

210. *Dehydrogenation. Part IV. Catalytic Disproportionation and Dehydrogenation of some Terpenes and Terpene Ketones.*

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A study has been made of the action of palladium and platinum catalysts on the following compounds of the terpene and sesquiterpene groups: limonene, pinene, pinane, cadinene, *isocadinene*, selinene, pulegone, menthone, carvone, dihydrocarvone, carvomenthone, camphor.

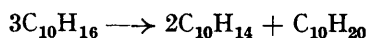
The results throughout were in harmony with the known structures. The experiments under mild conditions gave clear evidence of the skeleton structure and the number of double bonds. For instance, all the unsaturated substances underwent disproportionation into aromatic and saturated compounds at comparatively low temperatures (140° to 205°), the proportions formed being those predictable from the number of double bonds in the original terpene. Carvone was isomerised almost quantitatively to carvacrol. Pinene was converted into *p*-cymene and pinane, the cyclobutane ring being broken. Selinene was the least easily disproportionated hydrocarbon, owing to the presence of a quaternary carbon atom. Nevertheless it gave eudalene with surprising ease at 205°.

All the compounds studied, whether unsaturated or saturated (with the exception of camphor, which was completely resistant), gave their aromatic counterparts with elimination of hydrogen at higher temperatures. The yields of aromatic material were in general considerably better than those obtainable by other methods. Under vigorous dehydrogenating conditions, cadinene underwent elimination of the *isopropyl* group with the formation of 1:6-dimethylnaphthalene.

THE methods which gave satisfactory results (preceding papers and J., 1937, 1146) in effecting the catalytic dehydrogenation and disproportionation of hydronaphthalenes have now been applied to various naturally occurring terpenes, sesquiterpenes and terpene ketones. Dehydrogenation, although widely used in the determination of sesquiterpene structure, has been but little studied in the monoterpene field. Zelinski has, however, made some applications of his discoveries in the dehydrogenation of cycloparaffins to the terpene group, and there have been other isolated observations which are referred to later.

All the substances examined, with the possible exception of selinene, were of established structure. The results recorded below show that the catalytic methods, particularly when used at low temperatures, are capable of giving precise information on skeleton structure and degree of unsaturation. They have the advantage of cleanness in operation and can be used with small amounts of material.

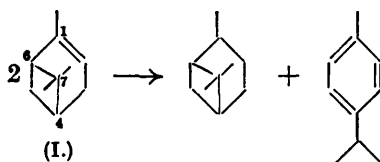
Limonene.—Zelinski (*Ber.*, 1924, 57, 2058) observed that, when limonene vapour was passed over platinised asbestos at 180°, the product was essentially saturated and contained *p*-menthane and an aromatic hydrocarbon, believed to be *p*-cymene. In agreement with this we find that, when pure limonene is boiled over platinised charcoal, no hydrogen is evolved but the unsaturated reactivity is lost. This occurs even at 140°, but no disproportionation could be observed after 24 hours' treatment at 102°. The product formed at 140° was shown to be a mixture of *p*-cymene and *p*-menthane in the approximate molecular ratio of 2 to 0.9. This agrees with the ratio demanded by the disproportionation:



The cymene was identified by conversion into terephthalic acid, under conditions which

permitted a semi-quantitative estimation to be made. The menthane, isolated by removing the cymene by sulphonation, was almost identical in properties with material prepared by direct hydrogenation of limonene. In the vapour phase at 305°, limonene was catalytically dehydrogenated to *p*-cymene in good yield.

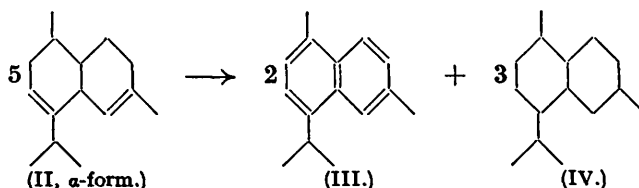
Pinene.—Zelinski (*Ber.*, 1925, 58, 864) observed that, when pinene vapour was passed over palladised asbestos at 190°, the product contained pinane and aromatic material. We find that, when pinene is boiled (156°) with platinised charcoal, it does not lose hydrogen but passes completely into a mixture of *p*-cymene and pinane. These are formed in approximately equimolecular proportion as required by the disproportionation :



p-Cymene was also formed at a temperature (154°) just below the boiling point, but we could detect none at 140°, showing that the fission of the *cyclobutane* ring requires rather more drastic conditions than are necessary for the straightforward dehydrogenation of limonene. Only the 6 : 7- and not the 4 : 7-bond (I) was broken in the dehydrogenation, for *o*-cymene could not be detected in the product.

