ON THE CATALYTIC ACTION OF ACTIVE CARBON UPON TERPENES AND THE RELATED COMPOUNDS.

By Seizo KIMURA.

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The investigations of Ruzicka and his co-workers(1) on the compounds of the higher terpene series with use of the dehydrogenation reaction of sulphur are too well known to need detailed statements. The present author has used active carbon together with sulphur in his studies and found that cyclic compounds of the terpene series can, in liquid phase, easily be transformed into aromatic compounds. This fact made him interested in the catalytic action of active carbon upon terpenes and the related compounds, so as to start an investigation on this reaction especially in the liquid phase.

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(1) *Helvetica Chim. Acta*, **4** (1921), 505.

The studies of catalytic action of active carbon have been made by various workers and some of the results have been already applied in industry. Most of them were, however, made by the reaction in the gaseous phase and up to 1932 there was none made upon the compounds of terpene series, except that of Asahina and Nakanishi(2) who reported the fact that cineol is converted to *p*-cymene by the action of palladium-charcoal or charcoal for bleaching purpose. The present author has also made investigations, in relation to the dehydrogenation reaction of sulphur, upon the action of active carbon alone on cineol. He then found a small quantity of *p*-cymene as the dehydration and dehydrogenation product of cineol.

(I) **Catalytic Action upon Menthone and Piperitone.** As active carbon exerts dehydrogenation action, it is expected to cause upon the terpene-ketones capable of existing in the enol form, such as menthone and piperitone, simultaneously a dehydrogenation action and a keto-enol metamerization. *l*-Menthone (b.p. 72°C./6 mm., $d_4^{25.5}$ 0.8905, n_D^{20} 1.4513, $[\alpha]_D^{30}$ -24.75) (50 g.) made by oxidation of menthol by Beckmann's method was heated with 25 g. of active carbon under a reflux condenser for 20 hours, the internal temperature being kept at 220°C. From the resulting oily material, about 2.7–3.4 g. of a phenolic substance was extracted with 5% NaOH solution. In this latter substance *m*-cresol was identified by elementary analysis and also by conversion into trinitro-*m*-cresol (m.p. 105–106°C.). A small quantity of thymol was also identified as thymol phenylurethane (m.p. 106–107°C.). The residue after the removal of the phenolic substance consisted of unacted menthone and it was noticed that during this reaction there was an optical transformation of *l*-menthone into *d*-menthone.

Piperitone (b.p. 90.5–92°C./5 mm., d_4^{24} 0.9305, $n_D^{26.8}$ 1.4831, $[\alpha]_D$ -48.22) (50 g.) prepared by refining oil of *Eucalyptus dives* of Australian origin was heated with 25 g. of active carbon for 20 hours, the internal temperature being kept at 200–240°. About 13.4 g. of a phenolic substance was extracted from the reaction product by treating it with 5% NaOH solution. As before, in this phenolic substance, *m*-cresol was identified by the elementary analysis and conversion into trinitro-*m*-cresol (m.p. 105–106°C.), and a small quantity of thymol was recognized by the elementary analysis and conversion into thymol phenylurethane (m.p. 106–107°C.). The residue after separating the phenolic substance consisted chiefly of the unacted piperitone which was identified by preparing α- and β-semicarbazones (m.p. 226–227° and 174–176° respectively). As expected, the keto-enol metamerization took place by which the enol form of menthone or piperitone was first formed. By their

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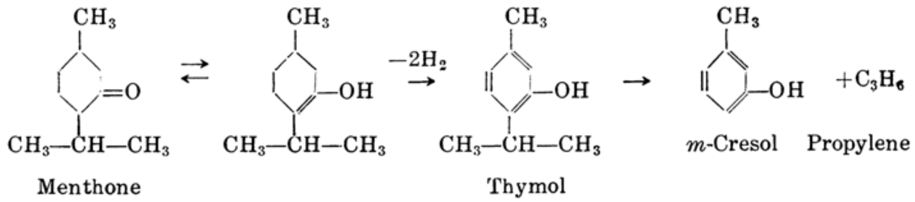
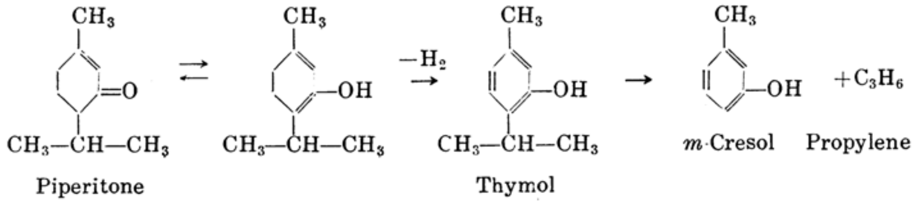
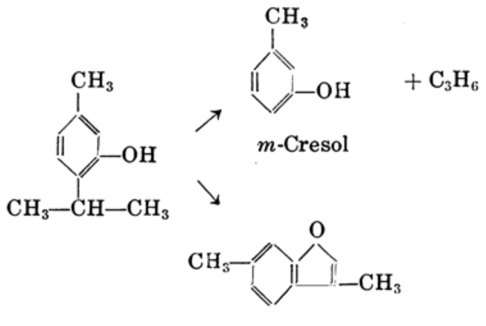
(2) *J. Pharm. Soc. Japan*, **52** (1928), 1.

