Anal. Calcd. for $C_6H_9(C{\equiv}CCl)$, $C_8H_{10}Cl_2$: Cl, 25.3, 40.1; mol. wt., 140.5, 177. Found: Cl, 32.0; mol. wt., 157, 159.

When 1-bromoethynyl-1-cyclohexanol was treated similarly with pyridine and thionyl chloride a mixture of 1-bromoethynyl-1-cyclohexene and 1-(chlorobromovinyl)-1-cyclohexene was formed. From 23 g. of the hexanol, there was produced 4 g. of product distilling at 120–130° (34 mm.) and 4.5 g. at 130–140°.

Summary

1-α-Chlorovinyl-1-cyclohexene was prepared by the action of thionyl chloride on ethynylcyclohexanol in pyridine and some ethynylcyclohexene was obtained also. 1-Ethynyl-1-chlorocyclohexane and cyclohexylidenevinyl chloride were proved absent.

1-Phenylethynyl-1-cyclohexanol, 1-chloroethynyl-1-cyclohexanol and 1-bromoethynyl-1-cyclohexanol underwent more dehydration than chlorination by thionyl chloride or phosphorus pentachloride.

1-Ethyl-1-chlorocyclohexane was prepared readily from 1-ethyl-1-cyclohexanol but 1-phenyl-1-cyclohexanol resisted chlorination.

EVANSTON, ILL. RECEIVED DECEMBER 11, 1933

[UNIVERSAL OIL PRODUCTS COMPANY RESEARCH LABORATORIES, RIVERSIDE, ILLINOIS]

The Action of Aluminum Chloride on Benzene and Cyclohexane

BY V. N. IPATIEFF AND V. I. KOMAREWSKY

In this study our observations are reported on the action of aluminum chloride on benzene and cyclohexane.

The numerous published references[1] on the action of aluminum chloride on benzene show quite different results on account of the use of different conditions in the experiments. Therefore, we decided to study this reaction under a definite set of conditions.

In a closed autoclave, in the absence of air and in the presence of dry hydrogen chloride, the action of aluminum chloride on benzene at 125° gave 1.7% of ethylbenzene and 0.84% of diphenyl calculated on the benzene charged.

To compare these results properly with the results of other investigators, it is necessary to note the following: (1) The absence of oxygen in our experiments accounts for the absence in our products of phenols and other oxygen-containing compounds (obtained by Wertyporoch and Sagel[1e] and Senff[1d]). It is evident that in the experiments of these investigators the oxygen of air and water has taken part in the reaction.

(2) The reaction of benzene with aluminum chloride under our conditions proceeds much more rapidly.

(3) The main products of reaction are ethylbenzene and diphenyl. The formation of these two compounds makes probable the following scheme of the reaction: (a) two parts of benzene combine to form diphenyl, liberating hydrogen; (b) a destructive hydrogenation of benzene occurs during which benzene decomposes, and the *decomposed fragments are hydrogenated* to form ethylene; (c) ethylene *alkylates* the unchanged benzene to form ethylbenzene.

The reaction of the first type (a) was observed by Friedel and Crafts,[1b] Scholl[2] and Scholl and Seer.[3] In the other two reactions, (b) and (c), we observed first a decomposition (destruction) and then an alkylation.

The proof that benzene decomposes in this manner follows: (1) from the formation of ethylbenzene, and (2) from the discovery, in the lower layer, containing aluminum chloride, of unsaturated ethylene polymers. Therefore, it is suggested that reactions (b) and (c) be called *destructive alkylation.*

From previous works by Aschan and others[4] it is known that cyclohexane isomerizes to methylcyclopentane in the presence of aluminum chloride.

In studying the action of aluminum chloride on cyclohexane under our experimental conditions, we have observed more fundamental changes.

By the action of aluminum chloride on cyclohexane in closed autoclaves in the presence of hydrogen chloride and in the absence of air at a

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[1] (a) Fr. Fischer and Niggemann, *Ber.*, **49**, 1475 (1916); (b) Friedel and Crafts, *Bull. de soc. chem. de Fr.*, **39**, 195, 306 (1883); (c) Gustavson, *Compt. rend.*, **146**, 640 (1908); (d) Senff, *Ann.*, **220**, 232 (1883); (e) Wertyporoch and Sagel, *Ber.*, **66**, 1306 (1933).

[2] Scholl, *Ber.*, **43**, 1737, 2202 (1910).

[3] Scholl and Seer, *Ann.*, **394**, 111 (1912).

