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

Destructive Hydrogenation of Indan and Hexahydroindan

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It has been shown[1] that bicyclic dihydroterpenic hydrocarbons, such as isobornylane and isocamphane, consisting of a five- and a six-membered ring, yielded only alkylcyclopentanes on destructive hydrogenation in the presence of a nickel–kieselguhr catalyst. It was of interest therefore to determine whether indan would also yield pentamethylenic hydrocarbons on destructive hydrogenation.

Indan on reacting with hydrogen at an initial pressure of 100 atmospheres and in the presence of a nickel–kieselguhr catalyst at 160° yielded only hexahydroindan. If, however, the hydrogenation was carried out at 240 to 250°, hydrogenolysis of the hexahydroindan presumably formed occurred, and the product was composed chiefly of alkylcyclohexanes; this reaction was also accompanied by demethylation. The alkylcyclohexanes formed consisted of 59 mole % of 1-methyl-2-ethylcyclohexane and 40 mole % of 1,2-dimethylcyclohexane. At 260° demethylation was more pronounced and the product consisted of lower boiling alkylcyclohexanes.

The relative activity of the nickel–kieselguhr catalyst was compared with a copper–alumina catalyst (67% CuO, 33% Al_2O_3), which previously was shown to catalyze the destructive hydrogenation of hydrocarbons.[2]

At 275° indan underwent hydrogenation in a stainless steel autoclave in the presence of copper–alumina and 100 atmospheres of hydrogen pressure; hexahydroindan to the extent of 65% was formed.

When the reaction was carried out at 325° 60% of the indan underwent hydrogenolysis to alkylbenzenes. From the infrared absorption spectral analysis it was calculated that on the basis of the indan reacted 57 mole % of toluene was produced. The other aromatic hydrocarbons present were *n*-propylbenzene, 33 mole % and benzene, 3 mole %. A small amount of naphthenic hydrocarbons such as methylcyclohexane and *n*-propylcyclohexane were also formed.

Since indan might have undergone hydrogenation prior to destructive hydrogenation, it was decided to subject hexahydroindan to the reaction with hydrogen at 325°; the copper–alumina catalyst was used and the experimental conditions were similar to that used in the case of indan. The product from this reaction consisted of gaseous and liquid hydrocarbons. The gases were composed of methane, ethane and propane; each of the gaseous hydrocarbons was produced in amounts ranging from 0.5–0.6 mole per mole of hexahydroindan charged. The liquid product, amounting to about 50% by weight of the starting material, was composed of 12% benzene, 17% toluene, 10% indan, 11% methylcyclopentane, 4% cyclohexane and 3% methylcyclohexane. The remainder of the product was not identified. The analysis was made by means of ultraviolet and infrared absorption spectra. The presence of toluene and benzene was also proved by means of solid nitro derivatives.

The presence of aromatic hydrocarbons in the products of destructive hydrogenation of hexahydroindan indicates that copper–alumina catalyst acts also as a dehydrogenation catalyst; it was not established however whether the dehydrogenation occurred before or after the destructive hydrogenation of hexahydroindan.

In order to compare further the relative activity of the copper–alumina and nickel–kieselguhr catalyst a destructive hydrogenation of hexahydroindan was carried out in the presence of the latter catalyst at 325°; only gaseous hydrocarbons, predominantly methane and ethane, were formed.

During the study of the hydrogenation of indan with copper–alumina catalyst, it was noticed that the degree of hydrogenation depended to a great extent upon the autoclave used; in an ordinary steel autoclave at 300° the hydrogenation proceeded only to the extent of 5%; this is in line with a similar observation noticed previously when *p*-cymene was subjected to hydrogenation.[3]

Experimental Part

Indan was prepared by hydrogenating indene (b. p. 176°, $n^{20}D$ 1.5770), dissolved in an equal volume of *n*-pentane. The hydrogenation was carried out in a rotating autoclave at 30°, under an initial hydrogen pressure of 100 atmospheres and in the presence of a nickel–kieselguhr catalyst. The indan produced was treated with 10% of its volume of 96% sulfuric acid in order to remove any unreacted indene present. This treatment was repeated several times, until no coloration of the acid layer was noticed. The indan produced, after washing and drying, distilled at 172°, $n^{20}D$ 1.5390.

