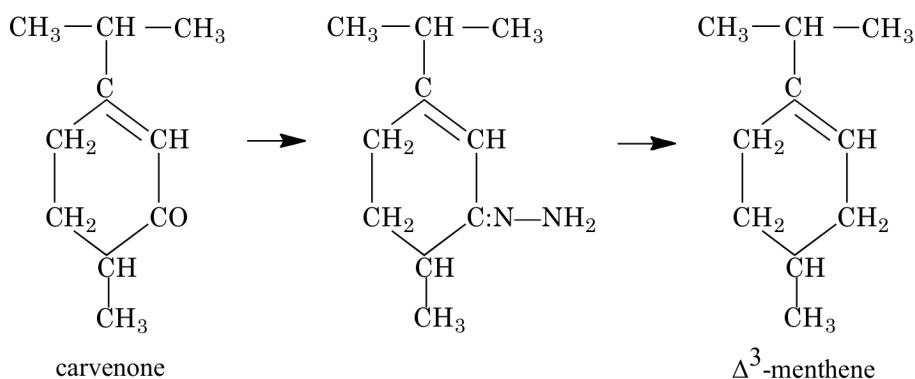
Determination of N

Weighed 0.2303 g: 14.4 cc N (21°, 754 mm)

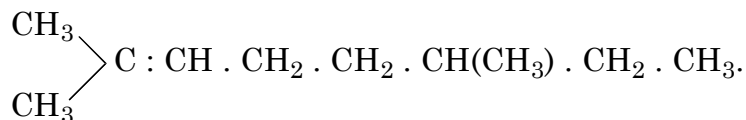
$C_{10}H_{18}NOCl$ calculated % N – 6.88

Found " N – 7.03

The conversion of carvenone to Δ^3 -menthene may be expressed as follows:



2. The conversion of citronellal to the hydrocarbon



A solution of 50 g. of Schimmel's citronellal (rotation $+9.84^\circ$ for 10 cm.) and 50 g of 50% hydrazine hydrate in 125 cc of alcohol was heated under reflux for 3 hours on a water bath, after which the alcohol was distilled off in an oil bath at 140° . The compound of citronellal with hydrazine $\text{C}_{10}\text{H}_{18}:\text{NNH}_2$ that remained was dried with fused potassium hydroxide.

The decomposition of the base in the presence of potassium hydroxide proceeds extremely vigorously; heating is necessary only in the beginning, to start the reaction, and then the decomposition proceeds to completion by itself so rapidly that, in order to avoid the loss of hydrocarbon, no more than 3.2 cc. of the base must be poured into caustic potash at once. The resulting hydrocarbon (35 g.) was washed with water, dried over calcium chloride, and distilled from sodium. The hydrocarbon boils at 164.5° at 756 mm.

Analysis.

Weighed	0.1743 g.:	$\text{CO}_2 - 0.5464 \text{ g.};$	$\text{H}_2\text{O} - 0.2231 \text{ g}$
$\text{C}_{10}\text{H}_{20}$.	Calculated	% C -	85.62
		" H -	14.38
	Found	% C -	85.49
		" H -	14.35

Specific gravity.

Weight of the substance at $20^\circ = 2.3853 \text{ g.}$

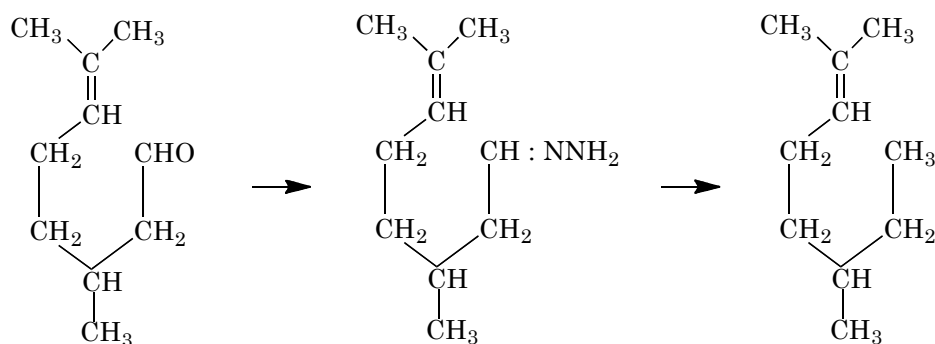
Weight of water at $0^\circ = 3.1670 \text{ g}$

$$d_{0}^{20} = 0.7533.$$

$n_D = 1.4304$; molec. ref. $R^2 = 48.06$. Calc. for $\text{C}_{10}\text{H}_{20}$ $R^2 = 47.74$.