[4] (a) Aschan, *ibid.*, **324**, 1 (1902); (b) Ipatieff and v. Grosse, in publication; (c) Nenitzescu and Cantuniari, *Ber.*, **66**, 1097 (1933); (d) Zelinsky, Turowa and Pollak, *ibid.*, **65**, 1171 (1932).

temperature of 150° for twenty-four hours, the hydrocarbon changes fundamentally. Besides isomerization to methylcyclopentane, dehydrogenation occurs with subsequent combination of two cyclohexyl radicals to form a mixture of dimethyldicyclopentyl and dicyclohexyl. An evolution of hydrogen occurs and a destructive alkylation reaction results in the production of *m*-dimethylcyclohexane. This experiment shows that (1) in order to combine two cyclohexyl radicals, it is not necessary to start with a mixture of cyclohexane and a halogen derivative ($C_6H_{11}Cl$) as is stated by Nenitzescu and Ionescu,[5] and (2) this reaction is not similar to that of Friedel and Crafts[1b] but a special reaction of a *destructive alkylation* with formation of dimethylcyclohexane. The yields of the reaction products, all calculated on the cyclohexane charged, are as follows: the product boiling up to 80° is a mixture of methylcyclopentane and unchanged cyclohexane; 34% is a liquid boiling from 80 to 289°, from which 6.5% of dimethylcyclohexane and 12.1% of a hydrocarbon, $C_{12}H_{22}$, were isolated and identified (calculated on cyclohexane charged). In addition, a certain amount (0.7–0.8%) of gas was evolved during the reaction.

Summarizing the results obtained, the most probable scheme of the reactions is as follows: (1) cyclohexane decomposes, giving ethylene. (2) Ethylene alkylates cyclohexane giving ethylcyclohexane, the latter isomerizing immediately to *m*-dimethylcyclohexane. (3) Other portions of cyclohexane dehydrogenate and two cyclohexyl radicals combine to form $C_{12}H_{22}$. (4) Destructive hydrogenation of cyclohexane produces paraffinic hydrocarbons, especially *i*-butane (see gas analysis).

It is interesting to note that during this reaction no formation of a lower layer was observed. The small increase in weight of aluminum chloride may be explained by a simple wetting of the catalyst by the products of the reaction.

Experimental Part

1. Benzene

About 100 g. of benzene (Baker C. P.) saturated with dry hydrogen chloride was placed in a glass cylinder and 10% by weight of aluminum chloride (obtained by sublimation) added. The glass cylinder was placed in a rotating Ipatieff bomb (750 cc. volume) in which the air had been displaced by nitrogen and heated for twenty-four hours at 125°. After completion of the experiment, no gases were evolved, the whole product consisting of two layers. The upper layer, after separation, was washed with water and 10% alkali solution, dried with calcium chloride and distilled in a Podbielniak apparatus.[6] The combined product from eight similar experiments was investigated. From 830.0 g. of benzene and 80.0 g. of aluminum chloride 903.7 g. of a product, consisting of two layers, was recovered. The upper layer amounted to 715.0 g. and the lower layer to 188.5 g. The upper layer gave on distillation 679.2 g. of an unchanged benzene and 35.8 g. of a higher boiling product. The lower layer, after decomposition with ice, gave 35.0 g. of an unchanged benzene, 10.0 g. of a higher boiling product (up to 250°) and 2.0 g. of unsaturated residues. From the upper layer 14.1 g. of a product boiling at 139–141° was isolated. An investigation of this product showed that it was pure ethylbenzene, n^{20}_{D} 1.4970.

Anal. Calcd. for $C_6H_5C_2H_5$: C, 90.56; H, 9.44. Found: C, 90.45; H, 9.50.

Oxidation with potassium permanganate gave pure benzoic acid of melting point 120°. Bromination in the presence of aluminum bromide, according to Klages and Allendorf,[7] gave a pure tetrabromide, $C_6HBr_4C_2H_5$, with a melting point of 139–140°. From the higher boiling fractions it was possible to isolate by fractionation 7 g. of a product boiling at 235–250° which solidified in the condenser. Recrystallization of this product from benzene gave pure diphenyl with a melting point of 70°.

Anal. Calcd. for $C_6H_5C_6H_5$: C, 93.50; H, 6.50. Found: C, 93.35; H, 6.63.

2. Cyclohexane

The same method was used for cyclohexane (Eastman C. P.), the temperature of the three experiments being 150°. From 307.4 g. of cyclohexane (three experiments) and 33.3 g. of aluminum chloride, 332.0 g. of liquid products consisting of two layers was recovered. In addition, 2175 cc. of gas was evolved during the reaction containing 61% of *i*-butane. The upper layer amounted to 289.5 g. and the lower layer to 42.5 g. The upper layer was separated into two fractions, using the Podbielniak apparatus: (1) 70 to 80°; (2) 80° and higher. The product boiling up to 80° is completely stable to the nitrating mixture and contains a mixture of methylcyclopentane and cyclohexane as can be seen from the boiling point 70 to 80° and refractive index n^{20}_{D} 1.4150. From the second fraction, 19.9 g. boiling at 120–123° was isolated by repeated fractionation, n^{23}_{D} 1.4215.

Anal. Calcd. for $C_6H_{10}(CH_3)_2$: C, 85.47; H, 14.53. Found: C, 85.68; H, 14.43.

This is a pure naphthenic hydrocarbon.