When pinene was passed over platinised charcoal at 300°, the preponderating reaction was dehydrogenation to *p*-cymene, but again there was some disproportionation to a more hydrogenated hydrocarbon. Pinane itself was slowly dehydrogenated to *p*-cymene at 300° over platinised charcoal with fission of the *cyclobutane* ring, in agreement with Zelinski and Lewina (*Annalen*, 1929, 476, 60).

Cadinene.—Cadinene (II) was unaffected by contact with platinised charcoal at 140°. At 186°, however, it was converted, practically without evolution of hydrogen, into a mixture of cadalene (III) and tetrahydrocadinene (IV). The cadalene was identical with material made by dehydrogenation of cadinene with sulphur, following Ruzicka and co-workers (*Helv. Chim. Acta*, 1921, 4, 508; 1922, 5, 356). The tetrahydrocadinene was almost identical in properties with the material of Semmler and Jonas (*Ber.*, 1914, 47, 2076) obtained by direct hydrogenation. The two compounds were formed in the ratio two mols. cadalene to 2.6 mols. of tetrahydrocadinene, *i.e.*, close to the 2 : 3 ratio required by the disproportionation :



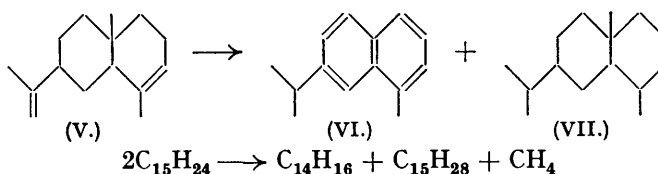
The smoothness of these reactions at this comparatively low temperature supports Ruzicka's formula for cadinene (II). When cadinene was boiled with palladised charcoal, the temperature rose from 243° to 282°. Hydrogen was evolved briskly, but the reaction ceased when only 36% of the quantity required for complete dehydrogenation had been eliminated. The liquid product yielded 50% of cadalene and 44% of tetrahydrocadinene. It is thus clear that more than half the hydrogen fails to escape from the system, but is used up in the reduction to (IV). It is remarkable for hydrogenation to proceed so freely in a boiling liquid at so high a temperature. Some other examples of high-temperature hydrogenation will be found later in this paper.

Ruzicka and Stoll dehydrogenated cadinene to cadalene over platinum in the vapour phase (*Helv. Chim. Acta*, 1924, 7, 85). Over an active platinised charcoal at 305°, we observed a very ready evolution of gas and the formation of a mixture of cadalene and 1 : 6-dimethylnaphthalene, which was identified by comparison of its picrate with authentic material. This seems to be the first example of such a degradation during dehydrogenation

over platinum; it recalls the elimination of the similarly branched side-chain of the steroids from C_{17} . It is probably connected with an abnormally high initial activity of the catalyst (compare this vol., p. 1130). When a second portion of cadinene was passed over the identical catalyst, there was less secondary decomposition and a higher yield of cadalene. Over the same catalyst at 335° there was a very considerable elimination of gaseous hydrocarbon fragments.

A portion of the cadinene fraction of oil of cade failed to give the solid dihydrochloride of cadinene, and from this a sample of *isocadinene* was isolated. This hydrocarbon has already been shown to yield cadalene by sulphur dehydrogenation (Ruzicka and Capato, *Helv. Chim. Acta*, 1925, **8**, 259). We find that over palladised charcoal at 185° *isocadinene* disproportionates without evolution of hydrogen, yielding cadalene. This supports the view that it has the same carbon skeleton as cadinene, but a different arrangement of double bonds.

Selinene.—The experiments were performed with β -selinene (probably V) regenerated from the dihydrochloride. Unlike all the other unsaturated substances described in this paper, it underwent no disproportionation when heated to 183° with an active catalyst. This shows a resistance to dehydrogenation comparable with that of the synthetic catalins containing an angular methyl group (Parts I and II; J., 1937, 1146; this vol., p. 1128) and supports Ruzicka's formula (V).



At 205° , however, prolonged treatment with palladised charcoal formed eudalene (VI) and tetrahydroselinene (VII). This novel type of disproportionation involved a primary elimination of two mols. of hydrogen and one mol. of methane, the hydrogen being almost completely used up in the reduction of the sesquiterpene. This is the first clear example of the elimination of a methyl group from a quaternary carbon atom under conditions sufficiently mild to permit of simultaneous hydrogenation. Both in this case and in that of cadinene, there seems no appreciable tendency for the reaction to stop at the tetrahydronaphthalene stage.

