ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. V. THE ACTION ON METHYLCYCLOHEXANOLS AND MENTHOL.*

By Harushige INOUE.

Received July 5th, 1934. Published September 28th, 1934.

Cyclohexanol is easily dehydrated to cyclohexene by the contact action of alumina, silica, or other dehydrating agents, at about 300°.[1] The conversion of cyclohexane derivatives into cyclopentane series, however, has been effected only by the action of the strong mineral acids such as hydriodic acid as Markonikoff[2] first observed, or only at higher temperatures as Ipatiew[3] reported. The present author[4] previously observed that when Japanese acid earth is used as a contact material, cyclohexanol is chiefly converted into methylcyclopentane at 350°, while at 250° it is mainly changed into cyclohexene. A similar isomerisation was also ascertained in the case of 1-methylcyclohexanol-(2).

The present experiment was undertaken to examine the relation between the position of the methyl group in methylcyclohexanols and the yield of each reaction product and further to study the catalytic action of the earth on menthol. The methylcyclohexanols used in the experiment were prepared by the hydrogenation of pure cresols. Their physical constants are shown in Table 1.

Table 1.

	B.p.	d_0^0	n_D^{20}
1-Methylcyclohexanol-(2)	167—170°	0.9473	1.45998
1-Methylcyclohexanol-(3)	173—176°	0.9300	1.45345
1-Methylcyclohexanol-(4)	172—174°	0.9320	1.46016

I. 1-Methylcyclohexanol-(3). By passing 70 g. of 1-methylcyclohexanol-(3) on the earth heated at 250°, 42.6 g. of oil (d_0^{20}, 0.8183) and 8.9 g.

* An epitomized translation of the paper published in Vol. 29 of the *Reports of the Tokyo Imperial Industrial Research Laboratory*.

(1) Ipatiew, *J. Russ. Phys. Chem. Soc.*, **38** (1906), 96; Sendrens, *Compt. rend.*, **144** (1907), 1110; Brunnel, *Bull. Soc. Chim.*, [3], **33** (1905), 270.

(2) *Ber.*, **30** (1897), 1226; *Ann.*, **307** (1899), 340.

(3) *J. Russ. Phys. Chem. Soc.*, **43** (1911), 1431.

(4) This Bulletin, **1** (1926), 219.

of water were obtained. The former, after subjected to fractional distillation ten times, gave the fractions shown in Table. 2.

Table 2.

B.p.	Yield (g.)	d_0^0	d_0^{20}	n_D^{20}	n_α^{20}	n_β^{20}	n_γ^{20}	Analysis (%)	
								C	H
92—95°	1.1	0.7800	0.7621	1.42090	1.41864	1.42646	1.43183	—	—
95—99°	2.2	0.7866	0.7691	1.42460	1.42230	1.43035	1.43521	85.85	14.01
99—102°	11.3	0.7909	0.7732	1.42790	1.42552	1.43368	1.43847	86.24	13.85
102—105°	8.5	0.7954	0.7787	1.43080	1.42859	1.43694	1.44164	86.45	13.55
105—110°	2.1	0.8024	0.7847	1.43482	1.43241	1.44105	1.44616	86.55	13.32
Residue	11.6	0.9342	0.9194	—	—	—	—	—	—
A	0.4	0.8836	0.8358	1.46375	—	—	—	—	—
B	4.3	0.9256	0.9110	1.49758	—	—	—	—	—
C	4.4	0.9634	0.9502	1.53174	—	—	—	—	—

The residue was further separated into three parts, A, B, and C, by fractional steam distillation as shown in the table.

The physical constants and results of elementary analyses of the fractions show that the main reaction product is methylcyclohexane, while in the case of 1-methylcyclohexanol-(2) methylcyclohexene is mainly produced under the same condition.[5]

When 1-methylcyclohexanol-(3) (150 g.) was treated similarly at 350°, 103.4 g. of oil (d_0^{20}, 0.8075) and 20.0 g. of water were obtained. The former gave the fractions shown in Table 3 after ten times fractional distillations.

Table 3.