This hydrocarbon was dehydrogenated over palladium catalyst at 320°, according to Zelinsky and Borisoff.[8] The dehydrogenated product is soluble in fuming sulfuric acid (15% SO_3 content), has n^{19}_{D} 1.4801, and gives after bromination, according to Klages and Allendorf,[7] a tetrabromide, $C_6Br_4(CH_3)_2$, with a melting point of 243°. This shows that the product investigated was a pure 1,3-dimethylcyclohexane. From the same fraction 37.1 g. of a product boiling at 220° was isolated, n^{16}_{D} 1.4675.

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[5] Nenitzescu and Ionescu, *Ann.*, **491**, 189 (1931).

[6] Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **5**, 119 (1933).

[7] Klages and Allendorf, *Ber.*, **31**, 1005 (1898).

[8] Zelinsky and Borisoff, *ibid.*, **57**, 150 (1924).

Anal. Calcd. for $C_{12}H_{22}$: C, 86.73; H, 13.27. Found: C, 86.48; H, 13.38.

This compound solidified when cooled in dry ice. The crystals were separated from the liquid by filtering through a cooled filter, and after recrystallization from methyl alcohol gave a pure white substance with a melting point of 46–47°.

Anal. Calcd. for $C_{12}H_{22}$: C, 86.73; H, 13.27. Found: C, 86.55; H, 13.30.

This compound corresponds exactly to dimethyldicyclopentyl isolated by Nenitzescu and Ionescu.[5]

Another portion of this product was dehydrogenated over palladium catalyst at 320°, according to Zelinsky and Borisoff.[8] After the dehydrogenation, the refractive index of the product increased from n_{16} 1.4675 to n_{18} 1.4815, and the following treatment by fuming sulfuric acid (15% SO_3 content) showed an aromatic content of 25%. The residue after sulfuric acid treatment could not be further dehydrogenated over palladium, and its analysis gave C, 86.78; H, 13.28. This investigation shows that 25% of the compound $C_{12}H_{22}$ is dicyclohexyl, the other 75% of this compound being dimethyldicyclopentyl, which could not be dehydrogenated over palladium.

Summary

1. The reaction of aluminum chloride on benzene has been confirmed and the formation of ethylbenzene and diphenyl has been studied quantitatively.

2. The action of aluminum chloride on cyclohexane has been investigated and the formation of dimethylcyclohexane and polycyclic hydrocarbons, $C_{12}H_{22}$, has been found.

3. The formation of ethylbenzene from benzene and dimethylcyclohexane from cyclohexane has been explained by assuming a simultaneous decomposition and alkylation designated by the term "Destructive Alkylation."

CHICAGO, ILLINOIS RECEIVED MARCH 22, 1934

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 137]

Reduction Studies in the Morphine Series. III. Dihydro-γ-isomorphine[1]

BY LYNDON SMALL AND ROBERT E. LUTZ

The extraordinary tendency of morphine derivatives of the pseudocodeine type, having a double linkage in the 6,7-position, to undergo "abnormal" reduction with addition of four hydrogen atoms, has heretofore made the normal dihydro derivatives of such bases inaccessible for pharmacological study. In the first paper of this series[2] it was demonstrated that the course of hydrogenation of pseudocodeine can be influenced by the reduction conditions in such a way that reductive scission of the ether ring is largely suppressed, and the principal product is a non-phenolic dihydropseudocodeine. This communication deals with the application of the special reduction conditions to γ-isomorphine and the development of a feasible preparative method for dihydro-γ-isomorphine.

As would be anticipated from the structural features present in ring III, γ-isomorphine is reduced catalytically under ordinary conditions with absorption of two moles of hydrogen, one of which is used in opening the ether ring, the other in saturating the alicyclic double linkage. The product is the diphenolic base tetrahydro-γ-isomorphine (III), which is very sensitive in neutral or alkaline solution, but so stable toward acids that it may be prepared by demethylation of tetrahydropseudocodeine (V) with boiling concentrated hydriodic acid.

By catalytic hydrogenation of γ-isomorphine under the conditions described in our previous communication, reductive scission of the ether linkage is diminished and the product consists of nearly equal amounts of tetrahydro-γ-isomorphine and the desired dihydro-γ-isomorphine (II). It is noteworthy that for γ-isomorphine the tendency to "abnormal" reduction appears to be much greater than for pseudocodeine under similar conditions.

The new dihydro-γ-isomorphine can be methylated with diazomethane, giving the known non-phenolic dihydropseudocodeine (IV).[2] The preparation of γ-isomorphine and the separation of the products obtained in its hydrogenation is an arduous process. As a preparative method it was found more advantageous to demethylate the relatively accessible dihydropseudocodeine with concentrated hydriodic acid, a reaction which gives an 84% yield of practically pure dihydro-γ-isomorphine.

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[1] The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia, and the University of Michigan.

[2] Lutz and Small, THIS JOURNAL, **54**, 4715 (1932).