ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH.
VI. THE ACTION ON CYCLOHEXYLAMINE AND ITS DERIVATIVES.*

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Cyclohexylamine as well as chloro- and iodo-cyclohexanes, when heated with hydrogen iodide in a sealed tube at 200° for several hours, produces methylcyclopentane.(1) One of the authors has previously(2) observed that cyclohexanol and its derivatives are converted chiefly into methylcyclopentane and its derivatives respectively by the catalytic action of Japanese acid earth heated at 300° under ordinary pressure, while at 200° they are mainly converted into cyclohexene and its derivatives respectively.

The present experiments were undertaken to ascertain whether cyclohexylamine and its derivatives also undergo the same isomeric change from the six-membered carbon rings to the five-membered ones by the contact action of the acid earth.

The amines used in the experiments were prepared from the corresponding phenols; pure carbolic acid and three isomeric cresols were reduced to hexahydrophenols by Sabatier and Sendrens's method, which were then oxidized with chromic acid, and the resulting ketones were changed into their oximes, from which the required amines were obtained by the reduction with metallic sodium and absolute alcohol. At every stage of the preparation, care was especially taken for purification, all the specimens being therefore very pure and entirely free from aromatic amines. The catalyst, dried at 300°, filled a glass tube with a length of 1 metre and a diameter of 2 cm., and was heated to 350° electrically, and then the weighed amount of an amine was passed on it. The liquid reaction product was passed through a condenser and collected in a receiver and the escaping gaseous product was bubbled into a series of washing bottles containing normal sulphuric acid to catch ammonia evolved.

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(1) Markonikoff, *Ber.*, **30** (1897), 1225; *Ann.*, **302** (1898), 36; ibid., **307** (1899), 336; Zelinsky, *Ber.* **30** (1897), 388. This work was carried out in 1927–1928. Recently Nenitzescu and Cantuniari (*Ber.*, **66** (1933), 1097) observed that cyclohexane is converted into methylcyclopentane when boiled with moist aluminium chloride.

(2) Inoue, This Bulletin, **1** (1926), 219; ibid., **9** (1934), 353.

I. **Cyclohexylamine.** The amine (b.p. 134°, d_4^{25} 0.8644, n_D^{25} 1.45757), (26.0 g.), being passed on the earth heated at 350° at the rate of 4.7 g. per hour, yielded 15.5 g. of an oily substance and 3.5 g. of gaseous ammonia. The oil was washed with cold dilute hydrochloric acid to remove basic substances, and then with a dilute soda solution and water, dried over anhydrous sodium sulphate, and thus 13.2 g. of a mixture of hydrocarbons (d_{20}^{20} 0.8264) were obtained, which, subjected to fractional distillation seven times, gave the fractions shown in Table 1.

Table. 1.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	70–76°	1.5	0.7654	1.4233
2	76–77°	2.0	0.7709	1.4263
3	77–80°	0.4	0.7741	1.4294
4	80–85°	0.1	—	—
5	Residue	2.5	0.9213	1.5135

As shown by the physical constants given in the table, the first fraction consists mainly of methylcyclopentane, whose presence was confirmed by the formation of succinic and acetic acids on oxidation according to Aschan.⁽³⁾ As the yield of the fourth fraction was too small to determine its physical constants, the same experiment was repeated and the fraction with the boiling point 82–85° was collected, which was found to be almost pure cyclohexene by its physical constants (b.p. 82–85°, d_4^{20} 0.8046, n_D^{20} 1.44466).

The second and third fractions are mixtures of methylcyclopentane and cyclohexene, and the residue is a mixture of higher hydrocarbons, probably the polymers, condensed products, or both, of the above mentioned substances.