B.p.	Yield (g.)	d_0^0	d_0^{20}	n_D^{20}	n_α^{20}	n_β^{20}	n_γ^{20}	Analysis (%)	
								C	H
To 80°	1.3	0.7103	0.6901	1.39172	1.38973	1.39724	1.40280	84.25	15.75
80—90°	4.1	0.7643	0.7458	1.41192	1.40990	1.41756	1.42221	84.57	15.37
90—93°	5.6	0.7736	0.7571	1.41710	1.41492	1.42264	1.42725	85.25	14.86
3—96°	9.0	0.7787	0.7615	1.41970	1.41728	1.42538	1.42998	85.40	14.56
96—99°	13.5	0.7855	0.7685	1.42380	1.42149	1.42961	1.43434	85.72	14.32
99—102°	15.9	0.7940	0.7769	1.42920	1.42673	1.43526	1.44028	85.86	14.19

(5) Inoue, This Bulletin, **1** (1926), 219.

Table 3. (*Concluded*)

B.p.	Yield (g.)	d_0^0	d_0^{20}	n_D^{20}	n_α^{20}	n_β^{20}	n_γ^{20}	Analysis (%)	
								C	H
102—105°	6.3	0.7997	0.7835	1.43367	1.43110	1.44001	1.44528	86.05	13.89
105—110°	3.6	0.8051	0.7896	1.43792	1.43535	1.44462	1.45048	86.67	13.34
110—115°	2.4	0.8129	0.7956	1.44301	1.44008	1.44993	1.45608	—	—
115—125°	2.8	0.8201	0.8038	1.44857	1.44551	1.45585	1.46199	—	—
125—140°	2 1	0.8378	0.8217	1.46105	1.45783	1.46940	—	—	—
Residue	25.1	0.9642	0.9506	—	—	—	—	—	—
A	0.9	0.8760	0.8606	1.48515	—	—	—	—	—
B	20.0	0.9603	0.9472	1.54432	—	—	—	—	—
C	2.6	—	—	—	—	—	—	—	—

The first fraction of Table 3 mainly consists of methylcyclopentane, as its physical constants and chemical composition clearly show. The fractions with h'gher boiling points are, in th's case, chiefly composed of dimethylcyclopentane, ethylcyclopentane, methylcyc ohexane, and a small amount of methylcyclohexenes. Δ^1-Methylcyclohexene, which was confirmed to occur in the reaction product by the oxidation wi h nitric acid, yielding thereby adipic acid (m. p. 150°) and β-methyladipic acid (m. p. 88—90°), can not be considered to have been formed by the simple dehydration of 1-methylcyclohexanol-(3). It is probab'e that Δ^2- or Δ^3-methylcyclohexene, originated by the dehydration of 1-methylcyclohexanol-(3) re-arranges itself to Δ^1-methylcyclohexene, the most stab'e form of the three isomers, by the contact action of the acid earth. The same experimental fact was observed by Wallach[6] when 1-methylcyclohexanol-(3) was treated with zinc chloride and also by the present author and Ishimura[7] when methylcyclohexylamines were treated with Japanese acid earth.

In orde:r to get the more precise knowledge of the reaction products, the following experiment was performed.

1-Methylcyclohexanol-(3) (76.0 g.) was passed on the earth heated at 350° and 54.6 g. of oil (d_0^0, 0.8248) and 9.6 g. of water were obtained. The oily substance was treated with concentrated sulphuric acid to remove unsaturated hydrocarbons, and 30.9 g. of saturated hydrocarbons were left unaffected by the acid, which were then submitted to fractional distillation ten times, giving the fractions shown in Table 4.

(6) *Ber.* **35** (1902), 2823.

(7) To be reported in next paper.

Table 4.

B.p.	Yield (g.)	d_0^0	d_0^{20}	n_D^{20}	n_α^{20}	n_β^{20}	n_γ^{20}	Analysis (%)	
								C	H
To 85°	0.9	0.7347	0.7169	1.40059	1.39383	1.40550	1.41021	—	—
85—89°	2.8	0.7611	0.7438	1.41153	1.40841	1.41659	1.41992	85.16	14.81
89—92°	—	0.7695	0.7522	1.41381	1.41171	1.41903	1.42326	85.30	14.69
92—95°	2.9	0.7720	0.7551	1.41525	1.41311	1.42038	1.42470	85.53	14.50
95—98°	8.9	0.7769	0.7602	1.41840	1.41582	1.42322	1.42763	85.72	14.28
98—101°	2.3	0.7804	0.7641	1.42000	1.41783	1.42528	1.42970	85.91	14.12
101—105°	1.0	0.7835	0.7672	1.42165	1.41944	1.42686	1.43134	86.24	13.80
Above 105°	0.7	0.7977	0.7816	1.42930	1.42708	1.43467	1.43925	—	—
Residue	6.3	0.9091	0.8957	1.49412	—	—	—	—	—

As is seen in Table 4, the third fraction boiling between 89° and 92° is noticed to consist mainly of dimethylcyclopentane from its physical constants and the result of elementary analysis, whereas the sixth fraction boiling between 98° and 101° is almost pure ethylcyclopentane.

