PRIMARY DOCUMENTS

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

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Zhurnal Russkago Fiziko-Khimicheskago Obshchestva, **1911**, *43*, 951-962.
Translated by Vladislav Suntsov and David E. Lewis

Supplemental Material

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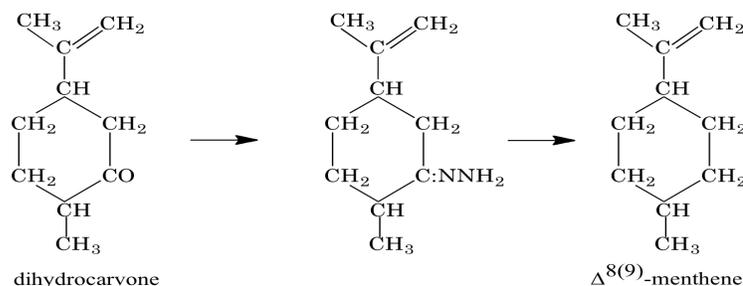
$\Delta^{8(9)}$-Menthene from Dihydrocarvone

Dihydrocarvone was obtained by Wallach (1) by direct reduction of dextrorotatory carvone (from Schimmel: $[\alpha]_D = +61.58°$) with zinc dust and caustic potash in aqueous alcohol solution; the properties of dihydro-

carvone (from the bisulfite compound): boiling point 222.5° at 752 mm.; $[\alpha]_D = -18.36°$.

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

dihydrocarvone $\Delta^{8(9)}$-menthene

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.

... [For the characterization data, see the Supplemental material.]

Since it is derived from dihydrocarvone, the hydrocarbon should have the structure of $\Delta^{8(9)}$-menthene [see scheme above].

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 $C_{10}H_{19}Br$ 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; $d\frac{20}{0} = 0.8182$; $n_D = 1.4560$; 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:

$\Delta^{8(9)}$-menthene $\Delta^{4(8)}$-menthene
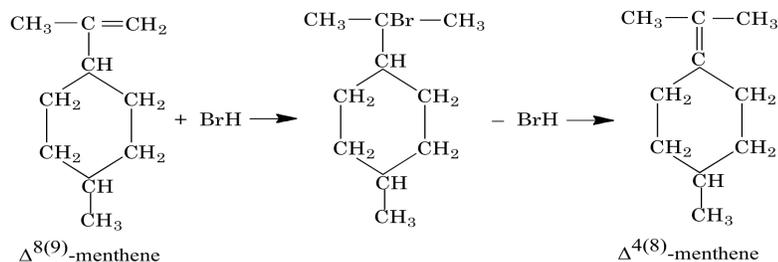
$\Delta^{4(8)}$-Menthene, obtained by Wallach (4) by the slow distillation of 4-methylcyclohexene-isobutyric acid boils at 172-174°; $d_{21} = 0.831$; $n_D = 1.4647$; when boiled with dilute sulfuric acid, $\Delta^{4(8)}$-menthene is isomerized to Δ^8-menthene (5). With this purpose, the hydrocarbon 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.; $d\frac{20}{0} = 0.8156$; $n_D = 1.4540$.

... [For the characterization data, see the Supplemental material.]

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

carvenone Δ^3-menthene
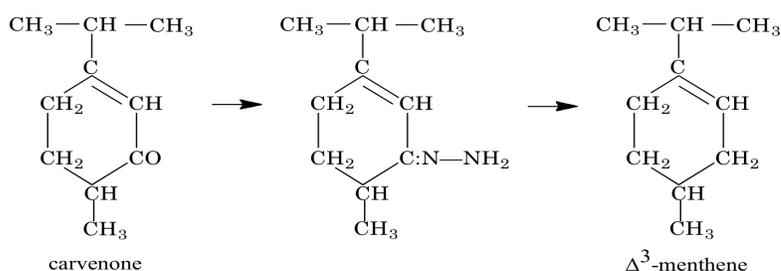
a dense bromide precipitated, from which carvenone with the following properties was obtained by decomposition with alcoholic alkali by heating on a water bath: b.p.

