The Catalytic Action of Reduced Nickel in the Hydrogenation of Geraniol, Citronellol and Linalool.

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Catalytic hydrogenation is usually reversible when the products remain in the same phase. As Sabatier and Mailhe(1) demonstrated benzene is hydrogenated with hydrogen in the presence of reduced nickel at about 200° to cyclohexane, but at 270-280° it is dehydrogenated to benzene with the same catalyst. Zelinsky(2) found that the vapour of benzene, when passed over palladium black in the presence of hydrogen at 100–110°, gave the good yield of cyclohexane, while on the contrary at 300° it gave almost the quantitative yield of benzene and hydrogen with the same catalyst. In a more recent work Zelinsky and Shujkin(3) found that benzene decomposes to form free methylene radical when heated in the hydrogen atmosphere at 330–350° in the presence of nickel precipitated on aluminium hydroxide. Thus the process of hydrogenation takes place generally at low temperatures and with the elevation of temperature dehydrogenation begins to occur and the resulting unsaturated product is liable to further decomposition.

Reduced nickel promotes on the other hand the elimination of carbonyl group from aldehyde molecule at higher temperatures. According to Ebert(4) acetaldehyde is easily decomposed into carbon monoxide and methane at 175° in the presence of nickel prepared by precipitating from a nickel nitrate solution by sodium hydroxide and reducing with hydrogen at 400°.

It is expected, therefore ,that when an alcohol, which can easily be obtained by hydrogenation of the corresponding aldehyde, is passed over nickel catalyst at higher temperatures, a part of it is dehydrogenated and aldehyde is regenerated and thus an equilibrium is established between the two reactions. But if the resulting aldehyde subsequently decomposes into carbon monoxide and hydrocarbon the equilibrium will be shifted to the side of dehydrogenation even in the atmosphere of hydrogen, and more aldehyde will be produced and be continuously decomposed. It has really been found by the present authors that geraniol, an unsaturated primary alcohol, is reduced mainly to dihydrogeraniol (citronellol) when passed over reduced nickel at 100° in the hydrogen atmosphere, but at 200° it gives a product consisting chiefly of 2,6-dimethylheptane, while at 300° it is mixed with a large quantity of 2,6-dimethylheptene-(2) and 2,6-dimethylheptadiene-(2,6). Methane also was found in the product obtained at temperatures above 200°. It was

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(1) *Compt. rend.*, **137**(1903), 240; *Bull. soc. chim.*, [3] **29**(1903), 975.

(2) *Ber.*, **44**(1911), 3121.

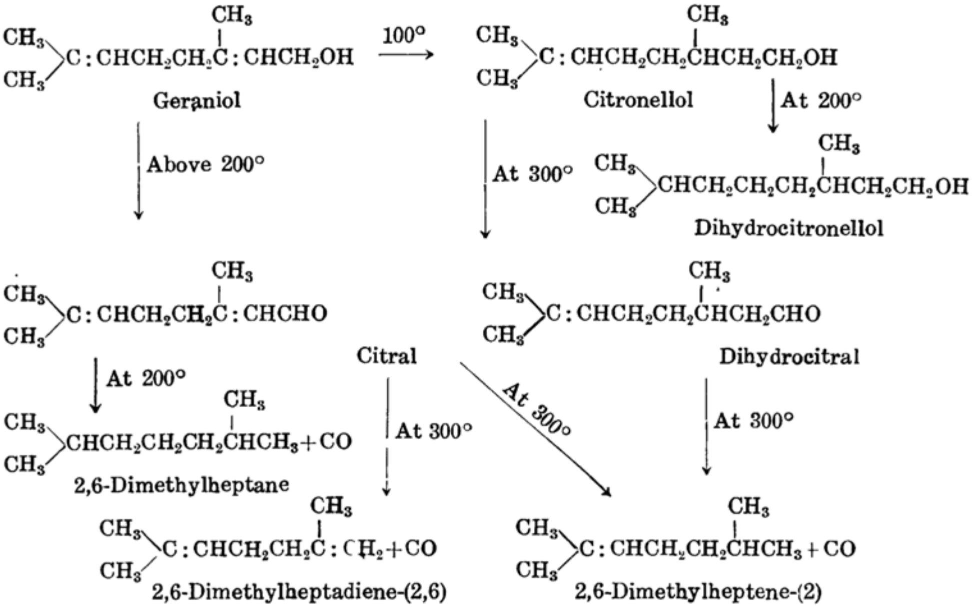
(3) *Chem. Zentr.*, **1935** I, 3540.