II. 1-Methylcyclohexanol-(4) By passing 70.0 g. of 1-methylcyclohexanol-(4) on the earth heated at 250°, 42.0 g. of oil (d_0^{20}, 0.8112) and 9.8 g. of water were obtained. The former, after ten times fractional distillations, gave the fractions shown in Table 5.

Table 5.

B.p.	Yield (g.)	d_0^0	d_0^{20}	n_D^{20}	n_α^{20}	n_β^{20}	n_γ^{20}	Analysis (%)	
								C	H
93—96°	0.8	0.7746	0.7571	1.41900	1.41673	1.42450	1.42960	—	—
96—99°	3.6	0.7853	0.7693	1.42410	1.42185	1.42981	1.43454	85.20	14.82
99—102°	12.6	0.7927	0.7752	1.42830	1.42587	1.43407	1.43881	86.18	13.84
102—105°	7.0	0.7985	0.7823	1.43281	1.43030	1.43892	1.44420	86.30	13.67
105—110°	1.3	0.8065	0.7894	1.43803	1.43545	1.44745	1.45019	86.73	13.35
110—115°	0.9	0.8169	0.7997	1.44426	1.44149	1.45102	1.45707	—	—
Residue	11.8	0.9412	0.8737	1.51723	—	—	—	—	—
A	1.5	0.9302	0.9164	1.50126	1.49767	1.51008	—	—	—
B	4.5	0.9313	0.9220	1.51098	1.50711	1.52010	—	—	—
C	4.9	0.9793	0.9664	1.54760	—	—	—	—	—

The residue was further separated by fractional steam distillation into three parts, A, B, and C.

The numerical data of Table 5 tell us that almost the same reaction took place as in the case of 1-methylcyclohexanol-(3) (cf. Table 2).

When 1-methylcyclohexanol-(4) (150.0 g.) was passed on the earth heated at 350°, 111.5 g. of oil (d_0^{20}, 0.8141) and 20.4 g. of water were obtained, and the former was divided into fifteen portions by ten times fractional distillations (Table 6).

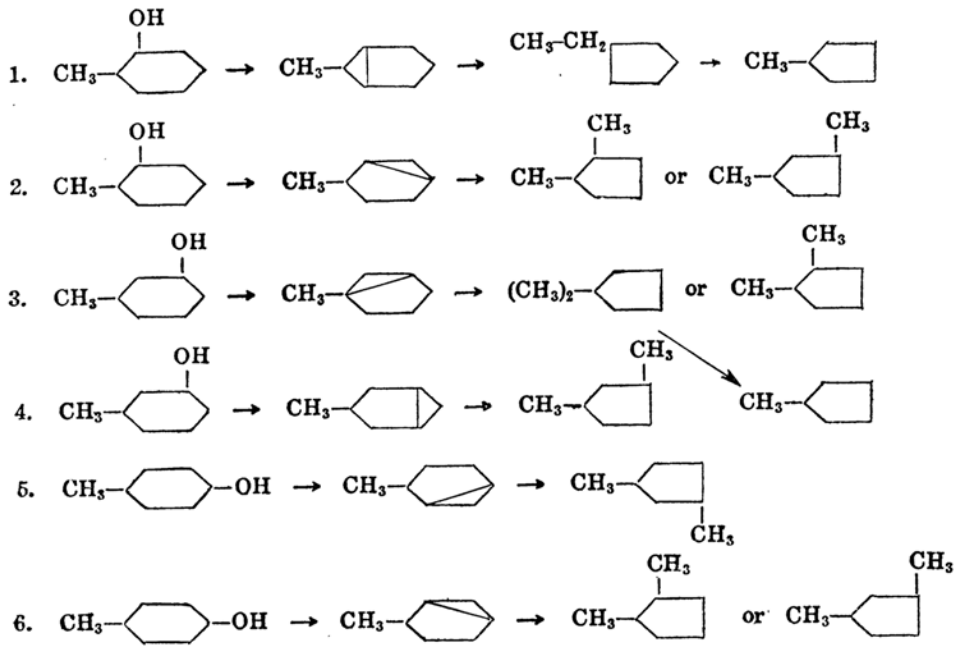
Table 6.