The basic substances were, as already stated, separated from the other reaction products by washing with dilute hydrochloric acid. The washing liquid was neutralized with caustic soda and extracted with ether. After the ether was driven off the free amines were weighed (Yield 0.4 g.). The amines were again dissolved in ether and left to stand. Some days after a white crystalline substance deposited on the wall of the vessel containing the ethereal solution, which was identified to be carbazole by its melting point (238°) and also by the characteristic colour reaction. Into the remaining ethereal solution dry carbon dioxide was passed under cooling with ice and common salt, thereby some unchanged cyclohexylamine was thrown down as carbonate. The solution separated from the insoluble carbonate was treated with benzoyl chloride and alkali. The benzoyl derivative pro-

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(3) *Ber.*, **31** (1898), 1804.

duced was recrystallized from dilute alcohol and was found to be benzanilide (m.p. 159–160°). The presence of aniline in the basic reaction product was further confirmed by the colour reactions with bleaching powder and with potassium bichromate.

From the above results it may be concluded that ammonia is first split off from cyclohexylamine, cyclohexene being yielded just in the same manner as water is split off from cyclohexanol, and then the resulting cyclohexene undergoes the isomerization from the six-membered carbon ring to the five-membered one producing methylcyclopentane, some polymerization or condensation products being formed simultaneously. The dehydrogenating property of Japanese acid earth is also noticed in the fact that carbazole and aniline are produced.

II. **1-Methylcyclohexylamine-(2).** By passing 66.7 g. of 1-methylcyclohexylamine-(2) (b.p. 148–150°, d_4^{14} 0.8639, n_D^{16} 1.45917) on the acid earth heated at 350° at the rate of 3.3 g. per hour, 41.0 g. of an oily substance and 7.8 g. of gaseous ammonia were obtained. From the former 1.0 g. of basic substances was separated in the same manner as in the former experiment and 35.0 g. of a neutral oil (d_{20}^{20} 0.8066) was obtained, which was fractionated into nine parts after the seventh fractional distillation (Table 2). The parts boiling below 100° were again fractionated three times (Table 3).

Table 2.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	To 85°	4.2	0.7586	1.4201
2	85—90°	2.0	0.7716	1.4263
3	90—95°	2.5	0.7748	1.4282
4	95—100°	4.9	0.7763	1.4296
5	100—102°	3.8	0.7794	1.4325
6	102—104°	3.1	0.7841	1.4351
7	104—108°	3.9	0.7893	1.4388
8	108—112°	0.7	0.7961	1.4435
9	Residue	7.4	0.9133	—

Table 3.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	70—75°	1.0	0.7492	1.4144
2	75—80°	1.5	0.7630	1.4216
3	80—85°	1.3	0.7686	1.4245
4	85—90°	1.3	0.7727	1.4266
5	90—95°	2.4	0.7750	1.4282
6	95—100°	2.8	0.7776	1.4298
7	Residue	0.7	—	—

The physical constants and the result of elementary analysis of the eighth fraction of Table 2 and the melting point (92–93°) of the nitrosochloride prepared from it by Faworsky and Bergmann's method,(4) well

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(4) *Ber.*, **40** (1907), 4863.

accord with those of Δ^1-methylcyclohexene. (Found: C, 87.16; H, 13.02. Calc. for C_7H_{12}: C, 87.50; H, 12.50%.)

From the physical constants it may be safely stated that the fractions boiling between 102° and 108° consist mainly of Δ^2- and Δ^3-methylcyclohexenes. A greater yield of the liquid nitrosochloride of bluish green colour is obtained from the lower boiling fraction than from the higher boiling, which shows that the lower boiling parts are richer in Δ^3-methylcyclohexene, for, according to Markonikoff,(5) the nitrosochloride of Δ^3-methylcyclohexene is a bluish green liquid. (The nitrosochloride of Δ^2-methylcyclohexene is not yet found in literature.)

The fifth fraction of Table 2 (b.p. 100–102°), united with the corresponding fraction in another experiment carried out under the same conditions, was treated with concentrated sulphuric acid to remove unsaturated hydrocarbons, and 5.0 g. of the resulting saturated hydrocarbons was fractionated five times over metallic sodium (Table 4).

The physical constants of the first fraction of Table 4 indicate that it is almost pure ethylcyclopentane.