dehydrogenation, thymol was then produced from which the isopropyl group was split off to form *m*-cresol as represented in the following scheme :





In order to make the final mechanism clear, 50 g. of thymol (m.p. 50–51°C.) was mixed with 25 g. of active carbon and subjected to the same treatment as before by which about 7.3 g. of a phenolic substance was obtained. This latter substance was proved by elementary analysis and by the formation of trinitro-*m*-cresol to be chiefly *m*-cresol itself. It was interesting here to find that about 5.4 g. of a neutral substance was obtained which was identified as 2,5-dimethylcumarone by the physical constants of its principal distillate (b.p. 212–217°C., $d_4^{25.5}$ 1.0352, $n_D^{22.5}$ 1.5521), molecular refraction (found : 44.66–44.99, theoretical : 43.76 for $C_{10}H_{10}O|^{=}_{4}$), colour reaction, elementary analysis, and the formation of its picrate (m.p. 75–76°C.). In this way, thymol is changed to *m*-cresol by splitting off of the isopropyl group by the action of active carbon. At the same time it undergoes dehydrogenation and is changed into a compound of cumarone series. This is represented by the following scheme :



2,5-Dimethyl-cumarone

This formation of dimethylcumarone is presumed to take place also when menthone or piperitone is acted upon by active carbon ; though its identification is expected to be impossible on account of a too small trace of it present.

(II) Catalytic Action upon Cyclic Terpene Alcohols. From the resemblance of the properties of active carbon with those of acid clay, Florida earth, etc., it is inferred that it will also exert a dehydration action upon terpene alcohols. For examining the action of active carbon, *d*- and *l*-terpineol were taken as representative members of cyclic tertiary terpenealcohols. *d*-*α*-Terpineol (m.p. 35°C., d_4^{15} 0.9390, n_D^{14} 1.4843, $[\alpha]_D^{25}$ +9.85) (100 g.) made by refining pine oil of the American origin was heated with 20 g. of active carbon for 5 hours at about 200°C. About 67.9 g. of an oily product and 9.8 g. of water were obtained. By repeated refining of the oil, it was proved by the physical constants, molecular refraction, elementary analysis, and by the formation of dipentene-tetrabromide (m.p. 124°C.) that it consisted almost entirely of dipentene.

By the action of boric acid upon brown comphor oil, after the removal of safrol, an alcoholic substance was obtained which was separated as boric acid ester. By refining the latter product, *l*-*α*-terpineol (m.p. 35°C., $d_4^{24.8}$ 0.9323, n_D^{25} 1.4802, $[\alpha]_D^{25}$ −13.70) was prepared. This substance (25 g.) was mixed with 5 g. of active carbon and heated for 6 hours at about 200°C. About 19.6 g. of an oily product and 4.3 g. of water were obtained. In this oil, dipentene was also identified.