B.p.	Yield (g.)	d_0^0	d_0^{20}	n_D^{20}	n_α^{20}	n_β^{20}	n_γ^{20}	Analysis (%)	
								C	H
To 80°	+	0.6887	—	—	—	—	—	—	—
80—85°	0.7	0.7574	0.7403	1.41197	1.40970	1.41766	1.42240	85.80	14.23
85—90°	3.2	0.7764	0.7588	1.41980	1.41743	1.42548	1.43051	85.92	13.95
90—93°	4.4	0.7802	0.7621	1.42190	1.41944	1.42764	1.43259	86.30	13.73
93—95°	4.2	0.7822	0.7656	1.42380	1.42124	1.42951	1.43464	86.33	13.64
95—97°	9.9	0.7866	0.7693	1.42640	1.42385	1.43234	1.43755	86.36	13.62
97—99°	7.9	0.7923	0.7746	1.42970	1.42718	1.43585	1.44106	86.41	13.55
99—102°	14.4	0.7993	0.7824	1.43442	1.43181	1.44080	1.44626	86.66	13.35
102—105°	12.0	0.8071	0.7915	1.44060	1.43777	1.44725	1.45293	87.15	12.92
105—110°	9.4	0.8143	0.7979	1.44496	1.44202	1.45192	1 45805	87.22	12.77
110—115°	1.9	0.8201	0.8036	1.44917	1.44611	1.45640	1.46277	87.48	12.46
115—130°	3.9	—	—	—	—	—	—	—	—
Residue	21.2	—	—	—	—	—	—	—	—
A	5.7	0.9198	0.9062	—	—	—	—	—	—
B	10.0	0.9338	0.9204	—	—	—	—	—	—
C	2.7	0.9761	0.9632	—	—	—	—	—	—

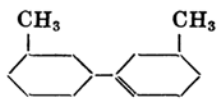
As shown in Table 6, results quite analogous to those in the case of 1-methylcyclohexanol-(3) (cf. Table 4) were obtained.

The above-mentioned experiments show that all the three isomers of methylcyclohexanols undergo the similar isomerisation from the six-membered carbon-rings to the five-membered by the catalytic action of Japanese acid earth heated at 350°, cyclopentane derivatives being produced. As regards the influence of the position of the methyl group in the molecules of methylcyclohexanols on the total yield of cyclopentane derivatives, it is noticed that 1-methylcyclohexanol-(2) is the most easy to be converted into cyclopentane derivatives and 1-methylcyclohexanol-(3) and -(4) follow next, any distinguishable difference being hardly recognized between the latter

two. 1-Methylcyclohexanol-(2) gives, however, the largest yield of cyclopentane and 1-methylcyclohexanol-(4) the smallest, whilst 1-methylcyclohexanol-(3) stands between the two. The mechanism of the formation of cyclopentane derivatives from methylcyclohexanols may be, therefore, explained schematically as follows:



Since ethylcyclopentane and 1,1-dimethylcyclopentane tend to be decomposed to methylcyclopentane and it is difficult for 1,2- and 1,3-dimethylcyclopentanes to produce it, it is very natural that 1-methylcyclohexanol-(2) gives the largest yield of methylcyclopentane and 1-methylcyclohexanol-(4) the smallest as stated above. The yield of methylcyclohexane in the reaction carried out at 250°, on the contrary, is very small in the case of 1-methylcyclohexanol-(2), while in the case of 1-methylcyclohexanol-(3) and -(4), methylcyclohexane is the main reaction product, and the yield of polymers is also in the same order. Markonikoff[8] obtained the hydrocarbon (I) from Δ^3-methylcyclohexene by shaking it with 50 per cent. sulphuric acid.



I

When the above hydrocarbon undergoes the thermal decomposition, it may m st probably be decomposed to methylcyclohexane and Δ^3-methyl-

(8) *Chem. Zentr.*, 1904, **I**, 1346.

cyclohexene or methylcyclohexadiene and therefore cyclohexene is most easy to occur in the reaction product which is originally rich in Δ^3-methylcyclohexene as in the case of 1-methylcyclohexanol-(3) or -(4), whereas there is no possibility for 1-methylcyclohexanol-(2) to produce Δ^3-methylcyclohexene and it is not difficult to anticipate the poor yield of methylcyclohexane in the latter case, which the above experiments have actually shown.