The fifth and sixth fractions of Table 3 (b.p. 90–100°) were combined together, treated with concentrated sulphuric acid, and fractionated again over metallic sodium (Table 5).

Table 4.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	90—98°	0.4	0.7632	1.4203
2	98—100°	1.6	0.7663	1.4221
3	Residue	0.7	0.8667	—

Table 5.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	90—96°	0.5	0.7591	1.4177
2	96—98°	1.1	0.7621	1.4195
3	98—100°	0.8	0.7646	1.4211
4	Residue	1.0	0.8625	—

The physical constants and results of elementary analysis of the first fraction of Table 5 (b.p. 90–96°) well accord with those of 1,2-dimethylcyclopentane. (Found: C, 85.49; H, 14.60. Calc. for C_7H_{14}: C, 85.71; H, 14.29%.) The second fraction (b.p. 96–98°) (Table 5) is ethylcyclopentane. (Found: C, 85.56; H, 14.47. Calc. for C_7H_{14}: C, 85.71; H, 14.29%.)

Ethylcyclopentane thus obtained may be contaminated with a small quantity of methylcyclohexane which is produced from methylcyclohexene by the contact action of concentrated sulphuric acid as one of the authors (H.I.) observed previously(6).

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(5) *Bull. soc. chim.*, [3] **34** (1905), 219.
(6) This Bulletin, **1** (1926), 225.

The first fraction of Table 3 (b.p. 70–75°) is obviously methylcyclopentane. (Found: C, 85.92; H, 14.10. Calc. for C_6H_{12}: C, 85.71; H, 14.29%.)

In order to examine the presence of toluene in the reaction products, the fraction boiling between 108° and 112° (Table 2) was treated with concentrated nitric acid under cooling with ice and salt and then the resulting nitro-compound was reduced with tin and hydrochloric acid. The reduction product showed the colour reaction with β-naphthol, which is characteristic of aromatic amines. It was then converted into a benzoyl derivative and this was recrystallized from alcohol. Its melting point was 130°, identical with that of benzo-*o*-toluide. Toluene was therefore actually present.

It was thus possible to detect methylcyclpentane, ethylcyclopentane, dimethylcyclopentane, the three isomeric methylcyclohexenes, and toluene in the neutral reaction product. Methylcyclopentane may here be considered to have been formed not only from cyclohexene but also from ethylcyclopentane by the decomposition analogous to that of ethylcyclohexane into methylcyclohexane⁽⁷⁾. Other hydrocarbons are polymers boiling above 112°. The residue of Table 2 combined with those obtained by other experiments was distilled in steam. Thirteen grams distilled over out of 17.6 g., the distillate was then twice distilled under the pressure of 2 mm., and the fractions shown in Table 6 were obtained.

Table 6.

Fraction	B.p. (2mm.)	Yield (g.)	d_4^{20}	n_D^{20}
1	40—60°	0.4	0.8707	1.4913
2	60—70°	0.5	0.8857	1.4966
3	70—80°	1.2	0.8969	1.5021
4	80—90°	1.6	0.9082	1.5101
5	90—95°	1.8	0.9200	1.5198
6	95—100°	0.5	0.9310	1.5296
7	100—105°	0.3	—	—
8	105—115°	0.2	—	—
9	115—125°	0.8	0.9557	1.5313
10	125—135°	1.6	0.9685	1.5700
11	Residue	1.2	—	—

The largest portion of Table 6 is the fifth fraction boiling between 90° and 95°, which on analysis gave the following results⁽⁸⁾:

Found: C, 88.42; H, 10.96. Calc. for $C_{14}H_{20}$: C, 89.29; H, 10.71%.
Mol. wt. found: 174. Mol. wt. calc. for $C_{14}H_{20}$: 188.

The acid-soluble reaction product amounted to 1.0 g., from which *o*-toluidine was isolated as the benzoyl derivative, and unchanged methylcyclohexylamine as the carbonate.

