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Influence of Cyclohexene Concentration in the Alkylation of Benzene by Cyclohexene. Dealkylation of Cyclohexylbenzenes

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Direct alkylation of benzene with cycohexene, using aluminum chloride[1] or sulfuric acid[2] as catalyst, offers a convenient method for the preparation of cyclohexylbenzenes.

Bodroux employed a large excess of benzene and obtained monocyclohexylbenzene together with a small quantity of substance melting at 169–170° which had the carbon–hydrogen ratio of diphenylcyclohexane. He assumed that the latter resulted from the dehydrogenation and rearrangement of dicyclohexylbenzene. Truffault obtained monocyclohexylbenzene and 1,4-dicyclohexylbenzene.

This paper describes the effect of varying the amount of cyclohexene. Using aluminum chloride as catalyst, the following products were obtained: monocyclohexylbenzene, 1,4-dicyclohexylbenzene, 1,3,5-tricyclohexylbenzene and 1,2,3,5-tetracyclohexylbenzene. The tri and tetra derivatives are new. With sulfuric acid as catalyst, the products were: monocyclohexylbenzene, 1,4-dicyclohexylbenzene and 1,2,3,5-tetracyclohexylbenzene. The yields of the various products depend upon the relative proportions of benzene and cyclohexene, catalyst and conditions being constant.

Both catalysts gave some liquid product which analyzed for di derivative. Von Braun,[3] also, obtained liquid di derivative as by-product from the reaction between benzene and cyclohexylbromide. Although our product remained liquid at −77°, it still contained 1,4-dicyclohexylbenzene as shown by dehydrogenation.

Mono-, di- and tricyclohexylbenzenes can be alkylated to higher derivatives by cyclohexene. Both mono- and dicyclohexylbenzenes can be converted to tetra derivative. Tricyclohexylbenzene was not isolated. Tri derivative can be alkylated to tetra derivative, but the yield is small, the main product being liquid. Attempts to obtain penta- and hexacyclohexylbenzenes were unsuccessful.

Di-, tri- and tetracyclohexylbenzenes can be dealkylated to lower derivatives by the action of benzene in the presence of aluminum chloride. 1,4-Dicyclohexylbenzene and 1,3,5-tricyclohexylbenzene are converted to monocyclohexylbenzene. 1,2,3,5-Tetracyclohexylbenzene is dealkylated to monocyclohexylbenzene and 1,3,5-tricyclohexylbenzene. From the di, tri and tetra derivatives there was also obtained a small yield of material melting at 168–169° which had the carbon–hydrogen ratio of diphenylcyclohexane.[4]

The proof of structure of the mono derivative consisted in dehydrogenation by bromine to diphenyl. The di derivative was identical with 1,4-dicyclohexylbenzene prepared according to the method of von Braun,[3] who established its structure by dehydrogenation to 1,4-diphenylbenzene and by oxidation to terephthalic acid. Hydrogenation of the di derivative gave the two isomeric 1,4-dicyclohexylcyclohexanes described by von Braun.[5] The structure of the tri derivative was established by dehydrogenation to 1,3,5-triphenylbenzene and by hydrogenation to 1,3,5-tricyclohexylcyclohexane.[6]

The structure of the tetra derivative was based upon its easy dealkylation to 1,3,5-tricyclohexylbenzene and also upon its hydrogenation (accompanied by dealkylation) to 1,4-dicyclohexylcyclohexane and 1,3,5-tricyclohexylcyclohexane.[7]

Experimental

Benzene, Cyclohexene and Aluminum Chloride.—To a stirred, ice-cooled mixture of 176 g. (2.3 moles) of benzene and 60 g. of anhydrous aluminum chloride was added 246 g. (3 moles) of cyclohexene (b. p. 82–85°; $d^{20}{}_4$ 0.811; $n^{20}{}_D$ 1.446). The time of addition was two and eight-tenths hours. The reaction temperature was 3–18°. After stirring an additional hour, the catalyst was decomposed with dilute acid and the mixture was filtered. Distillation and crystallization separated four cyclohexylbenzenes: 58 g. of monocyclohexylbenzene, 31 g. of 1,4-dicyclohexylbenzene, 158 g. of 1,3,5-tricyclohexylbenzene and 1 g. of 1,2,3,5-tetracyclohexylbenzene.

The constants of monocyclohexylbenzene are: b. p. 238.6–238.8° (756 mm.); m. p. 6.6–7.0°; $d^{20}{}_4$ 0.944; $n^{20}{}_D$ 1.5254.

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[1] Bodroux, *Ann. chim.*, [10] **11**, 511 (1928); see Berry and Reid, THIS JOURNAL, **49**, 3142 (1927).

[2] Truffault, *Compt. rend.*, **202**, 1286 (1936); the work described below was done before the appearance of Truffault's paper.