The vapour-phase dehydrogenation of selinene also gave eudalene. It was hoped, by using platinised asbestos, to bring about some migration of the methyl group to an adjoining carbon atom. This catalyst, however, failed to give any picrate-forming product. The easy formation of eudalene in comparatively good yield, 37%, as against a best yield of 10% by the use of sulphur (Ruzicka, Meyer, and Mingazzini, *Helv. Chim. Acta*, 1922, **5**, 356) strengthens the evidence for Ruzicka's formula, but the results of catalytic dehydrogenation throw no further light on the position of the quaternary atom.

Pulegone.—Treibs and Schmidt observed that pulegone and piperitone vapours underwent disproportionation into thymol and menthone over nickel or copper catalysts (*Ber.*, 1927, **60**, 2335; compare Read and collaborators, J., 1929, 2068). We found that at 175° over palladised charcoal liquid pulegone was rapidly converted into an equimolecular mixture of menthone and thymol without evolution of hydrogen:

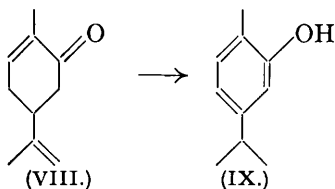


When pulegone was boiled with the same catalyst, some of the hydrogen escaped and the proportion of thymol in the product was increased. In the vapour phase at 300° , thymol was the main product, there was a little dehydration to *p*-cymene, and, surprisingly, still some hydrogenation to menthone (11%).

The menthone formed by disproportionation of *d*-pulegone at 175° was optically inactive, in contrast to that obtained by hydrogenation at room temperature (Skita and Ritter, *Ber.*, 1910, **43**, 3394; Vavon, *Compt. rend.*, 1912, **155**, 287; Read, *Chem. Rev.*, 1930, **7**, 19). It consisted mainly of *dl*-isomenthone, for it yielded a semicarbazone of m. p.

210°. The m. p. of the α -form of this semicarbazone is 219–220° (Hughesdon, Smith, and Read, J., 1923, **123**, 2916; cf. Pickard and Littlebury, J., 1912, **101**, 109; Wallach, *Annalen*, 1913, **397**, 217); other semicarbazones of menthones and isomenthones melt below 190° (Read and Cook, J., 1925, **127**, 2783). The racemisation which accompanies the disproportionation may be attributed to the temporary removal of the hydrogen atom from the asymmetric carbon atom (C_1); it may then return to give either enantiomorph. This process is presumably facilitated by the metallic catalyst, but it is possible that it might be effected by the heat alone (cf. the easy racemisation of piperitone; Read and Smith, J., 1923, **123**, 2267).

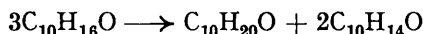
Carvone (VIII).—This doubly-unsaturated ketone stands at the same level of reduction as an aromatic substance with saturated side chains, and its enolate is a double-bond isomeride of carvacrol (IX). No evolution of hydrogen could be detected when it was heated with palladium, and it was converted into carvacrol, the yield of the latter being 95% after 12 hours at the boiling point.



The conversion of carvone into carvacrol has been known for nearly a century (Schweizer, *J. pr. Chem.*, 1841, **24**, 257); this is a particularly smooth method of effecting it. A trace of carvacrol—which is easily identified as the 4-nitroso-derivative—could even be detected after carvone had been kept over the catalyst at room temperature. This isomerisation accounted for the difficulty we experienced in bringing about complete catalytic hydrogenation of carvone to carvomenthone. The uptake of hydrogen, at first rapid, became very slow in the final stages. The reason was that the catalyst had caused some conversion into carvacrol, the aromatic ring of which was comparatively resistant to hydrogenation. Carvacrol was, in fact, found as an impurity in the final product. This recalls the fact that Read, Watters, Robertson, and Hughesdon (J., 1929, 2068) isolated thymol from the products of the catalytic “hydrogenation” of piperitone at room temperature.

Other Ketones.—Dihydrocarvone was converted into carvacrol both at the boiling point and at 175°. The yield at the boiling point was very good and there was little or no hydrogenation. Camphor was unaffected by active catalysts over the range 250° to 420°, as expected from the presence of the five-membered rings. Carvomenthone and menthone were dehydrogenated at the boiling points to carvacrol and thymol respectively. The yield of the latter was particularly good (84%), coming from a saturated ketone.

In comparison with the hydronaphthalene ketones discussed in Part III (preceding paper), the dehydrogenation of terpenic ketones appears to be considerably smoother and there is less tendency for the elimination of oxygen. There was no indication of the hydrogenation of ketones to alcohols under the conditions of disproportionation, *e.g.*, of pulegone to menthol by the process :



The tables on p. 1143 summarise the best yields of aromatic material, and the results of disproportionation of the various compounds.

EXPERIMENTAL.

The apparatus and procedures were those described in Part I (J., 1937, 1153). The suffixes to the catalysts have the significance denoted in Part II (this vol., p. 1130).