Hexahydroindan was prepared by hydrogenating indene at 160° under an initial hydrogen pressure of 100 atmospheres and in the presence of nickel–kieselguhr catalyst. The hexahydroindan produced distilled at 166°, $n^{20}D$ 1.4724.

Copper oxide–alumina catalyst which contained 67% of copper oxide and 33% alumina was prepared and reduced according to the procedure described previously.[4]

The nickel–kieselguhr catalyst was of the standard UOP grade and contained 65% nickel.[5]

Destructive Hydrogenation of Indan in the Presence of a Nickel–Kieselguhr Catalyst.—Indan, 60 g., was heated at

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[1] V. N. Ipatieff, H. Pines and M. Savoy, THIS JOURNAL, **69**, 1948 (1947).

[2] V. N. Ipatieff, H. Pines and R. C. Olberg, *ibid.*, **70**, 2123 (1948).

[3] V. N. Ipatieff, H. Pines and E. E. Meisinger, *ibid.*, **71**, 2934 (1949).

[4] V. N. Ipatieff and V. Haensel, *ibid.*, **64**, 520 (1942).

[5] V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

240 to 250° for five hours in a 450-ml. capacity stainless steel rotating autoclave with 6.0 g. of nickel-kieselguhr catalyst and in the presence of an initial hydrogen pressure of 100 atmospheres. When the pressure dropped to 70 atmospheres at 240°, the autoclave was recharged to 118 atmospheres with hydrogen and the autoclave temperature was raised to 250°. From the amount of hydrogen charged and the analysis of the discharged gases, it was calculated that for each mole of indan used in the reaction, 4.2 moles of hydrogen was absorbed and 0.8 mole of methane was formed.

The liquid product obtained from the reaction was distilled on a column of about seven-plate efficiency and a reflux ratio of 6:1. The following fractions were separated from 67.0 ml. charged: (1) b. p. 118-125°, 4.0 ml., n^{20}D 1.4275; (2) 125-130°, 9.1 ml., n^{20}D 1.4300; (3) 130-135°, 9.0 ml., n^{20}D 1.4320; (4) 135-141°, 9.5 ml., n^{20}D 1.4345; (5) 141-150°, 21.4 ml., n^{20}D 1.4387; (6) 150-151°, 11.9 ml., n^{20}D 1.4400; (7) > 151°, 2.0 ml., n^{20}D 1.4429.

The structure of the alkylcyclohexanes was determined by conversion of the various fractions to the corresponding aromatic hydrocarbons by dehydrogenation at 240 to 250° over platinized alumina.[6] By passing the hydrocarbons thrice over the catalyst, a yield of 80 to 90% of aromatics was obtained. The aromatic hydrocarbons were separated from the unreacted saturated hydrocarbons by means of chromatographic adsorption over activated silica.[7] The structure of the aromatic hydrocarbons was determined by means of infrared absorption spectra and by chemical derivatives. The composition of the lower boiling cuts was determined in the same manner.

Cuts 1 to 4.—Twenty-four ml. of the composite was dehydrogenated by passing it over platinized alumina; the aromatic hydrocarbons formed, amounting to 80%, after chromatographic separation, consisted of 54% *o*-xylene, 44% 1-methyl-2-ethylbenzene and 2% toluene.

Cuts 5 and 6.—Thirty-one ml. of the products was dehydrogenated; the aromatic hydrocarbons consisted of 95% 1-methyl-2-ethylbenzene and 5% *o*-xylene.