Active carbon was also made to act upon *l*-menthol and *d*-borneol as representative of cyclic secondary terpene alcohols.

l-Menthol (m.p. 42–43°C., $[\alpha]_D^{12}$ −49.07 in alcoholic solution) (50 g.) was heated with 10 g. of active carbon for 5 hours at 200°C. An oily distillate (16.9 g.) and 3.6 g. of water were obtained. The principal distillate was shown to be Δ^3-*p*-menthene by its physical constants (b.p. 166-167°C., d_4^{22} 0.8108, n_D^{22} 1.4532, $[\alpha]_D^{21}$ +15.22), molecular refraction (Found: 45.958, theoretical: 45.713 for $C_{10}H_{18}|\overline{\overline{1}}$), and elementary analysis. The dextro-rotatory property of this substance is especially to be noted. The residual part in the flask was extracted with ether and proved to be unchanged *l*-menthol.

d-Borneol (m.p. 203–204°C.) (50 g.) was heated with active carbon (50 g.) for 4 hours over direct flame. On distilling, 31.4 g. of an oil and 6 g. of water were obtained. By repeated distillation, the principal distillate was found to correspond well to camphene in its physical constants (b.p. 158–161°C., d_4^{15} 0.8651, $n_D^{22.5}$ 1.4685), molecular refraction (found: 44.025, calculated for $C_{10}H_{16}|\overline{\overline{1}}$: 43.513), and the results of elementary analysis. The trial to separate a crystalline sample of camphene from this material by cooling was rewarded only with a minimum quantity of crystals melting at 49°C. and with a camphor-like odour.

Judging from these experimental results, the dehydration activity of active carbon resembles that of acid clay though it is not so violent as the latter. With acid clay, the action is quickly completed in 20–30 minutes, while with active carbon it proceeds slowly and at a rather high temperature.

(III) Catalytic Action upon Acyclic Terpene Alcohols. Upon the presumption that the action of active carbon must be the same on acyclic compounds as on cyclic compounds, its reaction was studied upon geraniol and linalool representing cyclic terpene-alcohol compounds.

Geraniol to be used was separated and refined from citronella oil of the Javanese origin and had d_4^{15} 0.8807, n_D^{17} 1.4769, and $[\alpha]_D^{15} \pm 0$. It (200 g.) was heated with 40 g. of active carbon for 21 hours at 225°C. About 130 g. of an oily matter and 16.1 g. of water were obtained. By repeated distillation, the lower boiling portion (b.p. below 70°C./8 mm.) yielded myrcene which was identified by its physical constants (b.p. 47–49°C./7.5 mm., d_4^{15} 0.8062–0.8081, n_D^{15} 1.4667–1.4692, $[\alpha]_D^{16} \pm 0$), molecular refraction (found: 46.846–46.982, calculated for $C_{10}H_{16}|\overline{3}$: 46.979), and the results of elementary analysis. Besides myrcene thus identified, there was also found dipentene recognizable by conversion into its tetrabromide. The portion of the intermediate boiling points (b.p. 100–110°C./8 mm.) consisted chiefly of the unchanged geraniol. When the latter was removed, the residue showed physical constants well approaching those of linalool. The higher boiling portion (b.p. above 110°C./8 mm.) was repeatedly distilled, but it gave nothing worth of being considered as the chief constituent. However, it is presumed to have been oxides of the diterpene series.

Linalool prepared by refining the linalool of bois de rose, had the constants: b.p. 74°C./5.5 mm., d_4^{23} 0.8687, $n_D^{23.5}$ 1.4590, $[\alpha]_D^{24}$ −14.18. It (300 g.) was mixed with 60 g. of active carbon and subjected to the same procedure as before. An oily product weighing 159.7 g. was obtained together with 29.6 g. of water. The oily matter gave by repeated fractional distillation a lower boiling portion (b.p. below 70°C./7 mm.) which yielded as the chief constituent dipentene (tetrabromide m.p. 124°C.) besides a small quantity of a substance corresponding to myrcene (b.p. 43–44°C./5.5 mm., d_4^{20} 0.8087, n_D^{20} 1.4671). The portion of the intermediate boiling points (b.p. 70–85°C./7 mm.) consisted chiefly of the unchanged linalool. The higher boiling portion (b.p. above 85°C./7 mm.) gave a compound showing physical constants (b.p. 150–155°C./5 mm., d_4^{18} 0.8858, n_D^{17} 1.5014), molecular refraction (found: 90.467, calculated for $C_{20}H_{32}|\overline{4}$: 90.484), and the results of elementary analysis well agreeing with those of α-camphorene, which was synthesized by Semmler and Jonas(3) from myrcene and had the constants: b.p. 178–180°C./8.5 mm.,

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(3) *Ber.*, **46** (1913), 1566.

d_{18} 0.8844, n_D 1.50199, $[\alpha]_D$ ±0. This must have been formed by polymerization of myrcene produced by dehydration of linalool.