Limonene.—The terpene was purified by regeneration from the tetrabromide, m. p. 105°, by the method of von Braun and Lemke (*Ber.*, 1923, **56**, 1652). It had b. p. 176–177°, d_4^{20} 0.8415, n_D^{20} 1.4739.

(1) 10 C.c. of limonene were heated with 0.85 g. of platinised charcoal-*c* in a bath of boiling xylene (140°) for 21 hours. The product (A), freed from catalyst by filtration, was almost unchanged in density and refractivity but was no longer unsaturated to bromine in chloroform. 1.19 G. were agitated at 110° for 20 minutes with 10 c.c. of oleum containing 9% of sulphur trioxide (this procedure had been shown in preliminary experiments to extract cymene from a mixture with menthane). The liquid was cooled and extracted with light petroleum, free from aromatic hydrocarbon. The extract was dried over potassium carbonate, the solvent

removed, and the *p*-menthane distilled. Yield, 300 mg. (Found : C, 85.9; H, 14.2. Calc. for $C_{10}H_{20}$: C, 85.6; H, 14.4%). Its properties are compared below with those of *p*-menthane prepared by direct catalytic hydrogenation of limonene :

	$n_D^{20^\circ}$	$d_4^{20^\circ}$	$[R_L]_D$
<i>p</i> -Menthane by disproportionation	1.4408	0.8010	46.16
<i>p</i> -Menthane by hydrogenation	1.4429	0.8062	46.08

Results obtained by Catalytic Disproportionation and Dehydrogenation of some Terpenes and Terpene Ketones.

Terpene.	Optimum conversion into aromatic counterpart.
Limonene	80% <i>p</i> -Cymene. Vapour-phase dehydrogenation at 305°.
Pinene	75% <i>p</i> -Cymene. Vapour-phase dehydrogenation at 300°.
Cadinene	50% Cadalene. Liquid-phase disproportionation at 243°.
Selinene	37% Eudalene. Liquid-phase disproportionation at 205°.
Pulegone	59% Thymol. Vapour-phase dehydrogenation at 300°.
Carvone	95% Carvacrol. Liquid-phase rearrangement at 220°.
Dihydrocarvone	80% Carvacrol. Liquid-phase dehydrogenation at 225°.
Menthone	84% Thymol. Liquid-phase dehydrogenation at 204°.

Disproportionation.

Terpene.	Temp.	Products.	Proportions.	
			Found.	Calc.
Limonene	140°	<i>p</i> -Cymene + <i>p</i> -menthane	2 : 0.9	2 : 1
Pinene	156	<i>p</i> -Cymene + pinane	1 : 1.1	1 : 1
Cadinene	186	Cadalene + tetrahydrocadinene	2 : 2.6	2 : 3
Selinene	205	Eudalene + tetrahydroselinene	2 : 2.9	2 : 3
Pulegone	175	Thymol + menthone	1 : 0.9	1 : 1

The following procedure was devised for the estimation of *p*-cymene in small quantities of products of this type : 0.5 C.c. of *p*-cymene was boiled for 3 hours with 3.5 g. of chromium trioxide, 15 c.c. of water, 15 c.c. of acetic acid, and 5 c.c. of sulphuric acid. The product was cooled and diluted with water, and the solid collected by filtration, dried, and weighed. Yield of terephthalic acid, 370 mg. It was identified by conversion into the methyl ester. The yield of acid was repeatable and was not appreciably affected by variations in the time of heating or the excess of chromium trioxide used. Under similar conditions limonene gave a trace of terephthalic acid, but menthane gave no measurable amount.

1.12 G. of the product (A) were oxidised with 10 g. of chromium trioxide under the above conditions. 650 Mg. of terephthalic acid were produced, which yielded 850 mg. of the crystalline methyl ester, and corresponded to 760 mg. of cymene. In estimating the proportion of cymene to menthane, the menthane figure is obtained by difference. This corresponds to a higher amount than can actually be isolated, the reason being that oleum attacks menthane to a small extent.

(2) Limonene was unchanged when heated at 102° (boiling *n*-propyl acetate bath) for 24 hours with the same catalyst. The recovered liquid on oxidation gave a very small amount of terephthalic acid, hardly differing from that obtained in a blank experiment on pure limonene.

(3) Limonene (2.50 g.) was passed in the vapour phase over the same catalyst. There were formed 322 c.c. of hydrogen (75%) and 2.13 g. of a liquid, which was dried and distilled. It was nearly homogeneous; 220 mg. yielded on oxidation 170 mg. of terephthalic acid, corresponding to 210 mg. of cymene.

Pinene.—The terpene was twice fractionated from sodium. It had b. p. 156°, $n_D^{20^\circ}$ 1.4660.