The infrared analyses were made according to the general procedures given by Webb and Gallaway.[8] The spectra of the sample were obtained undiluted from 7.5 to 11.5 μ in a 0.1-mm. cell. From 11.0 to 14.5 μ, a dilution of 10% by volume was used. These spectrograms were then compared with those of the pure aromatics obtained under identical conditions of operation of the spectrogram. After the qualitative identification of the components present was complete, the quantitative determinations were made on the basis of appropriate absorption bands. The particular wave lengths used for calculation purposes were chosen for each sample so as to yield a minimum amount of interference. Typical spectrograms of the various aromatics may be found in the catalog issued by A. P. I. Project 44.

The Destructive Hydrogenation of Indan in the Presence of Copper Oxide-Alumina Catalyst.—Indan, 60 g., was heated at 325° for seven hours in a stainless steel autoclave with 6.0 g. of copper oxide–alumina catalyst and in the presence of an initial hydrogen pressure of 100 atmospheres. From the amount of hydrogen charged and the analysis of the discharged gases, it was calculated that for each mole of indan charged, 2 moles of hydrogen was absorbed and 0.8 mole of gaseous paraffins was formed. The liquid product of three experiments was combined and 145 ml. of it was distilled on the same column previously described.

The structure of the substituted benzenes was determined by infrared spectral analysis.

The product, distilled as follows: (1) 59-90°, 7.8 ml., n^{20}D 1.4560; (2, 3) 90-107°, 14.4 ml., n^{20}D 1.4848; (4) 107-110°, 22.5 ml., n^{20}D 1.4940; (5) 120-135°, 2.4 ml., n^{20}D 1.4904; (6) 135-150°, 7.9 ml., n^{20}D 1.4845; (7, 9) 150-160°, 25.6 ml., n^{20}D 1.4830; (10) 160-163°, 6.3 ml., n^{20}D 1.4880; (11, 13) 163-170°, 16.5 ml., n^{20}D 1.5098-1.5332; (14) 170-173°, 37 ml., n^{20}D 1.5361; (15) > 173°, 4 ml., n^{20}D 1.5400.

According to infrared analysis fractions 2,3 contained 81% toluene, 10% benzene and 8% methylcyclohexane. Fraction 4, 99% toluene. Fraction 7, 86% *n*-propylbenzene and 8% of 1-methyl-2-ethylbenzene. Fraction 8,9, 55% *n*-propylbenzene and 30% indan. Fraction 10, 40% *n*-propylbenzene and 35% indan. Fraction 11, 5% *n*-propylbenzene and 70% indan. Fraction 12-14 contain indan ranging from 85-95% and *n*-propylbenzene from 10-0%.

Destructive Hydrogenation of Hexahydroindan in the Presence of Copper Oxide-Alumina Catalyst.—Sixty grams (0.48 *M*) of hexahydroindan was destructively hydrogenated by heating it for six hours at 325° in a 450-ml. stainless steel bomb and in the presence of 6 g. of copper–alumina catalyst. The initial pressure of hydrogen measured at 25° was 100 atmospheres. At the end of the experiment the pressure gage registered 65 atm. at room temperature. The product resulting from the reaction consisted of 30.8 g. of liquid hydrocarbons, 7.3 g. of product collected in a Dry Ice–acetone cooled trap and 36.7 liters of non-condensable gas.

The non-condensable gases and those collected in the Dry Ice-trap were analyzed by means of a mass spectrograph. The following gaseous hydrocarbons were formed per one mole of perhydroindan charged: methane, 0.60 mole, ethane, 0.51 mole, propane, 0.52 mole, butanes, 0.05 mole and about 0.01 mole of each ethylene, propylene and butylenes.

The liquid product distilled as follows: (1) b. p. 47-73°, 29.2 vol. %, n^{20}D 1.4200; (2) 73-85°, 15.9%, n^{20}D 1.4394; (3) 85-107°, 12.7%, n^{20}D 1.4482; (4) 107-117°, 8.4%, n^{20}D 1.4800; (5) 117-137°, 11.2%, n^{20}D 1.4789; (6) > 137°, 16.1%, n^{20}D 1.5050.