[3] Von Braun, *Ber.*, **60**, 1180 (1927).

[4] The reaction responsible for this product will be discussed in a later paper.

[5] Von Braun, Irmisch and Nelles, *Ber.*, **66**, 1471 (1933).

[6] Adkins, Zartman and Cramer, THIS JOURNAL, **53**, 1425 (1931).

[7] Tetraphenylmethane also dealkylates during hydrogenation; Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Co., New York, 1936, p. 239.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.9; H, 10.1; mol. wt., 160. Found: C, 90.2; H, 9.9; mol. wt., 158.

1,4-Dicyclohexylbenzene (m. p. 102–103°) was found in the mother liquor from the crystallization of the tri derivative.

Anal. Calcd. for $C_{18}H_{26}$: C, 89.2; H, 10.8; mol. wt., 242. Found: C, 89.1; H, 10.8; mol. wt., 241.

Six cc. of oil was obtained which also had the carbon-hydrogen ratio of dicyclohexylbenzene. Its constants were: b. p. 335–340° (756 mm.); d^{20}_4 0.966; n^{20}_D 1.5357; C, 88.8; H, 10.9; mol. wt., 242. Dehydrogenation with bromine gave some 1,4-diphenylbenzene, showing that the original liquid contained 1,4-dicyclohexylbenzene.

1,3,5-Tricyclohexylbenzene melts at 68.5–69° after crystallizing from acetone. The air-dried material melts low, but after warming in a vacuum the melting point is sharp. It is very soluble in benzene, cyclohexane, carbon tetrachloride, and chloroform; less soluble in acetone, dioxane, and the lower alcohols.

Anal. Calcd. for $C_{24}H_{36}$: C, 88.8; H, 11.2; mol. wt., 324. Found: C, 88.5; H, 11.2; mol. wt., 350.

1,2,3,5-Tetracyclohexylbenzene melts at 264–265° after crystallizing from benzene. It is soluble in benzene, cyclohexane, carbon tetrachloride and chloroform; less soluble in acetic acid, acetone, ether and the lower alcohols.

Anal. Calcd. for $C_{30}H_{46}$: C, 88.6; H, 11.4; mol. wt., 406. Found: C, 88.3; H, 11.4; mol. wt., 414.

A fair yield of tetra derivative was obtained by increasing the ratio of cyclohexene to benzene, and using cyclohexane as solvent. In the absence of solvent, the mixture became too thick for effective stirring. To a mixture of 156 g. (2 moles) of benzene, 60 g. of aluminum chloride and 150 g. of cyclohexane was added 328 g. (4 moles) of cyclohexene. The time of addition was three and one-half hours. The reaction temperature was 3–20°. The products were: 20 g. of monocyclohexylbenzene, 35 g. of 1,4-dicyclohexylbenzene, 150 g. of 1,3,5-tricyclohexylbenzene and 80 g. of 1,2,3,5-tetracyclohexylbenzene.

Benzene, Cyclohexene and Sulfuric Acid.—Monocyclohexylbenzene was obtained as main product when 164 g. (2 moles) of cyclohexene was added to a stirred, ice-cooled mixture of 408 g. (6 moles) of benzene and 92 g. of 96% sulfuric acid. The time of addition was two hours. The hydrocarbon layer was washed with two 50-cc. portions of cold 96% sulfuric acid,[8] followed by water, 3% caustic, and water. The dried hydrocarbon was twice distilled through a short column. The yield of monocyclohexylbenzene was 200 g. (b. p. 239–245° at 760 mm.). The hydrocarbon fractions boiling at 78–83°, 83–235°, 235–239°, 245–265°, 265–300° and above 300° weighed 320, 2, 2, 11, 4 and 63 g., respectively.

The filtrate from the semi-solid bottoms was freed from unsaturates by shaking with cold 96% sulfuric acid, followed by distillation. The distillate did not solidify at −77°. Its constants were similar to those of the liquid mixture of isomeric dicyclohexylbenzenes obtained with aluminum chloride as catalyst (b. p. 332–335° at 742 mm.; d^{20}_4 0.969; n^{20}_D 1.5366; C, 88.8; H, 10.9; mol. wt., 253).

A satisfactory yield of 1,4-dicyclohexylbenzene could not be obtained by increasing the cyclohexene–benzene ratio.

A reaction mixture of 164 g. (2 moles) of cyclohexene, 156 g. (2 moles) of benzene, and 92 g. of sulfuric acid gave mono derivative as main product, 143 g. Fifty-one grams of crude solid was filtered from the bottoms (90 g.). Crystallization of the solid gave 26 g. of pure di compound and 11 g. of impure material melting at 95–99°.