(1) 1.0 C.c. of pinene was boiled with 0.1 g. of platinised charcoal-*c* for 11 hours in a stream of carbon dioxide. No significant quantity of gas was evolved but the recovered liquid was saturated to bromine in chloroform and had $n_D^{20^\circ}$ 1.4738. It contained about 50% of *p*-cymene (460 mg. yielded 190 mg. of terephthalic acid).

(2) 6.0 C.c. of pinene were boiled for 24 hours with 0.5 g. of the same catalyst. 3.56 G. of the recovered liquid were agitated for 20 minutes at 110° with 20 c.c. of 9% oleum. The non-aromatic product was isolated by extraction with light petroleum. Yield, 1.06 g. (Found : C, 87.4; H, 12.8. Calc. for $C_{10}H_{18}$: C, 86.9; H, 13.1%). Separate tests showed that pinane was appreciably attacked by oleum under these conditions.

(3) 1.0 C.c. of pinene was heated with 0.1 g. of catalyst for 24 hours at 154° (boiling anisole bath). 600 Mg. of the product yielded 150 mg. of terephthalic acid.

(4) After a similar experiment at 140° (boiling xylene bath) the product yielded no terephthalic acid.

(5) Over the same catalyst in the vapour phase at 300°, pinene (3.0 c.c.) gave 367 c.c. of gas (40% dehydrogenation) and 2.10 g. of a liquid with n_D^{20} 1.4787, d_4^{20} 0.8502. This contained 75% of *p*-cymene, for 600 mg. yielded 370 mg. of terephthalic acid, corresponding to 450 mg. of cymene. The comparatively low elimination of hydrogen corresponds with the occurrence of some hydrogenation. The reduced material was isolated as before. 1.37 G. of the product yielded 0.45 g. of a liquid, unaffected by oleum, with n_D^{20} 1.4463, d_4^{20} 0.8197 (Found : C, 86.6; H, 13.6%). This was probably a mixture of menthane and pinane.

Under the same experimental conditions, pinane was dehydrogenated to the extent of about 25% after one passage over the catalyst. 2.0 C.c. gave 293 c.c. of gas (24%) and a liquid, of which 0.35 g. yielded 0.07 g. of terephthalic acid, corresponding to 0.09 g. of *p*-cymene.

Cadinene.—The sesquiterpene was extracted from oil of cade following Henderson and Robertson (J., 1924, 125, 1992). The fractions of the oil boiling at 105–120°/1.5 mm. were shaken with alkali, dried, dissolved in acetic acid, and saturated with dry hydrogen chloride for 3 days. The crystalline product was recrystallised from glacial acetic acid saturated with hydrogen chloride, to a constant m. p. of 118°. The cadinene dihydrochloride was decomposed by heating with an equal weight of anhydrous sodium acetate in glacial acetic acid for 4 hours at 90° and for 1 hour at the b. p. The mixture was cooled and poured into water, and the sesquiterpene extracted by means of purified light petroleum and dried. Two fractionations, the second over potassium, gave pure cadinene, b. p. 130–131°/11 mm., $n_D^{18.5}$ 1.5090, $d_4^{18.5}$ 0.9240, $[R_L]_D$ 66.25. These values are very close to those reported by Henderson and Robertson. [The density recorded in Simonsen's "The Terpenes," Vol. II, p. 506, (d_4^{20} 0.9819) is a misprint for 0.9189.]

The liquid residues from the preparation of the crystalline dihydrochloride were hydrolysed in the same way to *isocadinene*, b. p. 130°/14 mm.

(1) 1.0 C.c. of cadinene was boiled with 0.1 g. of palladised charcoal-*c* for 160 minutes. The progress of the reaction is indicated below. The theoretical elimination of hydrogen for the complete dehydrogenation, $C_{15}H_{24} = C_{15}H_{18} + 3H_2$, is 319 c.c.

Time (mins.)	1	2	5	15	38	125	150	160
C.c. of hydrogen (corr.)	15	32	59	83	101	109	113	113
% Dehydrogenation	5	10	18.5	26	32	34	35.5	35.5
Temperature	243°	253°	265°	276°	280°	282°	282°	282°

The product was freed from the catalyst, and the picrate-forming material separated by treatment with a large excess of picric acid in alcohol, following Ruzicka's procedure, and then regenerated (450 mg.). It yielded 800 mg. of pure cadalene picrate, m. p. 114.5° alone or in admixture with a sample prepared by sulphur dehydrogenation following Ruzicka, Meyer, and Mingazzini (*loc. cit.*). The material which gave no solid picrate was freed from picric acid with ammonia and from alcohol by evaporation. Distillation yielded 420 mg. of an oil which had no action on bromine in chloroform. To free it from any possible contamination with a tetrahydronaphthalene derivative it was warmed for 30 minutes with 100% sulphuric acid, and isolated by dilution and extraction from ether. After distillation from potassium, 350 mg. of tetrahydrocadinene were isolated, n_D^{17} 1.4811 (lit., n_D^{20} 1.4805) (Found : C, 86.8, 86.7; H, 13.0, 12.85. Calc. for $C_{15}H_{28}$: C, 86.5; H, 13.5%).