Rotation $[\alpha]_D = +9.28^\circ$

The structure of the hydrocarbon, as shown by a study of the products of its oxidation with potassium permanganate, corresponds to the terpinolene form of citronellal:



For the oxidation of 18 g. of the hydrocarbon, a total of 39 grams KMnO_4 (3 atoms O(6)) were required. The first stage of oxidation, the formation of the corresponding glycol (13 g. KMnO_4), was carried out under cooling with ice water. After the potassium permanganate had been decolorized, a further 13 g. of KMnO_4 was added, and the mixture was heated in a water bath at 50° . After complete reduction of the permanganate, the volatiles were distilled off. The oily layer was separated from the remaining aqueous solution, and, after pre-saturation of the solution with potash, acetone was isolated by distillation. It was characterized by its iodoform reaction, and its conversion to the *p*-bromophenylhydrazone (by the action of *n*-bromophenylhydrazine in 50% acetic acid); shiny flakes, m.p. 93° from ligroin. No acetaldehyde was found.

The oily distillate containing unmodified hydrocarbon was treated with semicarbazide to give a crystalline precipitate of the semicarbazone, which was pressed on a porous plate and decomposed with 10% sulfuric acid. The oily product was isolated by steam distillation, saturated with potash, and dried with fused potash. The substance boils at 218° at 755 mm, and corresponds to a keto-alcohol, $\text{C}_{10}\text{H}_{20}\text{O}_2$.

Analysis.

Weight	0.1704 g.:	CO_2 – 0.4289 g.;	H_2O – 0.1773 g.
$\text{C}_{10}\text{H}_{20}\text{O}_2$.	Calculated	% C –	69.70
		" H –	11.71
	Found	% C –	68.65
		" H –	11.58

$$d_{0}^{20} = 0.9069; n_D = 1.4363.$$

Mol. ref. $R^2 = 49.62$. Calc. for $\text{C}_{10}\text{H}_{19}\text{O}$ $R^2 = 49.84$.

The keto-alcohol is recovered after heating with ammoniacal silver oxide solution; it does not give a color with fuchsinsulfurous acid [*Schiff's reagent; fuchsin and sodium bisulfite* — translators]. The semicarbazone is sparingly soluble in methyl alcohol, from which it crystallizes in rhombohedral plates; from hot benzene solution it crystallizes as needles, m.p. 125-126°.

Determination of N.

I. Weight,	0.1081 g.; 17.5 cc N (18°, 757 mm)	
II. Weight	0.1130 g.; 18.4 cc N (19°, 757 mm)	
C ₁₁ H ₂₃ O ₂ N ₃ calculated % N –	18.34	
	I	II
Found % N –	18.53	18.55

The semicarbanzone rotates the plane of polarized light to the right:

Solvent MeOH

1) concentration 0.5734 g. in 10 cc. of solution

$$[\alpha]_D = +1.78^\circ$$

2) concentration 0.3630 g. in 10 cc. of solution

$$[\alpha]_D = +2.20^\circ$$

To the residue after distillation of the neutral products of oxidation another 13 g. of KMnO₄ was added, and the mixture was heated at 50° until the permanganate had been decolorized. The solution was evaporated to dryness after filtering to remove manganese dioxide, and then decomposed with sulfuric acid. the oily acid liberated was extracted with light petroleum (b.p. 35-50°) and the extract was dried with sodium sulfate. The acid boils at 211-213° (uncorrected).

Specific gravity.

Weight of the substance at 20° = 0.8349 g.

Weight of water at 4° = 0.9047 g.

$$d_{\frac{20}{4}} = 0.9228;$$

$n_D = 1.4198$; $R^2 = 35.64$. Calc. for C₇H₁₄O₂ $R^2 = 36.03$.

Rotation.

Solvent ether;

concentration: 1.4198 g in 10 cc of solution;

$\alpha = +1.24^\circ$; $[\alpha]_D = +8.85^\circ$.

