g. or 71%. Recrystallization by concentration of its alcoholic solution *in vacuo*, at room temperature, gave white plates, m. p. 274–275° (dec.) (corr.). It was only sparingly soluble in alcohol.

Anal. Calcd. for $C_7H_{14}NI$: I, 53.10. Found: I, 53.20, 53.14.

To prove the identity of this dimethyl derivative, 0.25 g. dissolved in alcohol was shaken with 0.05 g. of Adams platinum oxide catalyst under hydrogen at atmospheric pressure. Reduction proceeded rapidly and the calculated quantity of hydrogen was absorbed. The solution was concentrated, yielding 0.2 g. of prismatic crystals; m. p. 332–333° (dec.). This was identical with an authentic sample of dimethylpiperidinium iodide, m. p. 334° (dec.), prepared from piperidine and methyl iodide.[9]

Anal. Calcd. for $C_7H_{16}NI$: I, 52.65. Found: I, 52.30, 52.32.

Summary

1. Δ^3-Tetrahydropyridine has been prepared and isolated as the hydrochloride.

2. Dimethyl-Δ^3-tetrahydropyridinium iodide has been prepared for physiological testing.

[9] Wedekind and Oechslen, *Ber.*, **35**, 1076 (1902).

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Action of Aluminum Chloride on Cyclohexylbenzene

BY B. B. CORSON AND V. N. IPATIEFF

Bodroux[1] obtained a compound melting at 169–170° as by-product in the alkylation of benzene with cyclohexene in the presence of aluminum chloride. He assumed that it was 1,2-diphenylcyclohexane and that it resulted from the dehydrogenation and rearrangement of dicyclohexylbenzene. The object of our study was to discover the source of this by-product and to determine its structure.

Corson and Ipatieff[2] obtained the same compound in the dealkylation of polycyclohexylbenzenes, and in the present work it also was obtained by the action of aluminum chloride upon monocyclohexylbenzene. Bodroux's suggested mechanism is probably incorrect. The more likely source of the diphenylcyclohexane is monocyclohexylbenzene rather than dicyclohexylbenzene.

Bodroux's evidence for the structure of the 169–170° compound was carbon–hydrogen analysis and melting point. Its melting point was the same as that of a compound described by Kursanoff[3] as 1,2-diphenylcyclohexane, which he obtained from the reaction between 1,2-dichlorocyclohexane and benzene in the presence of aluminum chloride.

We prepared Kursanoff's compound by the interaction of 1,2-dibromocyclohexane with benzene in the presence of aluminum chloride. Mixed melting point showed that it was identical with the product previously obtained[2] in the dealkylation of polycyclohexylbenzenes and also with that obtained in the present work by the action of aluminum chloride on monocyclohexylbenzene.

However, this 169–170° compound is 1,4-disubstituted and not 1,2- as assumed by Kursanoff and Bodroux. We confirm the recent findings of Nenitzescu and Curcaneanu[4] on this point. This rearrangement illustrates the well-known fact that structure cannot be based upon reactions which are catalyzed by aluminum chloride. Our evidence for the 1,4-structure of the 169–170° compound is that it hydrogenates to give a mixture of the two isomeric 1,4-dicyclohexylcyclohexanes.[5]

Cyclohexylbenzene yields a number of products when it is heated at 80–85° with aluminum chloride. The main products—dicyclohexylbenzene, benzene, diphenylcyclohexane, and cyclohexane—indicate the following reactions, in which both phenyl and cyclohexyl groups act as hydrogen donors.[6]

$$2C_6H_{11}C_6H_5 \longrightarrow C_6H_{11}C_6H_4C_6H_{11} + C_6H_6$$
$$2C_6H_{11}C_6H_5 \longrightarrow C_6H_5C_6H_{10}C_6H_5 + C_6H_{12}$$

The lowest boiling fraction contained, besides benzene and cyclohexane, also some hexane (from the opening and hydrogenation of cyclohexane) and probably some methylcyclopentane (from the isomerization of cyclohexane). The second fraction was unchanged cyclohexylbenzene.