(2) 940 Mg. of cadinene were heated at 140° (boiling xylene bath) for 24 hours with 100 mg. of platinised charcoal-*c*. 900 Mg. were recovered which yielded no picrate.

(3) 900 Mg. of cadinene were heated at 186° (boiling *trans*-decalin bath) for 20 hours with 100 mg. of palladised charcoal-*c*. The evolution of gas was only 22 c.c., and 870 mg. of liquid were collected. This was separated as before into 380 mg. of cadalene, which gave 700 mg. of picrate (m. p. 113.5°, mixed m. p. 114°), and 490 mg. of tetrahydrocadinene, which after distillation over potassium had b. p. 128°/11 mm., n_D^{18} 1.4868 (Found : C, 86.8; H, 13.2%).

(4) 1.02 G. of cadinene were passed over platinised charcoal-*c* at 305°. 384 C.c. of gas were evolved, corresponding to 105% dehydrogenation; hence gaseous hydrocarbon must have been eliminated. The recovery of liquid was 710 mg. The aromatic portion, isolated in the usual manner, was converted into the picrate, which melted at about 108° and was clearly a mixture. The hydrocarbon was accordingly regenerated (290 mg.) and fractionally distilled. Four fractions of approximately 50 mg. each were collected. The lowest-boiling fraction gave a yellow picrate, m. p. 108°, and 113° after crystallisation, not depressed by the picrate of 1 : 6-dimethylnaphthalene (m. p. 113°) but depressed to about 90° by cadalene picrate (Found : C, 56.8, 56.9;

H, 4.0, 4.1. Calc. for $C_{12}H_{12}, C_6H_3O_7N_3$: C, 56.1; H, 3.9%). The slightly high carbon figure shows that the elimination of cadalene was not complete. The second fraction also gave mainly the same picrate (m. p. 111° after crystallisation; mixed m. p. with the picrate of 1:6-dimethylnaphthalene 111.5°). The highest fraction was mainly cadalene. The picrate after three crystallisations melted at 111° alone, and at 112° in admixture with cadalene picrate. A mixture with the picrate of 1:6-dimethylnaphthalene melted at about 90° .

(5) When 1.23 g. of cadinene were passed over the identical catalyst at 300° there were formed 340 c.c. of gas (76% dehydrogenation) and 1.05 g. of a liquid containing 700 mg. of picrate-forming material. The picrate from this was a mixture from which pure cadalene picrate was isolated by two crystallisations (m. p. and mixed m. p. 113.5°).

(6) *iso*Cadinene (1.0 c.c.) was heated at 186° for 24 hours with 0.1 g. of palladised charcoal-*d*. There was no significant evolution of gas. The aromatic product (500 mg.) yielded cadalene picrate (m. p. and mixed m. p. 114.5°).

Selinene.—The fraction from celery seed oil boiling at 110 – $160^\circ/18$ mm. was washed with alkali, dried, and fractionated over sodium. The portion, b. p. 132 – $142^\circ/18$ mm., was collected in five 2° fractions, which were separately converted into the dihydrochloride. 10 G. of the sesquiterpene fraction in 30 c.c. of dry ether at -10° were treated with hydrogen chloride for 6 hours. The ether was removed by reducing the pressure; the oily product then solidified (yield, after crystallisation from petroleum, 10 g.). In agreement with Ruzicka, Koolhaas, and Wind (*Helv. Chim. Acta*, 1931, 14, 1132) the freshly prepared dihydrochloride melted at 52° (cf. Schimmel's Report, 1910, 95). α -Selinene was regenerated by methyl-alcoholic potash; b. p. 128 – $130^\circ/11$ mm., $n_D^{18.5}$ 1.5106, $d_4^{18.5}$ 0.9191, in close agreement with Semmler and Risse (*Ber.*, 1912, 45, 3301).