The attempt to detect geraniol in the distillates was made in vain.

From the above-given results, it is positively ascertained that active carbon exerts a power of dehydration, of ring formation, and of polymerization upon acyclic terpene alcohol compounds like geraniol and linalool.

(IV) Catalytic Action upon Acyclic Terpene Aldehydes. Citral and citronellal were taken as representatives of acyclic terpene aldehydes upon which the action of active carbon was tested.

Citral was separated from lemongrass oil of the Indian origin and showed the constants: b.p. 96–97°C./6.5 mm., d_4^{15} 0.8918, n_D^{20} 1.4872, $[\alpha]_D^{10}$ ±0. It (200 g.) was mixed with 40 g. of active carbon and slowly heated in an oil-bath with constant stirring. At about 135°C. the reaction became very brisk. The yield of the oily reaction product was about 50% of the citral used. By repeated fractional distillation a lower fraction was obtained which proved to be *p*-cymene by its physical constants (b.p. 174–177°C., d_4^{15} 0.8593–0.8624, n_D^{20} 1.4912–1.4940), molecular refraction (found: 45.390–45.445, calculated for $C_{10}H_{14}|\overline{\overline{3}}$: 44.845), the results of elementary analysis, and the property of forming *p*-oxyisopropyl-benzoic acid (m.p. 155–156°C.). The higher boiling fraction (b.p. 160–165°C./4 mm., d_4^{15} 0.9379, n_D^{20} 1.5251) showed in elementary analysis the presence of a hydrocarbon of the molecular formula $C_{20}H_{28}$. Besides, the presence of a small quantity of a terpene was inferred, which resembled citral-terpene detected by Horiuchi⁽⁴⁾ among the reaction products obtained by the action of 20% sulphuric acid upon citral.

Citronellal (b.p. 69–71°C./5 mm., d_4^{15} 0.8553, n_D^{20} 1.4467, $[\alpha]_D^{10}$ +11.02) was obtained by refining citronella oil of the Javanese origin. It (300 g.) was mixed with 60 g. of active carbon and subjected to the treatment as before. When the temperature of the oil bath reached about 99°C., a brisk reaction commenced, and the yield of the oily reaction product was about 57% of the citronellal taken. Upon fractional distillation, about 45 g. of a distillate having properties of isopulegol was obtained. After repeated purification by distillation, it showed physical constants (b.p. 66–68°C./4 mm., d_4^{15} 0.9148, n_D^{20} 1.4704, $[\alpha]_D$ +2.15), molecular refraction (found: 47.209, calculated for $C_{10}H_{18}O|\overline{\overline{1}}$: 47.238), and the results of elementary analysis proving it was isopulegol. By oxidation with the chromic acid mixture, it formed isopulegone which was converted to the oxime (m.p. 122–123°C.).

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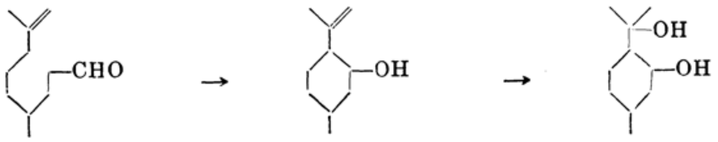
(4) *Mem. Coll. Sci., Kyoto Imp. Univ.*, **11** (1928), 190.

The higher boiling fraction had as the chief constituent di-isopulegol ether (b.p. 160–170°C./4 mm.) showing upon a further purification the physical constants (b.p. 157–158°C./4 mm., d_4^{15} 0.9188, n_D^{20} 1.4819, $[\alpha]_D^{13}$ -0.87), and the results of elementary analysis corresponding to the formula $C_2\,H_{34}O$. Besides this, a very small quantity of a terpene hydrocarbon was detected with the constants: b.p. 47–55°C./4 mm., d_4^{15} 0.8594, n_D^{20} 1.4826, $[\alpha]_D$ $+39.92$.

It was thus recognized that active carbon possesses dehydration activity as well as the action of ring formation and polymerization upon acyclic terpenealdehyde compounds. Especially interesting was the fact that isopulegol was very easily formed from citronellal without use of any solvent. This fact makes the present author concur to the view⁽⁵⁾ that isopulegol is formed by the direct ring formation of citronellal:



In order to corroborate this view, the temperature of the oil bath was kept comparatively low at about 70°C. to avoid the formation of water by the decomposition of citronellal. After a slow reaction taking place during three hours, there was found a large quantity (about 22%) of isopulegol formed which could not be thought as having come through the stage of menthoglycol.