Two solids were isolated from the third fraction, 1,4-diphenylcyclohexane (m. p. 169–170°) and 1,4-

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[1] Bodroux, *Ann. chim.*, [10] **11**, 511 (1929).

[2] Corson and Ipatieff, THIS JOURNAL, **59**, 646 (1937).

[3] Kursanoff, *Ann.*, **318**, 309 (1901).

[4] Nenitzescu and Curcaneanu, *Ber.*, **70**, 346 (1937).

[5] (a) Von Braun, Irmisch and Nelles, *ibid.*, **66**, 1471 (1933); (b) Corson and Ipatieff, THIS JOURNAL, **59**, 646 (1937).

[6] In a recently described cleavage reaction [Ipatieff and Pines, THIS JOURNAL, **59**, 56 (1937)] only the cyclohexyl group functioned as hydrogen donor.

dicyclohexylbenzene. The liquid which was separated from the crystals analyzed for $C_{18}H_{26}$ (presumably dicyclohexylbenzene, but it could be phenylcyclohexylcyclohexane). Hydrogenation of this liquid gave two solids, 1,3- and 1,4-dicyclohexylcyclohexanes, and a liquid which also analyzed for dicyclohexylcyclohexane.

The highest boiling fraction from the original reaction product did not crystallize. Its analytical figures ($C_{24}H_{30}$) corresponded to a combination of two phenyl groups and two cyclohexyl groups. Hydrogenation of this liquid gave another liquid which analyzed for $C_{24}H_{42}$ (tricyclohexylcyclohexane).

Experimental

A mixture of 825 g. of cyclohexylbenzene and 65 g. of anhydrous aluminum chloride was stirred for two hours at 80–85° under a reflux condenser to which was attached an ice trap and a dry ice trap in series. Liquid did not collect in the traps. The reaction mixture was decomposed with dilute acid, and washed with caustic, followed by water. The dried mixture was distilled through a Podbielniak column with a reflux ratio of about 10/1. The lowest boiling fraction was redistilled through the same column and the highest boiling fraction was distilled from a Claisen flask. The corrected boiling points used in the distillation curve (Fig. 1) were estimated from the data of Coats and Brown:[7]

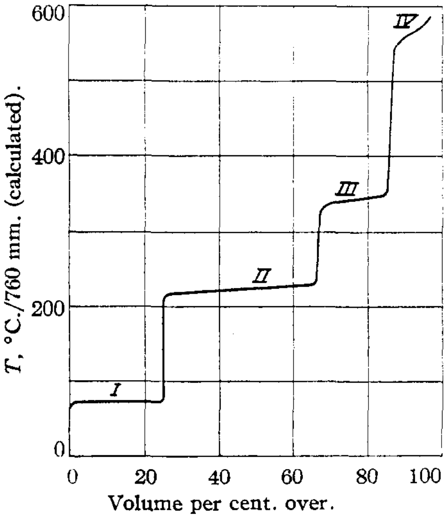

Fig. 1.—Distillation curve.

First Plateau (b. p. 68–78.5° at 755 mm.; n^{20}_{D} 1.4574; d^{20}_{4} 0.816).—This material was stable to 3% permanganate and, therefore, free from olefins. It reacted violently with nitrating mixture and 1,3-dinitrobenzene was isolated. The benzene content as determined by the volume decrease on shaking with cold 15% fuming sulfuric acid was about 65%.

The residual hydrocarbon (n^{20}_{D} 1.4174) from the fuming sulfuric acid was stable to nitrating mixture and, therefore, free from benzene. The presence of cyclohexane in the residual hydrocarbon was established by catalytic dehydrogenation over platinized asbestos at 250°. Hydrogen was liberated and the liquid catalysate contained benzene as shown by the formation of 1,3-dinitrobenzene with nitrating mixture. The estimated cyclohexane content was 30%.