(1) 960 Mg. of selinene were heated at 205° (boiling nitrobenzene bath) with 100 mg. of palladised charcoal-*c*. After 48 hours 45 c.c. (corr.) of gas had been evolved. 940 Mg. of a liquid material were recovered which was separated into 370 mg. of aromatic and 540 mg. of non-aromatic material. The former boiled at $138^\circ/11$ mm. and yielded 710 mg. of eudalene picrate. This melted at 92 – 93° alone or in admixture with a sample of picrate (m. p. 92°) prepared by sulphur dehydrogenation (Found: C, 58.2, 58.4; H, 4.5, 4.8. Calc. for $C_{14}H_{16}, C_6H_3O_7N_3$: C, 58.1; H, 4.6%). Eudalene, regenerated from the picrate, was converted into the styphnate, m. p. 119° , and the *trinitrobenzene* addition compound, m. p. 113° (Found: C, 60.85, 60.65; H, 4.8, 5.0. $C_{14}H_{16}, C_6H_3O_8N_3$ requires C, 60.4; H, 4.8%). Ruzicka, Meyer, and Mingazzini (*loc. cit.*), from eudalene obtained by sulphur dehydrogenation of selinene, obtained a picrate, m. p. 90 – 91° , and a styphnate, m. p. 119 – 120° .

The material which yielded no picrate was refluxed with potassium and distilled. It had b. p. $126^\circ/11$ mm., $n_D^{18.5}$ 1.4850, $d_4^{18.5}$ 0.8920 in close agreement with the properties of tetrahydro-selinene recorded by Semmler and Risse (*loc. cit.*—b. p. 125 – $126^\circ/10$ mm., n_D^{20} 1.4838, d_4^{20} 0.8889).

(2) When selinene was heated at 183° with the same catalyst for 20 hours, it gave no gas and its properties were practically unaltered.

(3) As a preliminary to a dehydrogenation in the vapour phase a sample of selinene was passed over a platinised charcoal catalyst (*-c*) at 325° to subdue its initial activity, after which the catalyst tube was thoroughly swept out with a current of hydrogen. 1.18 G. of fresh selinene were then passed over the same catalyst at 310 – 315° . There were formed 198 c.c. of gas and 950 mg. of a liquid product. The material which formed no picrate (600 mg.) boiled at 126 – $130^\circ/13$ mm. and had n_D^{19} 1.5435, d_4^{19} 0.9400; whence it was probably a tetralin derivative or an equivalent mixture. The picrate-forming material (320 mg.) was separated by distillation into five fractions, all of which yielded eudalene picrate. The main fraction is typical: After two crystallisations, the picrate from it melted at 92° alone and in admixture with eudalene picrate (Found: C, 58.1; H, 4.5. Calc. for $C_{14}H_{16}, C_6H_3O_7N_3$: C, 58.1; H, 4.6%).

(4) Attempted dehydrogenation of selinene over platinised asbestos-*c* at 320° and at 340° yielded practically no picrate-forming material.

Pulegone.—The commercial ketone was twice fractionated. The fraction, b. p. 105 – $110^\circ/12$ mm., was converted into the semicarbazone, which was crystallised from alcohol to constant m. p. 172° (cf. Baeyer and Henrich, *Ber.*, 1895, 28, 653). Regeneration yielded *d*-pulegone, b. p. 222° , n_D^{20} 1.4883, d_4^{20} 0.9402, $[\alpha]_D^{20} + 19.22^\circ$. The measurement of rotatory power was observed for the homogeneous liquid in a 1 dm. tube. The same is true for all the other measurements recorded below. The physical properties agree satisfactorily with those given in the literature, although the rotatory power is rather lower.

(1) 5.0 C.c. of pulegone were heated at 175° for 135 minutes with 0.5 g. of palladised charcoal-*d*. No hydrogen was evolved. The product was extracted in ether, filtered from catalyst, recovered by careful evaporation, and separated by fractional distillation and freezing into 2.05 g. of thymol, m. p. 52°, and 1.91 g. of *dl*-isomenthone, which yielded a semicarbazone, m. p. 210°. To confirm the yield and lack of rotation of the menthone formed, the experiment was repeated on a larger scale (20 g.) and the heating prolonged for 24 hours. Yield of menthone, 51%. It showed no detectable rotation in a 1 dm. tube.

(2) 2.82 G. of pulegone were boiled with 10% of the same catalyst for 4 hours at 220°. The recovered liquid (2.51 g.) was separated into pure thymol (1.56 g.) and menthone (0.80 g.). No cymene could be detected; but a small quantity was isolated in a similar experiment which was allowed to proceed for 24 hours. It had b. p. 60°/14 mm., n_D^{20} 1.4870, and was identified as before. The other two products were the same.

(3) 3.0 C.c. of pulegone were passed over a column of the same catalyst at 300°. The evolution of hydrogen corresponded to 55% dehydrogenation. The product was separated into *p*-cymene (0.15 g.), b. p. 61°/14 mm., n_D^{20} 1.4870, identified as before, and a high fraction (2.0 g.), b. p. ca. 112°/15 mm. This gave 1.66 g. (59%) of thymol, m. p. 52°, and 11% of *dl*-isomenthone (semicarbazone, m. p. 210°).