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(7) Sabatier and Sendrens, *Compt. rend.*, **132**, (1901), 856; ibid., **132**, 1255; *Ann. chim.*, [8] **4**, (1905), 365.

(8) The analysis was carried out after long standing of the sample, so a small amount of atmospheric oxygen seems to have been absorbed by it, some oxidation products being thereby formed.

III. **1-Methylcyclohexylamine-3.** The amine (b.p. 149–151°, d_4^{20} 0.8472, n_D^{20} 1.45357) (68.5 g.) was passed on the acid earth heated at 350° at the rate of 2.7 g. per hour and 34.5 g. of a neutral oil (d_{20}^{20} 0.8053), 8.5 g. of gaseous ammonia, and 1.4 g. of a basic substance were obtained.

The neutral oil was submitted to fractional distillation seven times over metallic sodium and the fractions shown in Table 7 were obtained. The fractions boiling below 100° were further fractionated three times over metallic sodium (Table 8.) Compared with 1-methylcyclohexylamine-(2), 1-methylcyclohexylamine-(3) produces a much less quantity of the portion boiling below 90°, which in the latter case consists mainly of dimethylcyclopentane as shown by its physical constants and the result of elementary analysis (Found: C, 85.97; H, 14.10. Calc. for C_7H_{14}: C, 85.71; H, 14.29%), but the presence of ethyl- and methyl-cyclopentanes was not definitely confirmed. The physical constants of the third fraction (b.p. 95–100°) of Table 7 are nearly equal to those of methylcyclohexane, which was not confirmed to be present in the reaction products of 1-methylcyclohexylamine-(2). The fractions boiling above 100° consist mainly of three isomeric methylcyclohexenes as in the former case. The nitrosochloride prepared from the seventh fraction (b.p. 108–112°) melts at 92°, indicating the presence of Δ^1-methylcyclohexene, which was further confirmed by analysis. (Found: C, 87.01; H, 12.83. Calc. for C_7H_{12}: C, 87.50; H, 12.50%.) Toluene was again found in the same fraction, which was isolated as benzo-*o*-toluide. (Found: N, 6.48. Calc. for $C_{14}H_{13}ON$: N, 6.63%.) Its amount was,

Table 7.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	To 90°	0.3	—	—
2	90—95°	1.7	0.7617	1.4223
3	95—100°	4.7	0.7741	1.4294
4	100—102°	5.5	0.7808	1.4334
5	102—104°	6.9	0.7876	1.4377
6	104—108°	6.5	0.7942	1.4431
7	108—112°	1.2	0.8010	1.4485
8	Residue	5.7	0.9144	—

Table 8.

Fraction	B.p.	Yield (g.)	d_4^{20}	n_D^{20}
1	To 90°	0.8	0.7552	1.4181
2	90—95°	0.9	0.7660	1.4233
3	Residue	4.1	0.7777	1.4295

Table 9.

Fraction	B.p. (5 mm.)	Yield (g.)	d_4^{20}	n_D^{20}
1	To 100°	0.4	0.8795	1.4992
2	100—115°	0.7	0.9251	1.5250
3	115—125°	0.4	0.9382	1.5359
4	125—135°	0.8	0.9632	1.5617
5	Residue	0.2	—	—

however, much larger than in the case of 1-methylcyclohexylamine-(2). The residue of Table 7 was submitted to steam distillation, then distilled under the pressure of 5 mm. into the fractions given in Table 9.

In the basic reaction product a trace of *m*-toluidine was noticed together with some unchanged 1-methylcyclohexylamine-(3).

IV. **1-Methylcyclohexylamine-(4).** The amine (b.p. 149–151°, d_4^{20} 0.8470, n_D^{20} 1.45157) (110.0 g.) was passed on the earth heated at 350° at the rate of 3.1 g. per hour, and 61.5 g. of a neutral oil (d_{20}^{20} 0.8049), 12.8 g. of gaseous ammonia, and 1.8 g. of a basic substance were obtained.

The neutral substance gave the fractions given in Table 10 after ten times fractional distillation over metallic sodium.

Table 10.