III. Menthol. With regard to the catalytic action of Japanese acid earth on menthol, Ono's paper[9] was published some years ago. While his experiment was carried out in liquid state, the present author treated menthol in vapour phase with the earth and some interesting facts hitherto unknown were manifested.

By passing 150.0 g. of menthol (m.p., 42°; $[\alpha]^{18}$,—48°19′) on the earth heated at 230°, 94.50 g. of oil (d_0^0, 0.8137) and 5.8 g. of water were obtained, and the former gave the fractions shown in Table 7 after subjected to fractional distillation ten times.

Table 7.

B.p.	Yield (g.)	d_0^0	d_0^{20}	n_D^{20}	n_α^{20}	n_β^{20}	n_γ^{20}	Analysis (%)	
								C	H
To 80°	0.8	0.6971	0.6805	1.38729	1.38534	1.39753	1.39635	—	—
80—100°	1.3	0.7713	0.7563	1.42060	1.41813	1.42636	1.43104	—	—
100—140°	1.4	0.7941	0.7789	1.43341	1.43080	1.43962	1.44489	—	—
140—150°	1.2	0.8015	0.7860	1.43762	1.43545	1.44337	1.44900	—	—
150—155°	0.7	0.8050	0.7913	1.43893	1.43625	1.44487	1.44989	—	—
155—159°	2.1	0.8081	0.7941	1.43944	1.43696	1.44537	1.45019	86.34	13.82
159—162°	4.9	0.8090	0.7948	1.43994	1.43734	1.44577	1.45058	85.99	14.02
162—165°	—	0.8108	0.7974	1.44095	1.43837	1.44656	1.45137	86.00	13.97
165—168°	26.9	0.8145	0.8000	1.44285	1.44038	1.44874	1.45362	86.17	13.84
168—171°	11.8	0.8203	0.8064	1.44657	1.44400	1.45252	1.45775	86.26	13.68
171—175°	4.6	0.8274	0.8140	1.45207	1.44932	1.45850	1.46396	86.49	13.44
175—180°	2.8	0.8349	0.8203	1.45906	1.45603	1.46593	1.47186	87.00	13.09
180—188°	1.9	0.8488	0.8350	1.46821	1.46509	1.47582	1.48228	87.63	12.58
188—189°	1.8	0.8540	0.8411	1.47176	1.46955	1.47958	1.48628	88.24	12.00
Residue	—	—	—	—	—	—	—	—	—
A	0.8	0.9129	0.9003	—	—	—	—	—	—
B	2.3	0.9470	0.9367	—	—	—	—	—	—

(9) This Bulletin, **1** (1926), 250.

As is seen in Table 7 it is obvious that the main reaction products are menthane and menthene.

When menthol (200.0 g.) was passed on the earth heated at 350°, 19.7 g. of light oil boiling under 100°, 155.0 g. of heavy oil boiling above 100° (d_0^0, 0.8061), and 18.2 g. of water were obtained. The oily substances were fractionated ten times and the fractions shown in Table 8 were obtained.

Table 8.