(4) *J. Phys. Chem.*, **39**(1935), 422.

produced undoubtedly by the reduction of carbon monoxide; in one run made without the passage of hydrogen the evolution of a large amount of carbon monoxide was really observed.

It is obvious therefore that geraniol is dehydrogenated to citral (geranial) above 200° even in the hydrogen atmosphere and that 2,6-dimethylheptadiene-(2,6), which is produced by the elimination of carbonyl group from citral, is reduced to 2,6-dimethylheptane at 200°, but at 300° a large part of it remains unchanged, while carbon monoxide set free is easily reduced to methane above 200°.

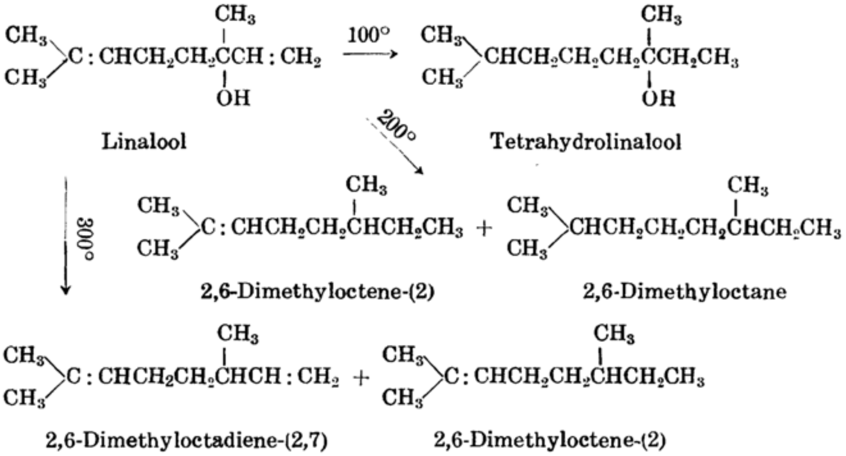
When citronellol is passed over reduced nickel in the hydrogen atmosphere, it is hydrogenated only to a small extent at 100° but to a considerable degree to dihydrocitronellol (tetrahydrogeraniol) at 200°, and the elimination of carbonyl group and the subsequent production of 2,6-dimethylheptene-(2) from citronellol becomes remarkable only at 300°. Thus it seems that the hydroxyl group in citronellol is more stable than in geraniol in the presence of the dehydrogenating catalyst.



The reduced nickel is a strong electron attracting substance, and therefore, when an aldehyde molecule is adsorbed on it, it induces the displacement of electrons within the molecule of the aldehyde. Thus the following electromeric displacement of electrons takes place and the carbonyl group will consequently be brought into an active state and tend to be eliminated:—

$$-\mathrm{C}:\mathrm{C}-\mathrm{C}:\mathrm{O} \rightarrow -\mathrm{C}-\mathrm{C}:\mathrm{C}\rightarrow\mathrm{O} \rightarrow -\mathrm{C}:\mathrm{C}+\mathrm{CO}$$

Linalool, an unsaturated tertiary alcohol, is very easily hydrogenated under the same condition; at 100° it is mainly changed to tetrahydrolinalool. At 200° the main reaction is dehydration accompanied by hydrogenation, and thus 2,6-dimethyloctene-(2) is produced together with 2,6-dimethyloctane. At 300° dehydration almost only takes place, the main product being 2,6-dimethyloctadiene-(2,7) mixed with a small quantity of 2,6-dimethyloctene-(2). The elimination of carbon monoxide and the subsequent production of methane was not confirmed to occur in this case.



Experimental.

The nickel catalyst was prepared electrolytically according to Dr. Inoue's method(5). It was oxidized at 350°, coarsely powdered, packed in a glass tube and reduced at 350°. The sample of the terpene alcohols were passed through the catalyst at required temperatures at a rate of 3 to 5 g. per hour. The liquid reaction products were cooled and gathered in a flask and the gaseous products were collected over a water reservoir and analyzed.

Geraniol.

(1) *Reaction temperature: 100°.* 10 g. of l-geraniol (b.p., 122–123°/20 mm.; d_4^{20}, 0.8782; n_D^{20}, 1.4771) gave fractions shown in Table 1.

Table 1.

Fractions	1	2	3	4
B.p. (10 mm.)	114–115°	115–117°	117–125°	Residue
Yield (g.)	3.5	2.8	0.7	1.2
d_4^{20}	0.8469	0.8526	—	—
n_D^{20}	1.4516	1.4538	1.4578	—

It appears that the fraction 2 mainly consists of citronellol. Longinow and Margoliss(6) gave the following data to *dl*-citronellol:—b.p. (15 mm.), 117–118°; d_4^{20}, 0.8560; n_D^{20}, 1.4543.