The residual hydrocarbon, after three passes over platinum and removal of benzene after each pass by means of fuming sulfuric acid, was stable to nitrating mixture. Its analytical figures, refractive index, and density (C, 84.6; H, 15.2; mol. wt., 87; n^{20}_{D} 1.3947; d^{20}_{4}, 0.711) indicated that it was a mixture of approximately equal amounts of methylcyclopentane (or cyclohexane) and hexane.

Second Plateau (b. p. 94–114° at 8 mm.; n^{20}_{D} 1.5268; d^{20}_{4} 0.946).—This fraction consisted of unchanged cyclohexylbenzene (about 35% recovery).

Anal. Calcd. for $C_{12}H_{16}$: C, 89.9; H, 10.1; mol. wt., 160. Found: C, 89.7; H, 10.1; mol. wt., 158.

Its identity was established by dehydrogenation to diphenyl by means of bromine.

Third Plateau (b. p. 166–170° at 3 mm.; n^{20}_{D} 1.5418; d^{20}_{4} 0.973).—This fraction deposited solid on standing. The solid was filtered by suction and fractionally crystallized, first from acetone, and finally from methyl alcohol. Four grams of 1,4-diphenylcyclohexane (m. p. 169–170°) was separated during crystallization from acetone.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.5; H, 8.5. Found: C, 91.2; H, 8.6.

Five grams of 1,4-dicyclohexylbenzene (m. p. 102–103°) was separated during subsequent crystallization from methyl alcohol.

The filtrate from the crude solid gave analytical figures agreeing with those of dicyclohexylbenzene (or phenylcyclohexylcyclohexane).

Anal. Calcd. for $C_{18}H_{26}$: C, 89.2; H, 10.8; mol. wt., 242. Found: C, 89.3; H, 10.5; mol. wt., 243.

The liquid was hydrogenated. A mixture of 48 g. of liquid, 100 cc. of cyclohexane, and 10 g. of nickel catalyst[8] was heated for fifteen hours at 220° under an initial hydrogen pressure of 100 kg./sq. cm. The product was crystallized from acetone.

Two solid compounds were separated, 2.3 g. melting at 159–161°, and 15.3 g. melting at 57–59°. The former was identified as the high-melting stereoisomer of 1,4-dicyclohexylcyclohexane.

The 57–59° compound also analyzed for dicyclohexylcyclohexane but mixed melting point showed that it was not the low-melting stereoisomer of the 1,4-derivative[2,5a] since a mixture of equal parts of the latter (m. p. 54–56°) and the 57–59° compound melted at 33–44°. The 57–59° compound was shown to be 1,3-dicyclohexylcyclohexane (see later).

Anal. Calcd. for $C_{18}H_{32}$: C, 87.0; H, 13.0; mol. wt., 248. Found: C, 87.1; H, 13.1; mol. wt., 246.

The mother liquor from the fractional crystallization of

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(7) Coats and Brown, University of Michigan, Dept. Eng. Research, Cir. series 2, 1928.

(8) A specially prepared nickel catalyst, supported on diatomaceous earth, of the same order of activity as Raney nickel, to be described in a subsequent publication by Ipatieff and Corson.

the 57–59° compound contained an oil, the major portion (11.5 g.) of which distilled at 211–215° at 39 mm. (n^{20}_D 1.5038; d^{20}_4 0.935). The analytical figures were those of dicyclohexylcyclohexane.

Anal. Calcd. for $C_{18}H_{32}$: C, 87.0; H, 13.0; mol. wt., 248; MR, 78.7. Found: C, 87.2; H, 12.9; mol. wt., 254; MR, 78.6.

Fourth Plateau (b. p. 330–370° at 2 mm.; n^{20}_D 1.5721; d^{20}_4 1.013).—The analytical figures corresponding to this plateau indicated a combination of two benzene rings with two cyclohexane rings. This material did not crystallize.

Anal. Calcd. for $C_{24}H_{30}$: C, 90.5; H, 9.5; mol. wt., 318. Found: C, 90.1; H, 9.7; mol. wt., 321.