(V) Catalytic Action upon Safrol and Isosafrol. Under the expectation that safrol and isosafrol would undergo the opening of their methylene-dioxy ring by active carbon, the reaction was tried under pressure, as it was known by experiments not to take place under ordinary pressure.

Safrol was prepared by separation and purification from brown camphor oil (b.p. 232.5–233°C., d_{15} 1.1050, n_D^{20} 1.5378, $[\alpha]_D$ ± 0). It (200 g.) was mixed with 40 g. of active carbon and slowly heated in an autoclave. At about 190°C., a brisk reaction commenced to taken place showing a pressure of 40 atmospheres and rising in temperature to 265°C. The reaction product was extracted with ether and the dark brownish oily matter was subjected to distillation under reduced pressure, when 40.3 g. of an oil was obtained. At the same time an increase of coaly matter was noted. The chief constituent consisting of about 22 g. of phenolic material had the properties (b.p. 118–130°C./4 mm., d_4^{15} 1.0942–1.0946, n_D^{20} 1.5441–1.5444), from

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(5) *Loc. cit.*; *J. Soc. Chem. Ind., Japan*, **34** (1931), 161.

which and from the result of elementary analysis there was attributed to it a formula $C_9H_{12}O_2$ containing two hydroxyl groups and no methoxyl group. To prove the constitution of the product, it was methylated in usual way when it showed physical constants: b.p. 95–100°C./4 mm. d_4^{15} 1.0167, n_D^{20} 1.5164. From this and from the results of elementary analysis and determination of methoxyl groups, the methylated oil was proved to have the molecular formula $C_{11}H_{16}O_2$ containing two methoxyl groups. It is clear then that the phenolic substance corresponding to it contains two hydroxyl groups.

The methylated oil gave on oxidation with potassium permanganate veratric acid (m.p. 179–181°C.). By nitration, it gave 6-nitro-3,4-dimethoxy-1-propyl-benzene (m.p. 80.5–81°C.).(6) These results show that the methylated oil is 3,4-dimethoxy-1-propyl-benzene and that the chief constituent of the higher boiling fraction of the phenolic matter produced from safrol is 3,4-dihydroxy-1-propyl-benzene. The 3,4-dihydroxy-1-propyl-benzene obtained by the present author was an difficultly crystallizable oil, so that it perhaps contained some impurities.

Another sample of 3,4-dimethoxy-1-propyl-benzene (b.p. 110–115°C./3 mm., d_4^{15} 1.0569, n_D^{20} 1.5652) was prepared by reduction of methyl-iso-eugenol with absolute alcohol and metallic sodium. The 6-nitro-3,4-dimethoxy-1-propyl-benzene (m.p. 80.5–81°C.) prepared by its nitration showed no change of melting point when mixed with the nitration product mentioned above. From the phenolic matter obtained as above, a small quantity of a substance of comparatively low boiling point (b.p. 85–115°C./5 mm., d_4^{26} 1.0266–1.0340, n_D^{26} 1.5291–1.5285) was obtained. When methylated, it gave an oil having physical constants: b.p. 65–70°C./4.8 mm., d_4^{15} 0.9809, n_D^{20} 1.5129. From the results of elementary analysis and from the fact that by oxidation it gave anisic acid (m.p. 179–181.5°C.), the methylated oil was found to be *p*-cresol-methyl-ether and the original phenolic matter was inferred to be *p*-cresol, although the formation of 4-hydroxy-1-propyl-benzene is not precluded. The material was too small in quantity to decide the question definitely.

The neutral material obtained had physical constants: b.p. 80–84°C./3.5 mm., d_4^{28} 1.0786–1.0768, n_D^{28} 1.5282–1.5255. It is quite different from safrol or isosafrol. From the fact that the phenolic substance contained a propyl group and that dihydro-safrol can be obtained in a large quantity from isosafrol, the formation of dihydrosafrol from safrol can be easily imagined, and the neutral substance mentioned above is safely presumed to be a mixture of safrol and dihydro-safrol.

A sample of isosafrol (b.p. 114–117°C./7 mm., d_{15} 1.1247, n_D^{20} 1.5757, $[\alpha]_D$ ±0) was obtained by isomerization of safrol in the usual way. It (200 g.)