The silver salt (prepared by precipitation from ammoniacal AgNO_3) crystallizes from boiling water as small needles.

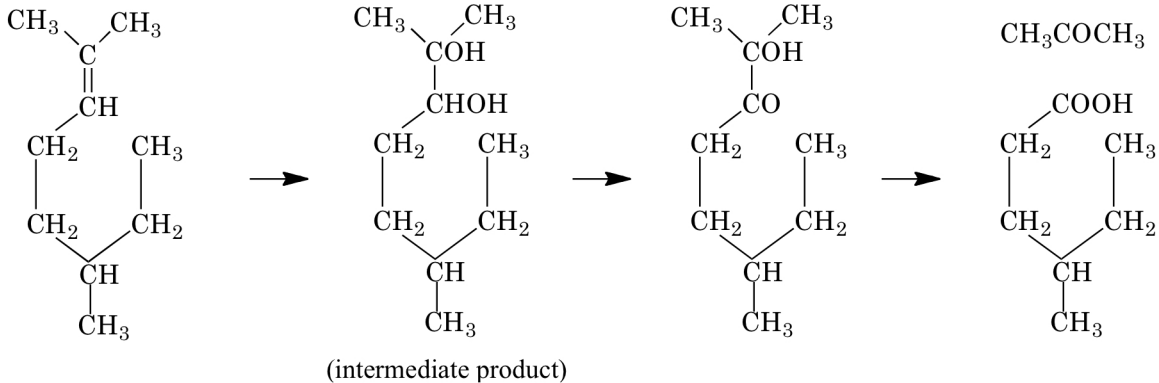
Analysis.

I. Weight 0.2784 g.; $\text{CO}_2 - 0.3592$ g.; $\text{H}_2\text{O} - 0.1356$ g. Ag - 0.1273 g.

II. " 0.1726 g.; Ag - 0.0784 g.

$\text{C}_7\text{H}_{13}\text{O}_2\text{Ag}$.	Calculated	% C -	35.44	
		" H -	5.53	
		" Ag -	45.53	
			I	II
	Found	% C -	35.22	-
		% H -	5.45	
		% Ag -	45.76	45.42

The active amylic acid C_5H_9 $\text{CH}(\text{CH}_3)\text{COOH}$ boils at $212-214^\circ$ (7); the corrected boiling point is 221° at 760 mm; $d_{20} = 0.9149$; $[\alpha]_D = +8.44^\circ$ at 20° (8). With these results, the study of oxidation products the structure of the hydrocarbon $\text{C}_{10}\text{H}_{20}$ is well established:



The Action of Hydrogen Bromide on C₁₀H₂₀

12 cc of the hydrocarbon were converted into the bromide C₁₀H₂₁Br by shaking with 35 cc of fuming hydrobromic acid, first at 0°, then at room temperature. The bromide was washed with water and soda and dried with calcium chloride. Yield: 12 g. Specific gravity of the bromide $d_{0}^{20} = 1.0772$; $n_D = 1.4578$. Mol. ref. $R^2 = 55.83$. Calc. for C₁₀H₂₁Br $R^2 = 56.01$. On distillation of the bromide with aniline, one obtains a hydrocarbon, C₁₀H₂₀, with physical properties very close to the original hydrocarbon: b.p. 163.5-164.5°, $d_{0}^{20} = 0.7515$, $n_D = 1.4293$; mol. ref. $R^2 = 48.12$; calc. for C₁₀H₂₀ $R^2 = 47.74$.

Rotation: $[\alpha]_D = +4.39^\circ$.

Reduction of the Hydrocarbon C₁₀H₂₀

3 cc of the hydrocarbon were heated in a sealed tube with 15 cc of hydriodic acid, sp. gr. 1.96, for 15 hours at 200°. The hydrocarbon boils at 159-159.5° at 742 mm.

Specific gravity.

Weight of the substance at 20° = 0.6616 g.

Weight of water at 4° = 0.9047 g.

$d_{4}^{20} = 0.7313$.

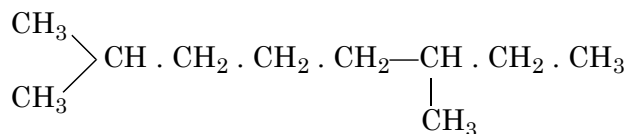
Index of refraction $n_D = 1.4110$; mol. ref. $R^2 = 48.02$. Calc. for C₁₀H₂₂ $R^2 = 48.13$.