(2) *Reaction temperature: 200°.* 20 g. of the *l*-geraniol gave 1.2 g. of water, 15.3 g. of oily product (d_4^{15}, 0.7388) and a large amount of methane. The oil gave fractions shown in Table 2.

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(5) *Reports of Tokyo Imp. Ind. Research Lab.*, **18**(1924), 4.

(6) *Bull. soc. chim.*, [4] **45**(1929), 163.

Table 2.

Fractions	1	2	3	4	5
B.p.	134–135°	135–136°	136–138°	138–145°	Residue
Yield (g.)	2.8	3.7	1.5	1.1	2.3
d_4^{15}	0.7149	0.7164	0.7183	0.7212	—
n_D^{15}	1.4057	1.4068	1.4078	1.4096	—

Fractions 1, 2 and 3 in Table 2 seem to consist chiefly of 2,6-dimethylheptane. Kishner⁽⁷⁾ gave to 2,6-dimethylheptane the following constants:—b p. (756 mm.), 133°; d_0^0, 0.7299; d_0^{20}, 0.7130; n_D, 1.4028; and Escourrou⁽⁸⁾, b.p. (740 mm.), 133–134°; d^{11}, 0.7209; $n_D^{10.5}$, 1.4067.

(3) *Reaction temperature: 300°.* 20 g. of the *l*-geraniol gave 12.2 g. of oily product (d_4^{15}, 0.7584) and a large amount of methane. The oil was fractionated three times and gave fractions shown in Table 3.

Table 3.

Fractions	1	2	3	4	5	6	7
B.p.	To 138°	138–142°	142–147°	147–155°	155–165°	165–175°	Residue
Yield (g.)	1.3	2.3	1.8	2.0	1.4	1.2	1.0
d_4^{15}	0.7293	0.7369	0.7421	0.7499	0.7631	0.7782	—
n_D^{15}	1.4187	1.4240	1.4275	1.4321	1.4392	1.4463	—

All the fractions in Table 3 seem to consist of the mixture of 2,6-dimethylheptane, 2,6-dimethylheptene-(2) and 2,6-dimethylheptadiene-(2,6). Auers and Moosbrugger⁽⁹⁾ gave the following data to 2,6-dimethylheptadiene-(2,6):—b.p. (766 mm.), 144–145°; $d_4^{17.4}$, 0.7649; $n_D^{15.4}$, 1.44319. According to Doeuvre⁽¹⁰⁾ 2,6-dimethylheptene-(2) has the following constants:—b.p. (760 mm.), 142–143°; d_4^{14}, 0.768; n_D^{14}, 1.4321, of which the last two values are evidently too high when compared with those of other dimethylheptenes, dimethylheptanes and dimethylheptadienes. Fraction 3 in Table 3 seems to consist of almost pure 2,6-dimethylheptene-(2). R_L: found, 43.62; $C_9H_{18}\vDash$ requires 43.30.

Citronellol.

(1) *Reaction temperature: 200°.* 20 g. of d-citronellol (b.p. at 5 mm., 99–101°; d_4^{18}, 0.8674; n_D^{18}, 1.4583) gave a small amount of water and 17.2 g. of oily product (d_4^{18}, 0.8144). The oil gave fractions shown in Table 4.

Table 4.

Fractions	1	2	3
B.p.	135–138°	138–142°	Residue
Yield (g.)	2.3	0.7	—
d_4^{18}	0.7191	0.7195	—
n_D^{15}	1.4109	1.4114	—

The residue in Table 4 was fractionated under the reduced pressure of 14 mm. and gave fractions shown in Table 5.

Table 5.

Fractions	1	2	3	4
B.p. (14 mm.)	50–112°	112–114°	114–116°	116–123°
Yield (g.)	0.1	3.9	3.7	1.5
d_4^{18}	0.8367	0.8455	0.8471	0.8485
n_D^{18}	1.4398	1.4411	1.4420	1.4438

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(7) *Chem. Zentr.*, **1913** II, 2130.

(8) *Bull. soc. chm.*, [4] **43** (1928), 1112.

(9) *Ann.*, **387** (1912), 183.

(10) *Bull. soc. chim.*, [4] **45** (1929), 409.

The main parts of the fractions 1, 2 and 3 seem to be dihydrocitronellol. According to Longinow and Margoliss(6) it has the following constants:—b.p. (16 mm.), 110.5°; d_4^{20}, 0.835; n_D^{20}, 1.4405.

(2) *Reaction temperature: 300°.* 20 g. of the citronellol gave 0.6 g. of water and 11.0 g. of oily product (d_4^{18}, 0.7769) which was fractionated as shown in Table 6.