B.p.	Yield (g.)	d_0^0	d_0^{20}	n_D^{20}	n_α^{20}	n_β^{20}	n_γ^{20}	Analysis (%)	
								C	H
45—50°	1.8	0.6527	0.6342	1.36390	1.36191	1.36819	1.37218	—	—
50—55°	0.5	—	—	1.37855	1.37698	1.38114	—	—	—
55—67°	1.8	0.7035	0.6846	1.38461	1.38263	1.38933	1.39367	84.32	15.76
67—72°	5.7	0.7343	0.7152	1.39780	1.39581	1.40282	1.40733	85.07	15.02
72—75°	1.2	0.7491	0.7310	1.40412	1.40204	1.40914	1.41366	85.30	14.71
75—80°	1.5	0.7561	0.7393	1.40747	1.40541	1.41266	1.41726	85.46	14.68
80—90°	1.7	0.7604	0.7429	1.41044	1.40820	1.41592	1.42029	85.58	14.57
90—100°	1.4	0.7737	0.7561	—	—	—	—	—	—
100—120°	1.9	0.7927	0.7763	1.41969	1.41663	—	1.42980	—	—
120—140°	2.8	0.8106	0.7945	1.43381	1.43070	—	1.44538	87.28	12.85
140—150°	2.8	0.8172	0.8018	1.44546	1.44220	—	1.45824	86.96	13.05
150—153°	1.9	0.8162	0.8007	1.44867	1.44531	—	1.46130	86.75	13.32
153—156°	4.2	0.8155	0.8001	1.44747	1.44420	—	1.45993	86.68	13.39
156—159°	3.0	0.8143	0.7987	1.44657	1.44330	—	1.45844	86.36	13.58
159—162°	12.0	0.8160	0.8003	1.44546	1.44240	—	1.45706	86.52	13.57
162—165°	12.0	0.8176	0.8028	1.44627	1.44320	—	1.45795	86.70	13.44
165—168°	12.2	0.8234	0.8092	1.44747	1.44440	—	1.45933	86.79	13.27
168—171°	8.8	0.8314	0.8174	1.45167	1.44852	—	1.46396	86.90	13.14
171—175°	6.5	0.8402	0.8262	1.45757	1.45423	—	1.47053	87.15	12.90
175—180°	5.7	0.8571	0.8419	1.46461	1.46097	—	1.47864	87.76	12.31
180—185°	5.7	0.8707	0.8550	1.47765	1.47381	—	1.49371	88.34	11.56
185—190°	5.3	0.8832	0.8694	1.48862	1.48426	—	1.50587	88.70	11.25
190—195°	7.1	0.8938	0.8795	1.49805	1.49361	1.50772	—	89.10	10.98
195—200°	1.8	0.8999	0.8859	1.50536	1.50065	1.51559	—	—	—
Residue	4.3	—	—	—	—	—	—	—	—

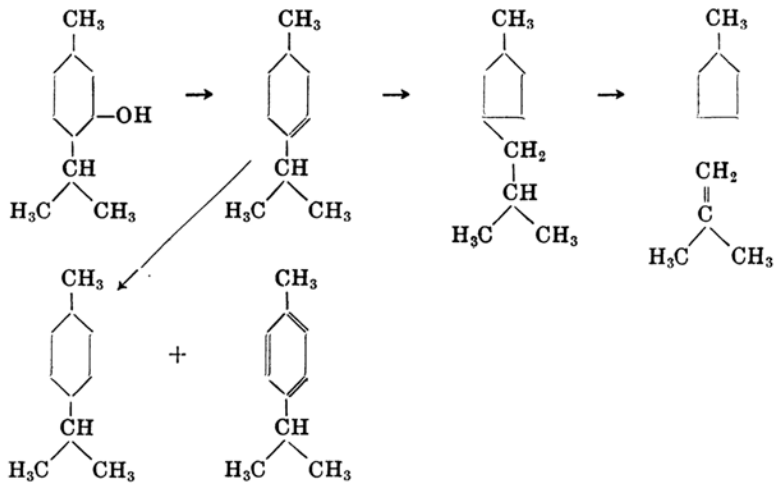
The fractions boiling near 70° in Table 8 are methylcyclopentane, which was confirmed by the examination of physical constants and results of elementary analyses and further by the oxidation with concentrated

nitric acid, succinic acid (m. p., 177—179°) and acetic acid being thereby found in the oxidation products. Among the fractions boiling between 100° and 200°, those boiling between 160° and 170° predominate in quantity, which seem to be composed of menthene when their densities and refractive indices are considered, but from the fact that they give nitrosochloride or nitrosite with difficulty and also from the calculation of bromine values, the content of menthene was found to be only less than 10 per cent. They probably consist of menthene, menthane, and *p*-cymene. The presence of *p*-cymene was confirmed as follows: the fraction boiling between 171° and 175° was nitrated and the resulting nitro-compound was reduced, amino-cymene being then isolated as benzoyl derivative (m. p., 135—136°, probably a mixture of two isomers). The physical constants of the fraction boiling between 140° and 150° well accord with those of isopropylcyclopentane. It is not determined, however, whether that substance is actually present or not. It is remarkable that the fraction boiling between 156° and 159° has a minimum density. This fraction was treated with concentrated sulphuric acid to remove unsaturated hydrocarbons and remaining saturated hydrocarbons were once more fractionated (Table 9).

Table 9.