Rotation: $[\alpha]_D = +1.75^\circ$.

Analysis.

Weight	0.1257 g.:	CO ₂ – 0.3899 g.;	H ₂ O – 0.1750 g.
C ₁₀ H ₂₂ .	Calculated	% C –	84.40
		" H –	15.60
	Found	% C –	84.59
		% H –	15.58

If the reduction of the hydrocarbon C₁₀H₂₀ with hydriodic acid is not accompanied by isomerization, then the saturated hydrocarbon C₁₀H₂₂ may be represented as 2,6-dimethyloctane



V. Markovnikov and A. Reformatskii (9) obtained a hydrocarbon $C_{10}H_{22}$ with b.p. 158-159° at 745 mm and $d_{0}^{20} = 0.7554$ on reduction of roseol (*l*-citronellol) with hydriodic acid. The boiling point of the M. and R. hydrocarbon coincides with the boiling point of our hydrocarbon; as for the difference in specific gravity, in the M. and R. paper, there is a note (10):

The specific gravity found inspires some doubt, as it is significantly higher than the specific gravity of all known decanes. Unfortunately, it could not be tested due to lack of material.

According to the method of their preparation, both hydrocarbons should be identical.

Recently, A. Skita and G. Ritter (11) isolated a decane with the following properties from the reduction of citral by the method of Sabatier: b.p. 148-152° (?); $d_{4}^{18} = 0.7348$; $n = 1.4138$.

The Hydrocarbon $C_{10}H_{18}$ from Citral

(Preliminary report)

The compound of citral with hydrazine $C_{10}H_{16}:NNH_2$ was prepared by refluxing an alcohol solution of 23 g. of citral (from Schimmel, b.p. 126° at 25 mm) and 23 g. of 50% hydrazine hydrate. After the alcohol was distilled off on an oil bath at 140°, the residue was dried with fused potassium hydroxide. The decomposition of the base in the presence of potassium hydroxide proceeds vigorously after a little warming. The distillate was washed several times with water, steam distilled and dried over calcium chloride; yield 11 g. After boiling over sodium, the hydrocarbon boils at 164-165° at 755 mm.

Analysis.

Weight	0.1671 g.:	CO ₂ – 0.5324 g.;	H ₂ O – 0.1967 g.
C ₁₀ H ₁₈ .	Calculated	% C –	86.87
		" H –	13.13
	Found	% C –	86.94
		% H –	13.18

Specific gravity.

Weight of the substance at 20° = 1.8647 g.

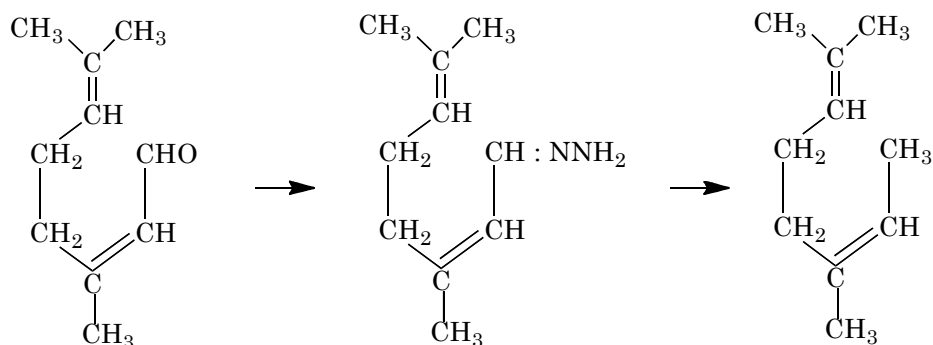
Weight of water at 0° = 2.4300 g.

$$d_{0}^{20} = 0.7674.$$

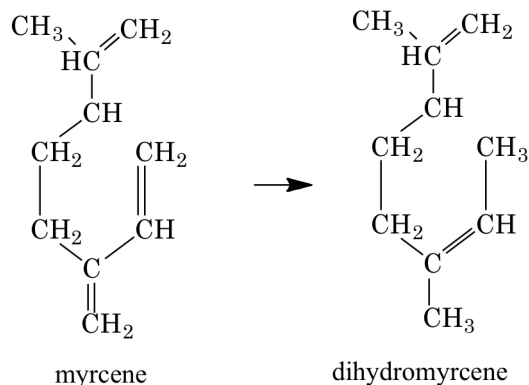
Index of refraction $n_D = 1.4443$; mol. ref. $R^2 = 47.80$. Calc. for $C_{10}H_{22}$ $R^2 = 47.34$.