Table 6.

Fractions	1	2′	3
B.p.	134–138°	138–144°	Residue
Yield (g.)	2.3	3.6	3.0
d_4^{18}	0.7294	0.7357	—
n_D^{18}	1.4183	1.4224	—

The residue in Table 6 was distilled under the reduced pressure of 17 mm. and gave 2.7 g. of a fraction with b.p. 115–127°; d_4^{18}, 0.8677; n_D^{18}, 1.4536. The fraction 2 in Table 6 seems to consist mainly of 2,6-dimethylheptene-(2).

Linalool.

(1) *Reaction temperature: 100°.* 10 g. of *l*-linalool (b.p. 98–100°/27 mm.; d_4^{18}, 0.8720; n_D^{18}, 1.4668) gave about 8 g. of oily product which was factionated under the reduced pressure of 21 mm. as shown in Table 7.

Table 7.

Fractions	1	2	3
B.p. (21 mm.)	To 92°	92–95°	95–98°
Yield (g.)	0.7	4.6	2.4
d_4^{18}	0.7877	0.8402	0.8288
n_D^{18}	1.4334	1.4391	1.4385

The fractions 2 and 3 in Table 7 consist mainly of tetrahydrolinalool. Locquin and Sung(11) gave the following constants to tetrahydrolinalool:—b.p. 88–88.5°, (14 mm.); d_4^{15}, 0.8360; n_D^{15}, 1.4388.

(2) *Reaction temperature: 200°.* 20 g. of the linalool gave 1.5 g. of water and 17.0 g. of oil (d_4^{18}, 0.7712) which was fractionated as shown in Table 8.

Table 8.

Fractions	1	2	3	4	5
B.p.	156–161°	161–165°	165–167°	167–175°	Residue
Yield (g.)	2.8	4.8	0.9	1.6	ca. 1
d_4^{20}	0.7520	0.7564	0.7647	0.7760	—
n_D^{20}	1.4239	1.4257	1.4277	1.4302	—

The fractions 2 and 3 in Table 8 consist mainly of 2,6-dimethyloctene-(1 or 2), while the fraction 1 is a mixture of 2,6-dimethyloctane and 2,6-dimethyloctene-(1 or 2). Kishner(12) gave to 2,6-dimethyloctene-(1 or 2) the following data:—b.p. (757 mm.), 163–164°; d_0^{20}, 0.7533; n_D^{20}, 1.4286. According to Willstätter and Mayer(13) 2,6-dimethyloctane has the following constants:—b.p. (724 mm.), 156.5–158°; d_4^{0}, 0.741, d_4^{20}, 0.730; while Enklaar(14) gave b.p. (760 mm.), 158–159°; d_4^{15}, 0.7340; n_D^{15}, 1.4135.

(3) *Reaction temperature: 300°.* 20 g. of the linalool gave 1.0 g. of water and 12.6 g. of oily product (d_4^{20}, 0.8113) which was fractionated as shown in Table 9.

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(11) *Compt. rend.*, **174** (1922), 1428.
(12) *Chem. Zentr.*, **1911** II, 1925.
(13) *Ber.*, **41** (1908), 1478.
(14) *Ber.*, **41** (1908), 2084.

Table 9.

Fractions	1	2	3	4
B.p.	90–160°	160–165°	165–170°	Residue
Yield (g.)	1.1	2.2	2.5	ca. 5
d_4^{20}	0.7555	0.7791	0.7923	—
n_D^{20}	1.4316	1.4412	1.4458	—

The fractions 2 and 3 in Table 9 ocnsist mainly of 2,6-dimethyloctadiene-(2,7). Chablay⁽¹⁵⁾ gave the following data to it:—b.p. (764 mm.), 169–171°; d^{20}, 0.775; n_D^{20}, 1.4482–1.4492 and Asahina⁽¹⁶⁾, b.p. (23 mm.), 68–70°; d_4^{17}, 0.7778; n_D^{20}, 1.4561.

The residue in Table 9 was distilled under the reduced pressure of 16 mm. and gave fractions shown in Table 10.

Table 10.

Fractions	1	2	3
B.p. (16 mm.)	75–85°	85–90°	90–99°
Yield (g.)	1.2	1.8	2.0
d_4^{20}	0.8198	0.8516	0.8730
n_D^{20}	1.4549	1.4600	1.4622

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(15) *Ann. chim.*, [9] **8** (1917), 194.

(16) *Acta Phytochim.* (Japan), 1 (1923), 79; *Chem. Zentr.*, **1923** III, 249.