Fractions 1-4 were analyzed by ultraviolet[9] and fractions 5 and 6 by infrared absorption spectra. The following is the composition of the various fractions: (1) 17% of benzene; (2) 35% of benzene; (3) 10% of benzene and 33% of toluene; (4) 40% of toluene; (5) 79% of toluene, 15% of indan (6) 50% of indan.

Fractions 1-4 (14.1 g. or 19 ml.) were passed over silica gel[7] in order to remove the aromatic hydrocarbons and therefore facilitate the analysis of the saturated hydrocarbons by infrared absorption spectra. About 7.2 ml. of saturated hydrocarbons were obtained of which 6 ml. distilled at 60-86° and were composed of 50% of methylcyclopentane, 15% of cyclohexane and 10% of methylcyclohexane.

Hydrogenation of Indan in the Presence of Copper Oxide-Alumina.—Sixty grams of indan was hydrogenated in a 450-ml. autoclave in the presence of 100 atmospheres of hydrogen pressure measured at 25°. The hydrogenation was carried out at 275° for six hours. The final pressure at room temperature was 50 atmospheres. The product obtained from the reaction distilled as follows: (1) 163-164°, 36%, n^{20}D 1.4837; (2) 164-168°, 46%, n^{20}D 1.4930; (3) 168-171°, 14%, n^{20}D 1.5170. The respective cuts contained according to infrared analysis 75, 65 and 35% of perhydroindan, the remainder being indan.

Summary

The destructive hydrogenation of indan and hexahydroindan was investigated.

Nickel–kieselguhr catalyst causes the hydrogenolysis to occur at 240–250°, 1-methyl-2-ethyl- and 1,2-dimethylcyclohexane are main products of the reaction.

The destructive hydrogenation of indan at 325° in the presence of copper oxide–alumina catalyst

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[6] H. Pines, R. C. Olberg and V. N. Ipatieff, *ibid.*, **70**, 533 (1948).

[7] B. J. Mair and A. F. Forziati, *J. Research Natl. Bureau Std.*, **32**, 151, 165 (1944).

[8] G. M. Webb and W. S. Gallaway, *Petroleum Processing*, **2**, 356 (1947). The authors wish to thank Dr. Gallaway for the infrared analyses.

[9] The ultraviolet analysis was made by Charles Berg.

yielded as the main product *n*-propylbenzene and toluene. Aromatic hydrocarbons were also formed when hexahydroindan was destructively hydrogenated in the presence of copper–alumina catalyst.

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The Fractionation of γ-Globulin by Electrophoresis-convection

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Introduction

A method of fractionation of proteins in solution utilizing an electrophoretic adaptation of the principles of the Clusius column was suggested by Kirkwood[1] in 1941 and tested experimentally by Nielsen and Kirkwood[2] several years later. Recently an electrophoresis-convection apparatus of improved design has been described and successfully used to fractionate horse diptheria antitoxin pseudoglobulin.[3] Fractionation occurs in a narrow vertical convection channel between two semi-permeable membranes, connecting an upper and lower reservoir. Separation depends upon the superposition of differential horizontal electrophoretic transport of the components on vertical convective transport of the solution as a whole. The vertical convective transport is controlled by the horizontal density gradient produced by the electrophoretic migration of the proteins across the channel.

The utility of the method of electrophoresis-convection and the effectiveness of the new fractionation unit have been well illustrated by the partial separation of the bovine serum proteins reported recently by the authors.[4] These separations were accomplished by the isoelectric procedure, *i.e.*, by successively immobilizing the components at their respective isoelectric points and transporting the mobile components from the top reservoir of the apparatus. It was suggested that electrophoresis-convection should supplement the ethanol fractionation of biological tissues and fluids as carried out by Cohn, *et al.*[5] It was apparent that subfractionation of the plasma protein fractions obtained by alcohol precipitation could be accomplished by electrophoresis-convection.