B.p.	Yield (g.)	d	d_0^{20}	n_D^{20}	n_α^{20}	n_γ^{20}	Analysis (%)	
							C	H
152—154°	1.8	0.7941	0.7805	1.43191	1.42940	1.43704	85.89	14.29
154—158°	1.3	0.7980	0.7836	1.43311	1.43070	1.43840	—	—
158—162°	0.9	0.8034	0.7865	1.43462	1.43210	1.43982	—	—

The main portion given in Table 9 is the first fraction boiling between 152° and 154°, which consists most probably of methylisobutylcyclopentane, by the thermal decomposition of which the above-mentioned cylcopentane may be produced. Thus the transformation of menthol by the contact action of Japanese acid earth heated at 350° may be represented by the following scheme:



Thus the author has reached the conclusion that in the case of menthol the contact isomerisation from the six-membered carbon-ring to the five-membered also takes place in a manner just analogous to the case of methylcyclohexanols or methylcyclohexylamines.

A more accurate information of the composition of the reaction products was furnished by the following experiment.

Menthol (200 g.) was treated similarly at 350° and 151.4 g. of oil (d_0^0, 0.8152) was obtained, which, giving 138.4 g. of saturated hydrocarbons after treated with concentrated suphuric acid, was fractionated as shown in Table 10.

Table 10.

B.p.	Yield (g.)	d_0^0	d_0^{20}	n_D^{20}	n_α^{20}	n_β^{20}	n_γ^{20}	Analysis (%)	
								C	H
30—40°	1.5	0.5724	—	—	—	—	—	—	—
40—60°	0.6	0.6780	0.6605	—	—	—	—	—	—
60—65°	1.5	0.7006	0.6825	1.38594	1.38209	1.39026	1.39456	—	—
65—70°	2.4	0.7248	0.7070	1.39521	1.39325	1.39997	1.40391	—	—
70—80°	4.9	0.7506	0.7305	1.40500	1.40293	1.41281	1.41405	85.20	14.64
80—90°	1.6	0.7598	0.7423	1.41163	1.40930	1.41679	1.42124	—	—
90—100°	2.5	0.7779	0.7604	1.42420	1.42165	1.43040	1.43541	86.38	13.66
100—110°	2.1	0.7989	0.7817	1.43732	1.43465	1.44427	1.44999	87.15	12.75
110—130°	2.9	0.8018	0.7846	1.43904	1.43615	1.44596	1.45185	—	—
130—150°	3.4	0.8199	0.8043	1.45107	1.44812	1.45849	1.46476	—	—

Table 10. (*Concluded*)

B.p.	Yield (g.)	d_0^0	d_0^{20}	n_D^{20}	n_α^{20}	n_β^{20}	n_γ^{20}	Analysis (%)	
								C	H
150—154°	3.8	0.8225	0.8069	1.45147	1.44852	1.45839	1.46456	—	—
154—158°	3.0	0.8186	0.8037	1.44887	1.44606	1.45561	1.46140	87.03	13.10
158—161°	7.7	0.8164	0.8021	1.44677	1.44405	1.45322	1.45869	86.67	13.54
161—164°	6.9	0.8174	0.8027	1.44657	1.44390	1.45292	1.45834	—	—
164—167°	10.8	0.8218	0.8069	1.44967	1.44691	1.45620	1.46169	—	—
167—170°	15.0	0.8265	0.8122	1.45317	1.45043	1.45999	1.46570	86.67	13.42
170—173°	10.7	0.8335	0.8238	1.46255	1.45953	1.46999	1.47638	—	—
173—175°	4.5	0.8534	0.8429	1.47755	1.47414	1.48612	1.50139	88.06	11.95
175—180°	6.3	0.8595	0.8544	1.48688	1.48321	1.49631	1.50429	88.62	11.51
180—185°	4.9	0.8851	0.8696	1.49862	1.49454	1.50876	1.51762	—	—
185—190°	5.8	0.8929	0.8784	1.50448	1.50028	1.51503	1.52415	—	—
190—200°	6.0	0.9003	0.8809	1.50924	1.50500	1.52001	1.52927	—	—
Residue	—	—	—	—	—	—	—	—	—

As is seen in Table 10, the presence of menthene, cyclopentane, and methylisobutylcyclopentane is manifested by the physical constants and results of elementary analyses of the fractions with the boiling points corresponding to these substances respectively.

The Tokyo Imperial Industrial Research Laboratory,
Hatagaya, Tokyo.