Carvone.—The commercial ketone was distilled, and the fraction of b. p. 90—95°/10 mm. converted into semicarbazone (m. p. 162°). The physical constants of the regenerated ketone were in excellent agreement with those in the literature: B. p. 229°, n_D^{20} 1.4995, d_4^{20} 0.9600, $[\alpha]_D + 58.12^\circ$.

In the following experiments, 3.0 c.c. of carvone were heated to the temperature named with 10% of palladised charcoal-*d*. In no case was any detectable quantity of hydrogen evolved.

Temperature	228°	230°	150°	95°	20°
Time (hours)	2	12	24	72	12
Yield of carvacrol, %	81	95	59	1	trace

The product in each case was washed out of the apparatus with light petroleum, and the carvacrol extracted from the solution with 50% aqueous sodium hydroxide (carvacrol cannot be extracted from an ethereal solution in this way). The carvacrol was then liberated by acidification and isolated by means of ether. In experiment 1, 2.43 g. were obtained, n_D^{20} 1.5223. In all cases the carvacrol was identified as follows: An ice-cold solution of 1 part of carvacrol in 4 parts of alcoholic hydrogen chloride, saturated at 0°, was treated with a concentrated aqueous solution of sodium nitrite. The 4-nitrosocarcacrol, so formed, melted at 153° after crystallisation from alcohol.

Dihydrocarvone.—This was prepared by reducing carvone with zinc and alkali, following Wallach and Schrader (*Annalen*, 1894, 279, 377). It had b. p. 221°, n_D^{20} 1.4713, d_4^{20} 0.9247, $[\alpha]_D - 14.78^\circ$. These physical constants agree closely with those found by Wallach (*Annalen*, 1893, 275, 116).

(1) 3.0 C.c. of dihydrocarvone were boiled for 3 hours with 10% of palladised charcoal-*d*. Hydrogen corresponding to 92% dehydrogenation was evolved. The product was worked up as described above for carvone, and yielded 80% of carvacrol, identified as the 4-nitrosoderivative.

(2) In similar experiments performed at 175°, carvacrol was also formed, although slowly. The yields were 19% in 7.5 hours and 37% in 22 hours. Owing to the large amount of unchanged material, the saturated ketone, which was presumably formed at the same time, was not isolated.

Carvomenthone.—Twice fractionated *d*-carvone was hydrogenated, palladised charcoal-*d* and then Adams's catalyst being used. The first 3 l. of hydrogen were taken up very rapidly, but the rate then fell off and the theoretical quantity (6.1 l.) was absorbed only after 48 hours. The product was freed from a small quantity of carvacrol by means of 50% aqueous potassium hydroxide. It had b. p. 222°, n_D^{20} 1.4554, d_4^{20} 0.900 (compare Wallach, *Annalen*, 1893, 277, 135), and yielded the semicarbazone, m. p. 195°, described by Baeyer (*Ber.*, 1895, 28, 1601).

Dehydrogenation over 10% of palladised charcoal-*d*, for 2 hours at the b. p., yielded 18% of hydrogen and 15% of carvacrol, isolated and identified as before.

Menthone.—45 G. of *l*-menthol, m. p. 43°, were oxidised with 60 g. of potassium dichromate, 50 c.c. of concentrated sulphuric acid, and 300 c.c. of water. The menthone had b. p. 204°, n_D^{20} 1.4510, d_4^{20} 0.8960, and yielded a semicarbazone, m. p. 179°.

When it was boiled with palladised charcoal-*d* (10%), the b. p. rapidly rose to 222°. After 2.5 hours the evolution of hydrogen corresponded to 98% of the theoretical for complete

dehydrogenation to thymol. The product was worked up as described above for the products from pulegone. Crystalline thymol was isolated in 84% yield.

Camphor.—The commercial ketone was sublimed to constant m. p. 178°. It was compressed into small pellets, which were introduced into a broad glass tube terminated by a small bulb. Through this bulb was fused a thin tube, by means of which hydrogen could be passed to assist in the sublimation of the camphor. The other end of the broad tube led by means of a ground joint to the tube containing the catalyst. Apart from this, the apparatus resembled that used in previous work for vapour-phase dehydrogenation. The catalyst tube was heated by means of an electric furnace, wired so as to give a temperature constant throughout its length to 2°. The temperature was read by means of a thermocouple. The catalyst was heated to 250° and the camphor was slowly sublimed in a slow stream of hydrogen. It collected unchanged at the far end of the apparatus. The experiment was repeated at 320° and at 420° with the same negative results.

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