The sub-fractionation of bovine γ-globulin prepared by ethanol precipitation, Fraction II of bovine plasma, is the subject of this paper. γ-Globulin was chosen because of its known heterogeneity and its immunological importance. In the case of a protein which migrates as a single boundary in an electric field but has a specified mobility distribution as revealed by reversible electrophoretic boundary spreading, fractionation is accomplished by means of a modified isoelectric procedure. In this procedure the *p*H of fractionation is so chosen as to be close to the average isoelectric point of the protein. Transport in the apparatus leads to a redistribution of the protein ions such that the fractions withdrawn from the top and bottom reservoir possess mobility distribution differing from that of the original protein. Using this procedure γ-globulin has been separated into four fractions of different mean mobilities and isoelectric points.

Experimental

Material.—The bovine γ-globulin[6] used in this investigation had a mobility of -1.73×10^{-5} cm.^{2} volt^{-1}sec.$^{-1}$ at a concentration of 1% in barbital buffer, *p*H 8.7 and ionic strength 0.1. In this buffer the γ-globulin migrated as a single peak during electrophoresis.

Electrophoretic Analysis.—The moving boundary technique of Tiselius[7] as modified by Longsworth[8] was used in the electrophoretic analysis. Mobilities were determined by electrophoresis of a 1% protein solution in barbital buffer *p*H 8.7 and ionic strength 0.1, at a field strength of 4 volts/cm. for four hours. Mobilities were calculated in accordance with the suggestions of Longsworth and MacInnes.[9]

Boundary spreading experiments were carried out on 0.5% solution of globulin and its fraction equilibrated against cacodylate buffer (0.08 *N* sodium chloride–0.02 *N* sodium cacodylate). These experiments were performed at the average isoelectric points of the proteins. The power consumption in boundary spreading experiments did not exceed 0.015 watt/cc. The refractive-index gradient curves were recorded photographically on Eastman Kodak Co. CTC plates using both the schlieren scanning technique of Longsworth and the cylindrical lens schlieren technique. In the cylindrical lens method a diagonal knife edge brought in from below the optical axis was used in the optical system. The standard deviations of the mobility distributions determined by the two methods agreed to within 5%. Since the γ-globulin fractions possessed Gaussian mobility distributions, the heterogeneity constant, *h*, is tabulated for these proteins. However, the original γ-globulin had a non-gaussian distribu-

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(1) J. G. Kirkwood, *J. Chem. Phys.*, **9**, 878 (1941).

(2) L. E. Nielsen and J. G. Kirkwood, THIS JOURNAL, **68**, 181 (1946).

(3) J. R. Cann, J. G. Kirkwood, R. A. Brown and O. Plescia, *ibid.*, **71**, 1603 (1949).

(4) J. R. Cann, R. A. Brown and J. G. Kirkwood, *ibid.*, **71**, 1609 (1949).

(5) (a) E. J. Cohn, J. A. Leutscher, Jr., J. L. Oncley, S. H. Armstrong, Jr., and B. D. Davis, THIS JOURNAL, **62**, 3396 (1940); (b) E. J. Cohn, L. E. Strong, W. L. Hughes, D. J. Mulford, J. M. Ashworth, M. Melin and H. L. Taylor, *ibid.*, **68**, 459 (1946).

(6) Armour Laboratories, Armour and Company, Chicago, Illinois, kindly supplied the bovine γ-globulin, Fraction II of Bovine Plasma.

(7) A. Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).

(8) (a) L. G. Longsworth, *Chem. Rev.*, **30**, 323 (1942); (b) L. G. Longsworth, *Ind. Eng. Chem., Anal. Ed.*, **18**, 219 (1946).

(9) L. G. Longsworth and D. A. MacInnes, THIS JOURNAL, **62**, 705 (1940).