It finally was hydrogenated at 240° under an initial hydrogen pressure of 100 kg./sq. cm. with nickel catalyst. The hydrogenated product was a liquid which gave analytical figures agreeing with those of tricyclohexylcyclohexane.

Anal. Calcd. for $C_{24}H_{42}$: C. 87.2; H, 12.8. Found: C, 87.4; H, 12.6.

Kursanoff's 169–170° Compound.—Two hundred and forty-two grams (1 mole) of 1,2-dibromocyclohexane[9] was added during two hours to a stirred mixture of 624 g. (8 moles) of benzene and 5 g. of anhydrous aluminum chloride. A second 5-g. portion of aluminum chloride was added at the end of an hour. The reaction was run at room temperature. Hydrogen bromide evolution started after about thirty minutes. After the addition of the dibromocyclohexane, the mixture was heated at 50° for two hours. After standing overnight the mixture was decomposed with dilute acid, and the hydrocarbon layer was separated, washed, dried, and twice distilled. Fifty-five grams of dibromocyclohexane was recovered. The 75-g. fraction distilling at 190–215° (9 mm.) became semi-solid on standing. The solid was filtered and crystallized from cyclohexane. Fifteen grams of 1,4-diphenylcyclohexane (m. p. 169–170°) was obtained, together with 0.3 g. of another solid (crystallized from acetone), which melted at 125.5–126.5° (C, 92.3; H, 7.9), whose structure was not determined. The composition of the oil which was filtered from the solid, and which represented the major part of the yield, was not studied.

Hydrogenation of Kursanoff's Compound.—Fourteen grams of the 169–170° compound, dissolved in 50 cc. of cyclohexane, was heated for twenty hours at 220° under an initial hydrogen pressure of 100 kg./sq. cm. with 5 g. of nickel catalyst. Fractional crystallization, first from acetone and later from methyl alcohol, separated the product into the two stereoisomers of 1,4-dicyclohexylcyclohexane.[2,5a] The major portion of the yield was the higher melting isomer.

1, 3 - Dicyclohexylcyclohexane.—1, 3 - Diphenylbenzene (Eastman) was heated for twenty-four hours with nickel catalyst at 200° under an initial hydrogen pressure of 100 kg./sq. cm. Crystallization of the product from acetone gave material melting at 62.5–63.5°.

Anal. Calcd. for $C_{18}H_{32}$: C, 87.0; H, 13.0; mol. wt., 248. Found: C, 87.1; H, 13.0; mol. wt., 249.

The mother liquor contained about 3 cc. of oil which was not analyzed.

A 50/50 mixture of the previously described 57–59° compound and 1,3-dicyclohexylcyclohexane melted at 58–60°. The 57–59° product was, therefore, mainly 1,3-dicyclohexylcyclohexane. The small amount of impurity which contaminated the 57–59° compound was difficult to remove.

1, 2 - Dicyclohexylcyclohexane.—1, 2 - Diphenylbenzene (Eastman) was heated for twenty-four hours at 220° with nickel catalyst under an initial hydrogen pressure of 100 kg./sq. cm. Crystallization of the product from acetone gave material melting at 44.5–46°. The yield was quantitative.

Anal. Calcd. for $C_{18}H_{32}$: C, 87.0; H, 13.0; mol. wt., 248. Found: C, 87.1; H, 13.1; mol. wt., 230.

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Summary

Cyclohexylbenzene, in the presence of aluminum chloride at 80–85°, gives benzene, cyclohexane, hexane, probably methylcyclopentane, 1,4-diphenylcyclohexane, 1,4-dicyclohexylbenzene, probably 1,3-dicyclohexylbenzene, and a still higher boiling material whose composition corresponds to $C_{24}H_{30}$ (a combination of two phenyl groups and two cyclohexyl groups).

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[9] Greengard, *Org. Syn.*, **12**, 26 (1932).