Starting with 246 g. (3 moles) of cyclohexene, 156 g. (2 moles) of benzene, and 92 g. of sulfuric acid gave 95 g. of crude monocyclohexylbenzene and 170 g. of bottoms distilling above 300°. The latter deposited solid on standing. Filtration gave 94 g. of solid and 69 g. of oil. Seventy-one grams of pure 1,4-dicyclohexylbenzene was obtained by recrystallizing the crude solid.

When the cyclohexene–benzene ratio was greater than 1.5, there was excessive tar formation. An experiment was made with 328 g. (4 moles) of cyclohexene, 156 g. (2 moles) of benzene, and 92 g. of sulfuric acid. The reaction mixture was so dark that it was difficult to separate the acid layer. Troublesome emulsions were encountered when the hydrocarbon layer was washed. Seventy-five grams of monocyclohexylbenzene and 199 g. of bottoms (above 300°) were obtained. From the latter was obtained 61 g. of 1,4-dicyclohexylbenzene and 1.5 g. of 1,2,3,5-tetracyclohexylbenzene. The filtrate (110 g.) was not investigated.

Alkylation of Mono-, Di- and Tricyclohexylbenzenes.—Ninety-eight grams (1.2 moles) of cyclohexene was added during one hour to a mixture of 160 g. (1 mole) of monocyclohexylbenzene, 80 g. of cyclohexane, and 92 g. of 96% sulfuric acid. The reaction temperature was 2–14°. The following compounds were isolated: 70 g. of monocyclohexylbenzene, 23 g. of 1,4-dicyclohexylbenzene and 12 g. of 1,2,3,5-tetracyclohexylbenzene. The greater part of the tetra derivative separated from the catalyst acid on standing.

Forty-one grams (0.5 mole) of cyclohexene was added to a mixture of 58 g. (0.24 mole) of 1,4-dicyclohexylbenzene, 80 g. of cyclohexane and 20 g. of anhydrous aluminum chloride. The time of addition was one hour. The reaction temperature was 3–7°. Forty-nine grams of 1,4-dicyclohexylbenzene and 16 g. of 1,2,3,5-tetracyclohexylbenzene were isolated. When the reaction was run at 80°, the products were 35 g. of 1,4-dicyclohexylbenzene and 9 g. of 1,2,3,5-tetracyclohexylbenzene, plus 25 g. of liquid boiling from 300 to 425°.

Twelve and three-tenths grams (0.15 mole) of cyclohexene was added to a mixture of 32.4 g. (0.1 mole) of 1,3,5-tricyclohexylbenzene, 80 g. of cyclohexane, and 20 g. of aluminum chloride. The time of addition was one hour. Different reaction temperatures were tried; 11–15°, 34–37° and 80–83°. The solid products isolated from these experiments were: 19 g. of tri and 1 g. of tetra derivative; 15 g. of tri and 0.3 g. of tetra derivative; 7.7 g. of tri derivative, respectively.

Dealkylation of Di-, Tri- and Tetracyclohexylbenzenes.—1,4-Dicyclohexylbenzene (24.2 g.; 0.1 mole) was stirred for two hours at 80–83° with 195 g. (2.5 moles) of benzene and 20 g. of aluminum chloride. Eighteen grams of monocyclohexylbenzene was obtained; also 5 g. of liquid which distilled at 330–350°, and 6 g. of bottoms. Both of the

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[8] The purpose of the sulfuric acid was to remove esters which would otherwise decompose to tar during distillation; see Ipatieff, Corson and Pines, THIS JOURNAL, 58, 919 (1936).

latter fractions deposited crystals which melted at 168–169° after crystallizing from acetone.

1,3,5-Tricyclohexylbenzene (32.4 g., 0.1 mole) was stirred for two hours at different temperatures with 195 g. (2.5 moles) of benzene and 20 g. of aluminum chloride. Depending on the temperature, the main product was monocyclohexylbenzene or unchanged tri derivative. At 22–27° the products were 4.2 g. of mono derivative and 20.8 g. of tri derivative; at 50–55°, 23 g. of mono derivative; at 80–83°, 15 g. of mono derivative. The amount of viscous bottoms increased with the temperature. There was also a small fraction boiling at 330–350° which deposited solid on standing which melted at 168–169° and which was identical with the solid obtained from the di derivative. With anhydrous ferric chloride as catalyst, neither monocyclohexylbenzene nor the 330–350° fraction was obtained. The viscous bottoms were not investigated.

1,2,3,5-Tetracyclohexylbenzene (40.6 g., 0.1 mole) was stirred at 20–23° for two and one-half hours with 98 g. (1.25 moles) of benzene and 20 g. of aluminum chloride. Eleven grams of monocyclohexylbenzene (b. p. 235–241°; n^{20}_D 1.525) and 20 g. of 1,3,5-tricyclohexylbenzene were isolated. The identity of the mono derivative was established by dehydrogenation to diphenyl (m. p. 68–69°; mixed m. p. 69–70.5°). The tri derivative melted at 67–68° and showed no depression when melted with an equal quantity of 1,3,5-tricyclohexylbenzene. A fraction boiling at 330–350° was also obtained. This liquid deposited solid melting at 168–169°, which was identical with that obtained in the dealkylation of 1,4- and 1,3,5-tricyclohexylbenzenes.