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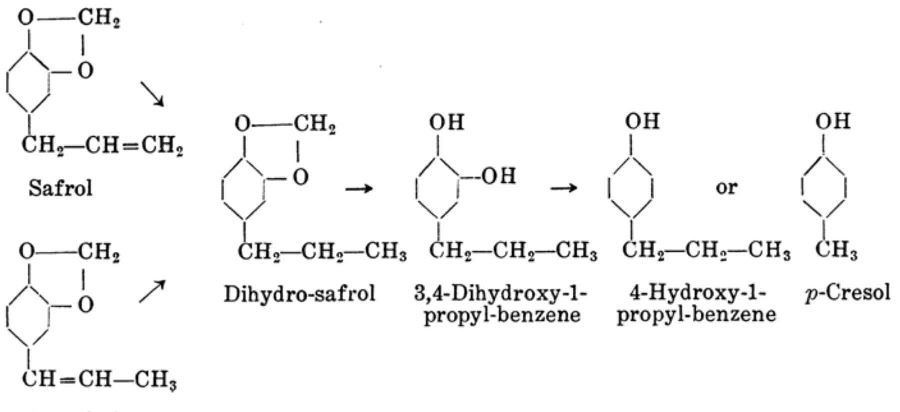
(6) H. Thoms, *Ber.*, **36** (1903), 860.

was heated with 40 g. of active carbon as before under pressure. At 198°C. the reaction began to take place very briskly and the pressure rose to 33 atmospheres with the rise of temperature to 284°C. At the completion of the reaction, 37.8 g. of an oily matter was distilled off at 61–125°C. under 4 mm. In about 10 g. of phenolic substance from the oily reaction product, 3,4-dihydroxy-1-propyl-benzene was identified as in the case of the experiment with safrol. The neutral substance was identified as almost pure dihydrosafrol from the physical constants (b.p. 80–83°C./4 mm., d_4^{29} 1.0626, n_D^{30} 1.5151), and the molecular refraction (found : 46.54, calculated for $C_{10}H_{12}O_2\overline{|\overset{=}{3}}$: 45.87), and the results of elementary analysis. From these results it is inferred that, by heating safrol and isosafrol with active carbon, the reaction runs in such a way that a portion is decomposed and carbonised producing hydrogen which is added to the double bonds of the allyl or propenyl group, changing it to a propyl group. At the same time the methylene-dioxy ring is split, chiefly to produce dihydroxy compounds, a small fraction of which is converted to hydroxy compounds by the loss of one hydroxyl group. This is made clear by the following scheme :



Safrol

Isosafrol

Dihydro-safrol

3,4-Dihydroxy-1-propyl-benzene

4-Hydroxy-1-propyl-benzene

or

p-Cresol

While in the experiments with safrol the neutral substance consists of a mixture of unchanged safrol and dihydro-safrol, in the case of isosafrol it consists almost wholly of dihydro-safrol. This is easily understood from the consideration that, generally in the reduction with metallic sodium and alcohol, the propenyl group is more easily hydrogenated than the allyl group.(7) The fact that carbon is liberated at the same time with the liberation of hydrogen

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(7) G. Ciamician and P. Siber, *Ber.*, **23** (1890), 1162; A. Klages, *Ber.*, **32** (1899), 1439.

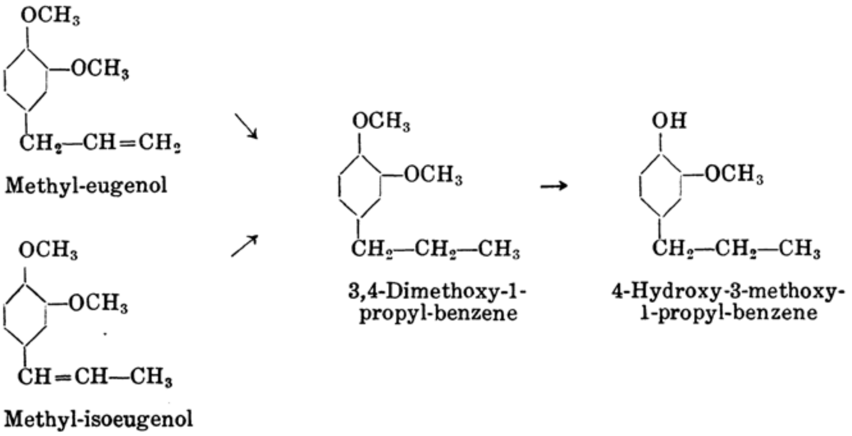
by the decomposition of the material, is made clear by the existence of a much larger quantity of carbon at the end of reaction than at the beginning.