233.5-234.5° at 750 mm.; $d\frac{20}{0} = 0.9263$; $n_D = 1.4828$;

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.

... [For the complete experimental details of this part of this section, see the Supplemental material.]

The conversion of carvenone to Δ^3-menthene may be expressed as follows [see scheme above].

2. The conversion of citronellal to the hydrocarbon

$$\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix} \Big> C : CH . CH_2 . CH_2 . CH(CH_3) . CH_2 . CH_3.$$
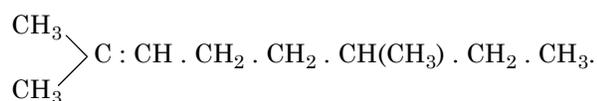
... [For the complete experimental details of this section, see the Supplemental material.]

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:

$$CH_3 \diagdown C \diagup CH_3 \quad CH : NNH_2 \quad CH_3$$
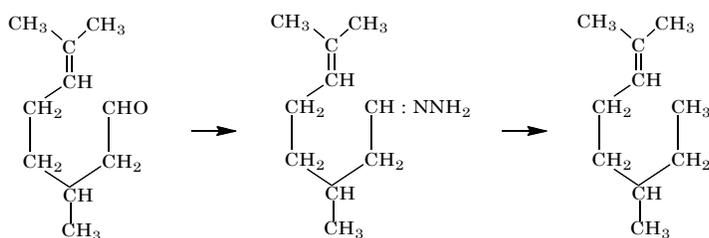
For the oxidation of 18 g. of the hydrocarbon, a total of 39 grams $KMnO_4$ (3 atoms O(6)) were required. The first stage of oxidation, the formation of the corresponding glycol (13 g. $KMnO_4$), was carried out under cooling with ice water. After the potassium permanganate had been decolorized, a further 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, $C_{10}H_{20}O_2$.

Analysis.

Weight	0.1704 g.:	CO_2 –	H_2O –
		0.4289 g.;	0.1773 g.

| $C_{10}H_{20}O_2$.	Calculated	% C –	69.70
	" H –		11.71
	Found	% C –	68.65
	" H –		11.58

$$d\frac{20}{0} = 0.9069; \; n_D = 1.4363.$$

Mol. ref. $R^2 = 49.62$. Calc. for $C_{10}H_{19}$:O $\diagup^{OH}$ $R^2 = 49.84$.

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°.

... [For the complete experimental details of the rest of this section, see the Supplemental material.]

$$\begin{matrix} CH_3 \\ \\ C_5H_9 \end{matrix} \Big> CHCOOH$$

The active amylacetic acid boils at 212-214° (7); the corrected boiling point is 221° at 760 mm; $d_{20} = 0.9149$; $[\alpha]_D = +8.44°$ at 20° (8). With these results, the study of oxidation products the structure of the hydrocarbon $C_{10}H_{20}$ is well established:

(intermediate product)
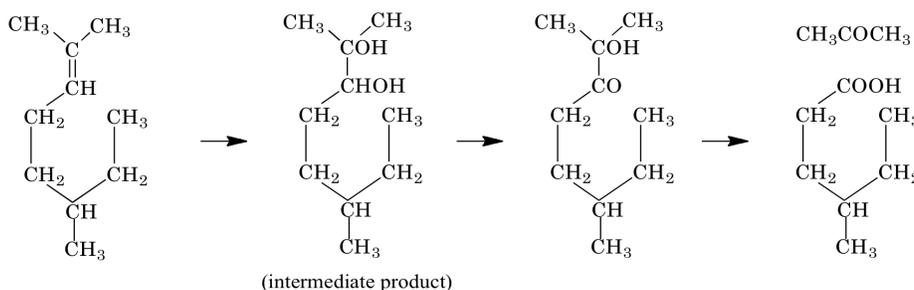
The Action of Hydrogen Bromide on $C_{10}H_{20}$