The hydrocarbon is optically inactive.

If we start from the terpinolene formula for citral, the transformation of citral into the hydrocarbon $C_{10}H_{18}$ may be represented as follows:



The hydrocarbon from citral is an isomer of the dihydromyrcene prepared by Semmler by the reduction of myrcene with Na and C_2H_5OH (12):



Dihydromyrcene boils at $171.5-173^\circ$; $d_{20} = 0.7802$; $n_D = 1.4501$.

Tomsk

1 May, 1911.

References and Notes

1. H. Schrader and O. Wallach, "Zur Kenntniss der Terpene und der ätherischen Oele. I. Ueber Verbindungen der Carvonreihe," *Justus Liebigs Ann. Chem.*, **1894**, 279, 366-390. Cited in the original as Lieb. Ann. **279**, 377.
2. W. H. Perkin Jr. and S. S. Pickles, "Versuche über die Synthese von Terpenen," *Chem. Zentralbl.*, **1905**, II, 239. Abstracted article: "LXIV.—Experiments on the synthesis of the terpenes. Part II. Synthesis of Δ^3 -*p*-menthenol(8), $\Delta^{3,8(9)}$ -*p*-menthadiene, *p*-menthanol(8), $\Delta^{8(9)}$ -*p*-menthene, and *p*-menthane," *J. Chem. Soc., Trans.*, **1905**, 87, 639-655. Cited in the original as Cbl. 1905, II, 239. 45,85
3. [Molecular refraction; it has the advantage that it is almost independent of the density, temperature and aggregation state of the compound, and that it can be predicted on the basis

of simple addition of the of contributions from bonds, atoms or groups. We do not know why Kizhner reports R^2 . See M. Born and E. Wolf, *Principles of Optics*, 4th ed. (Pergamon Press: Oxford, 1970), pp. 88-90. —translators]

4. O. Wallach, "Zur Kenntniss der Terpene und der ätherischen Oele," *Justus Liebigs Ann. Chem.*, **1908**, 360, 26-81. Cited in the original as Lieb. Ann. **360**, 72.
5. Cited in the original as loc. cit. 74.
6. [This is the number of oxygen atoms formally added to one molecule of the hydrocarbon on complete oxidation to acetone and the potassium salt of 4-methylhexanoic acid:
 $C_{10}H_{20} + 2 KMnO_4 \rightarrow C_3H_6O + C_7H_{13}O_2K + 2 MnO_2 + KOH$ —translators]
7. I. Welt, "Contribution à l'étude des dérivés amyliques actifs," *Ann. chim. phys.*, [7], **1895**, 6, 115-144. Cited in the original as Ida Welt. *Ann. chim. phys.* [7], **6**, 132.
8. The b.p. of 221° is too high if we take into account that the normal heptyl [*carboxylic*] acid boils at 222.4° at 743.4 mm.
9. V. Markovnikov and A. Reformatskii, "Issledovanie volgarskogo rozovogo masla [Investigation of the Volga rose oil]," *Zh. Russ. Fiz.-Khim. O-va.*, **1898**, 24, 663-686. Cited in the original as Ж. П. Ф. X. O. **24**, 679.
10. Cited in the original as Loc. cit. 680.
11. A. Skita and H. Ritter, "Über die Sabatiersche Reduktion und ihre Umkehrung," *Ber. dtsh. chem. Ges.*, **1911**, 44, 668-676. Cited in the original as Ber **44**, 668.
12. F. W. Semmler, *Die ätherischen Öle nach ihren chemischen Bestandteilen: unter Berücksichtigung der geschichtlichen Entwicklung*, Veit & Comp., Leipzig, 1906, vol. 1, p 356. Cited in the original as Semmler, "Die ätherischen Öle" v. 1, 356.