Fraction	B.p.	Yield (g.)	d_4^{25}	n_D^{25}
1	To 90°	0.2	—	—
2	90—95°	0.7	0.7531	1.4187
3	95—100°	2.3	0.7680	1.4253
4	100—102°	3.9	0.7754	1.4299
5	102—104°	10.9	0.7822	1.4335
	104—106°	12.2	0.7840	1.4376
7	106—108°	10.2	0.7948	1.4415
8	108—112°	3.8	0.7970	1.4444
9	Residue	8.0	0.8980	—

Table 11.

Fraction	B.p. (5 mm.)	Yield (g.)	d_4^{20}	n_D^{20}
1	To 97°	0.5	0.8776	1.4891
2	97—110°	1.2	0.9046	1.5046
3	110—115°	0.7	0.9129	1.5114
4	115—125°	0.8	0.9226	1.5198
5	125—135°	0.7	0.9450	1.5426
6	Residue	0.9	—	—

By the similar treatment of each fraction, three isomeric methylcyclohexenes, dimethylcyclopentane, and toluene were ascertained to occur. In this case, too, the presence of methyl- and ethyl-cyclopentanes was not confirmed.

The residue of Table 10 was distilled under the pressure of 5 mm. (Table 11). The fourth fraction of Table 11 (b.p. 125–135°) was analyzed.

Found: C, 89.38; H, 10.39. Calc. for $C_{14}H_{20}$: C, 89.29; H, 10.71%.
Mol. wt. found: 176. Mol. wt. calc. for $C_{14}H_{20}$: 188.

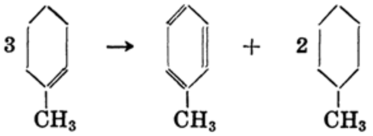
Here again a substance with a probable molecular formula of $C_{14}H_{20}$ was isolated, of which further study was not able to be done on account of the scantiness of the material. In the basic reaction product, *p*-toluidine, unchanged methylcyclohexylamine, and a small quantity of a white crystalline substance melting at 186–190°, probably a homologue of carbazole, were confirmed to occur.

Conclusion.

(1) One molecule of ammonia is first liberated from cyclohexylamine and its methyl derivatives when they are passed on Japanese acid earth heated at 350°, yielding cyclohexene and its methyl derivatives respectively. The molar yield of ammonia produced thereby corresponds to about 80 per cent. of the amine taken.

(2) Some part of cyclohexene thus produced then undergoes an isomeric change from the six-membered carbon ring to the five-membered one giving methylcyclopentane. Methylcyclohexenes suffer the similar isomerization giving ethyl- and dimethyl-cyclopentanes and some part of ethylcyclopentane is further decomposed to methylcyclopentane. The displacement of the double bond within the molecule of Δ^2- or Δ^3-methylcyclohexene must occur simultaneously giving Δ^1-methylcyclohexene, the most stable form of the three isomers, for, in the case of 1-methylcyclohexylamine-(4), Δ^1-methylcyclohexene can not be otherwise formed.

(3) The acid earth promotes also dehydrogenation, yielding aniline and carbazole from methylcyclohexylamine, and toluene from three isomeric methylcyclohexenes. Toluene is always accompanied by methylcyclohexane, and the yields of the two substances go parallel. The following mechanism may be therefore suggested, which Zelinsky(9) has proposed for the catalytic reaction of palladium.



The presence of benzene, however, was not confirmed in the reaction product of cyclohexylamine.

(4) Polymerization, condensation, or both, take place at the same time giving polymers or condensed products, whose amounts are about 15–20 per cent. of the total reaction product.

(5) The total quantity of cyclopentane derivatives is much larger in the case of cyclohexylamine than in the case of its methyl derivatives, while of the latter 1-methylcyclohexylamine-(2) gives the largest amount and 1-methylcyclohexylamine-(4) gives the least. It is also observed that the yield of polymers goes parallel to that of cyclopentane derivatives.

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(9) *Ber.*, **57** (1924), 2055.