12 cc of the hydrocarbon were converted into the bromide $C_{10}H_{21}Br$ 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 $d\dfrac{20}{0} = 1.0772$; $n_D = 1.4578$. Mol. ref. R^2 = 55.83. Calc. for $C_{10}H_{21}Br$ $R^2 = 56.01$. On distillation of the bromide with aniline, one obtains a hydrocarbon, $C_{10}H_{20}$, with physical properties very close to the original

hydrocarbon: b.p. 163.5-164.5°, $d\dfrac{20}{0} = 0.7515$, $n_D = 1.4293$; mol. ref. $R^2 = 48.12$; calc. for $C_{10}H_{20}$ $R^2 = 47.74$.

Rotation: $[\alpha]_D = +4.39°$.

Reduction of the Hydrocarbon $C_{10}H_{20}$

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.

... [For the characterization data, see the Supplemental material.]

If the reduction of the hydrocarbon $C_{10}H_{20}$ with hydriodic acid is not accompanied by isomerization, then the saturated hydrocarbon $C_{10}H_{22}$ may be represented as 2,6-dimethyloctane
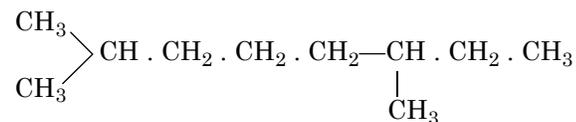
V. Markovnikov and A. Reformatskii (9) obtained a hydrocarbon $C_{10}H_{22}$ with b.p. 158-159° at 745 mm

and $d\dfrac{20}{0} = 0.7554$ 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° (?);

$d\dfrac{18}{4} = 0.7348$; $n = 1.4138$.

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
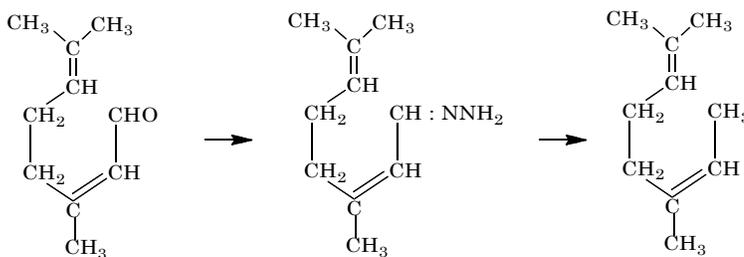

calcium chloride; yield 11 g. After boiling over sodium, the hydrocarbon boils at 164-165° at 755 mm.

... [For the characterization data, see the Supplemental material.]

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: [see scheme above].

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):

myrcene   dihydromyrcene
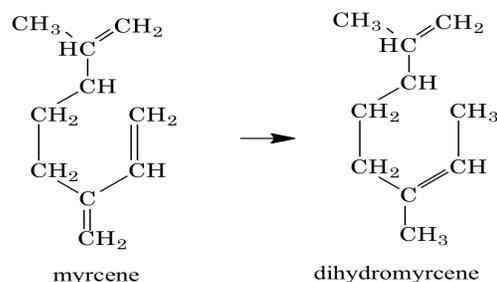
Dihydromyrcene boils at 171.5-173°; $d_{20} = 0.7802$; $n_D = 1.4501$.

Tomsk, 1 May, 1911.

Supplemental Material

An unabridged translation of this paper can be found in the Supplemental Material for the *Bulletin for the History of Chemistry* at the journal's website,

www.scs.uiuc.edu/~mainzv/HIST/bulletin/index.php.

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. Р. Ф. Х. О. **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. dtsch. 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.

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Registration is open for the International Committee for the History of Technology (ICOHTEC) Symposium 2016, scheduled for July 26-30 in Porto, Portugal. The title of the conference is "Technology, Innovation, and Sustainability: Historical and Contemporary Narratives."

Innovation and sustainability have become key words of our everyday life, extending from political and economic discourse to teaching curricula and from the lay public to academia. However, the use of these terms is often abstract and simplistic, ignoring the density of their interrelationships in different geographic, historical and civilizational contexts, and the boomerang character of today's world.

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