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

Repetition of this experiment at 80°, using 40.6 g. (0.1 mole) of tetra compound, 195 g. (2.5 moles) of benzene, and 20 g. of aluminum chloride gave 25 g. of monocyclohexylbenzene and 4 g. of material boiling at 300–350°. The latter deposited crystals of the 168–169° compound.

Proof of Structure.—Monocyclohexylbenzene was dehydrogenated to diphenyl. Forty-eight grams of bromine was added during two hours to 16 g. of monocyclohexylbenzene at 165°. The bromine was consumed quickly and hydrogen bromide was evolved. The product distilled at 253–273° (755 mm.) and the distillate solidified. The recrystallized solid melted at 68–69° (yield 14 g.). The mixed melting point with diphenyl was 69–70.5°.

Dicyclohexylbenzene was identical by mixed melting point with 1,4-dicyclohexylbenzene prepared according to the method of von Braun,[3] from cyclohexyl bromide, benzene and aluminum chloride.

Hydrogenation of dicyclohexylbenzene gave two isomeric dicyclohexylcyclohexanes. Forty-eight grams of di derivative (dissolved in 100 cc. of cyclohexane) was heated fourteen hours at 220° with 5 g. of nickel catalyst and an initial hydrogen pressure of 100 kg./sq. cm. The main product was the isomer melting at 159.5–161° (calcd.: C, 87.0; H, 13.0. Found: C, 86.9; H, 13.0). The other isomer melted at 54–56° (Found: C, 86.9; H, 13.0.)

Tricyclohexylbenzene was dehydrogenated to 1,3,5-triphenylbenzene. Thirty-six grams of bromine was added to 8 g. of tricyclohexylbenzene at 165°. Hydrogen bromide was evolved. The reaction product was distilled at 4 mm., 7 g. boiling at 230–250°. The distillate solidified. It was crystallized from absolute alcohol; m. p. 168–170°. Combustion gave low figures for carbon (calcd.: C, 94.07; H, 5.93. Found: C, 92.68, 92.74; H, 5.97, 5.98). A 50–50 mixture of 1,3,5-triphenylbenzene (m. p. 171–172°)[9] and dehydrogenation product melted at 170–171°.

Hydrogenation of the tri derivative gave tricyclohexylcyclohexane; m. p. 158–159° after crystallizing from cyclohexane–acetone. Thirty grams of tricyclohexylbenzene (dissolved in 100 cc. of cyclohexane) was heated for twenty hours at 240° with 5 g. of nickel catalyst and an initial hydrogen pressure of 120 kg./sq. cm.

Anal. Calcd. for $C_{24}H_{42}$: C, 87.2; H, 12.8. Found: C, 86.9; H, 12.9.

Tetracyclohexylbenzene was assumed to be the 1,2,3,5-derivative because of its easy dealkylation to 1,3,5-tricyclohexylbenzene.

Hydrogenation of the tetra derivative gave mainly 1,3,5-tricyclohexylcyclohexane, together with a smaller amount of 1,4-dicyclohexylcyclohexane. Fifty-one grams of tetracyclohexylbenzene (dissolved in 100 cc. of cyclohexane) was heated for twelve hours at 250° and twelve hours at 280° with 5 g. of nickel catalyst and an initial hydrogen pressure of 100 kg./sq. cm. A small amount of liquid product, obtained from the mother liquor, was not investigated.

Acknowledgment.—The authors express their thanks to Mr. Wilbur Shand for assistance in the experimental work and to Mr. Reno Moehl for carbon–hydrogen analyses.

Summary

Benzene reacts with cyclohexene to form mono-, di-, tri- and tetracyclohexylbenzenes. The nature of the product depends upon the relative amount of cyclohexene. The reaction is catalyzed by aluminum chloride and also by sulfuric acid.

Mono-, di- and tricyclohexylbenzenes react with cyclohexene to form higher derivatives.

Di-, tri- and tetracyclohexylbenzenes react with benzene, in the presence of aluminum chloride, to form lower derivatives.

Di- and tricyclohexylbenzenes are hydrogenated to di- and tricyclohexylcyclohexanes, respectively. Tetracyclohexylbenzene is dealkylated during hydrogenation, the products being di- and tricyclohexylcyclohexanes.

RIVERSIDE, ILLINOIS RECEIVED JANUARY 18, 1937

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[9] Dolgov and Volnov, *J. Gen. Chem.* (U. S. S. R.), **1**, 340 (1931).