From the results reported here it is concluded that active carbon exerts a splitting action upon the methylene-dioxy ring of safrol and isosafrol as well as the catalytic hydrogenation action.

VI. Catalytic Action upon Methyl-eugenol and Methyl-isoeugenol. From the above-mentioned experiments it was expected that active carbon may have a de-methylating action upon the methoxyl group. As it was also desired to extend the catalytic hydrogenation experiment to other kinds of compounds, the present author tested the activity of active carbon upon methyl-eugenol and methyl-isoeugenol. A sample of methyl-isoeugenol (b.p. 125–131°C./6 mm., $d_4^{18.8}$ 1.0590, $n_D^{18.5}$ 1.5707) was obtained by methylating isochavibetol and purifying the product in the usual way. It (200 g.) was mixed with 40 g. of active carbon and slowly heated in an autoclave up to 247°C., when a brisk reaction commenced raising the pressure to 24 atmospheres. At the completion of the reaction, the product was extracted with ether. The small quantity of the phenolic substance contained in the oily product showed physical constants (b.p. 90–93°C./4.5 mm., $d_4^{21.5}$ 1.0487, $n_D^{22.2}$ 1.5239), colour reactions, and results of elementary analysis proving that it consisted of 4-hydroxy-3-methoxy-1-propyl-benzene. The main fraction (about 20 g.) of the neutral matter was subjected to repeated fractionation and showed the physical constants: b.p. 108–110°C./6 mm., $d_4^{19.2}$ 1.0140, n_D^{21} 1.5159. From these figures and from the results of elementary analysis, it was identified as 3,4-dimethoxy-1-propyl-benzene. This conclusion was corroborated by further facts that it produces by oxidation with potassium permanganate veratric acid (m.p. 179–181°C.) and that it yields by nitration 6-nitro-3,4-dimethoxy-1-propyl-benzene.

A sample of methyl-eugenol (b.p. 123°C./9 mm., d_4^{17} 1.0372, $n_D^{17.8}$ 1.5337) was prepared by methylation of eugenol. It (200 g.) was heated with 40 g. of active carbon under pressure as before. From the reaction product, a small quantity of phenolic substance and a large amount of neutral substance were obtained. The main fraction of the neutral material was shown by the elementary analysis and by the nitration to 6-nitro-3,4-dimethoxy-1-propyl-benzene to consist chiefly of 3,4-dimethoxy-1-propyl-benzene. The physical constants (b.p. 110-112°C./6 mm., $d_4^{16.4}$ 1.0184, n_D^{16} 1.5208) did not, however, agree with those obtained before for the product from methyl-isoeugenol: this is due perhaps to the admixture of the unchanged material. This is again due to the different susceptibilities to hydrogenation of allyl group and propenyl group, endorsing the conclusion already drawn by the author in the case of safrol and isosafrol.

The reaction mechanism inferred from the above results is as follows. The hydrogen produced by thermal decomposition under pressure is added to the double bonds of allyl and propenyl groups by the catalytic action of active carbon to change them to a propyl group. The hydroxy compounds are then formed by de-methylation. Active carbon thus exerts a catalytic hydrogenation as well as de-methylation as in the previous instances. This is schematized as follows:



Cantelo⁽⁸⁾ has made investigations of catalysis by animal charcoal, silica gel, etc., upon the thermal decomposition of methane. Kusama and Uno⁽⁹⁾ have subjected methane to thermal decomposition under the catalysis of nickel with the formation of carbon and hydrogen. The latter concluded that the relation between the quantity of the catalyser and the percentage of the hydrogen formed depended upon the catalytic activity of carbon which accumulated in the reaction. In the experiments reported here, active carbon is considered to have exerted some catalytic activity of thermal decomposition.

The investigation here described was performed under the kind guidance of Dr. Kashichi Ono to whom a sincere acknowledgment is herewith rendered by the author.

Research Laboratory of
Nippon Koryo Yakuhin Kaisha, Ltd.,
Kobe.

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(8) *J. Phys. Chem.*, **28** (1924), 1036.

(9) *Sci. Pap. Inst. Phys. Chem. Research, Japan*, **8** (1929), 1.