HIGH-MOLECULAR-WEIGHT HYDROCARBONS AND HYDRO-CARBON INTERMEDIATES

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In a previous publication from this laboratory on "Chemical Structure of Lubricating Oils"¹ several series of synthetic hydrocarbons of high molecular weight were described and characterized as to their viscosities, viscosity indices, aniline points and other physical properties of interest to oil chemists and petroleum technologists.

By comparing the physical properties of one hydrocarbon with those of another, the two differing from each other in only one structural factor, as for instance, straight versus branched chain, saturated versus unsaturated side chains, or aromatic versus hydroaromatic nuclei, it was possible to draw certain definite conclusions with respect to the effect of various structural factors on the physical properties of the hydrocarbons involved. It was further concluded on the basis of the physical properties of these synthetic products, that it is possible, in a general way, to deduce the probable structure of the hydrocarbons constituting the various types of widely differing lubricating oils.

For the sake of brevity, the scope of the paper referred to above was limited to the consideration of the physical properties of the hydrocarbons in question. Description of the methods of preparation of the final products as well as of the intermediates was, therefore, postponed.

It is the purpose of this paper and of others to follow to give a concise description of the synthetic methods employed, as well as a complete description and characterization of not only the ultimate materials sought but of the intermediates as well.

This paper covers monosubstituted derivatives of benzene, diphenyl and naphthalene.

The numbers in brackets appearing after the names of the hydrocarbons described in this paper refer to the numbers connoting the individual hydrocarbons in Table I in the original article.¹

¹ MIKESKA, Ind. Eng. Chem., 28, 970 (1936).

EXPERIMENTAL

General method of procedure.—All the aromatic hydrocarbons were prepared by reduction of the appropriate ketones or else by the action of Grignard reagents on the ketones with subsequent dehydration of the resulting alcohols. The ketones were in turn prepared by condensing, in the presence of aluminum chloride, acid chlorides of the required structure and molecular weight with carefully chosen aromatic groups.

Reduction of the ketones to the corresponding hydrocarbons by Clemmensen's method was found unsatisfactory, probably because of their insolubility in aqueous hydrochloric acid. Modification of Clemmensen's method, however, yielded the desired hydrocarbons in a state of high purity in a relatively short time.

Naphthenes, insofar as they were studied, were obtained by exhaustive hydrogenation of the corresponding aromatics in the presence of platinum oxide.²

Inasmuch as the general method of preparation of the intermediate ketones was essentially the same in all cases, the preparation of only one ketone, stearophenone, is given in full detail. In the case of other ketones, only deviations from the standard procedure are recorded.

Stearophenone.-Stearophenone was prepared by the method of Claus and Häfelin.³

Three hundred grams of pure molten stearic acid (m.p. 69° C.) was poured with stirring into 75 g. of phosphorus trichloride. The mixture was heated to 70° for half an hour, during which time the phosphorous acid formed settled to the bottom of the flask as a viscous colorless liquid. The stearyl chloride was carefully decanted into 800 cc. of benzene contained in a two-liter Erlenmeyer flask.

The flask was then immersed in an ice bath, and cooled to 0° , whereupon 150 g. of aluminum chloride was added slowly with occasional shaking of the flask. When all the aluminum chloride had been added, which took about an hour, the flask was removed from the ice bath and allowed to stand overnight at room temperature. The next day the reaction product was poured into a mixture of ice and 200 cc. of concentrated hydrochloric acid.

The ketone was thus precipitated in snow-white crystalline form. The mixture was transferred into a separatory funnel, and extracted with ether. The extract was washed free of hydrochloric acid and dried over sodium sulfate. When dry, the filtered solution was saturated with ammonia gas to precipitate the small amount of unchanged stearic acid carried over. On removal of the ammonium stearate by filtration, the filtrate was treated with an equal volume of methyl alcohol and cooled to 0°. The ketone crystallized immediately. The first crop consisted of 236 g. of snow-white product melting at 63.5-64.5°. An additional 15 g., melting at 59-63°, was obtained from the mother liquors. In another experiment 887 g. of the pure ketone was obtained from 900 g. of stearic acid. Claus and Häfelin³ give the melting point as 59°, while N. K. Adam⁴ gives the melting point as 63-63.5°.

Anal. Calc'd for C24H40O: C, 83.64; H, 11.70.

Found: C, 83.67; H, 11.66.

In some cases, especially if the starting products are not quite pure, the original ketone may be obtained in various shades of darkness. In that case, it is better to distill the raw material before the recrystallization as outlined above.

² VOORHIES AND ADAMS, J. Am. Chem. Soc., 44, 1397 (1922).

³ CLAUS AND HÄFELIN, J. prakt. Chem., [2], 54, 399 (1896).

⁴ ADAM, Proc. Roy. Soc. (London), A103, 684 (1923).

Octadecylbenzene [1].—Octadecylbenzene was originally prepared by F. Krafft⁵ by the action of sodium on a mixture of bromobenzene and octadecyl iodide. Our product was obtained by reduction of stearophenone to the corresponding hydrocarbon.

Early attempts to reduce the ketone to hydrocarbon by Clemmensen's⁶ method were abandoned because of the long time required to bring the reaction to completion. A modification of Clemmensen's method which worked satisfactorily for all the ketones used was finally adopted.

About a three-inch layer of mossy zinc amalgamated according to Clemmensen's directions with 5% mercuric chloride, was placed in a two-liter Erlenmeyer flask, provided with an inlet tube for hydrogen chloride, and a return condenser. Two hundred fifty grams of stearophenone dissolved in 750 cc. of xylol was then added, followed by just enough concentrated hydrochloric acid to cover only about half of the zinc amalgam. This left the xylol solution of the stearophenone in direct contact with the other half of the zinc amalgam.

The mixture was then heated to boiling. During refluxing, hydrogen chloride was passed into the reaction mixture to replace the hydrochloric acid consumed. After a contact time of seven hours, the product was isolated, and was distilled under 5 mm. pressure. The product distilled at $220-235^{\circ}$ and weighed 228 g. The residue consisted of 30 g. of heavy oil. The distillate was redissolved in xylol and placed in contact with zinc-mercury amalgam as before for 7 hours. On isolation and distillation under 4 mm. pressure, 190 g. of a product boiling at 195-205° and melting at 33° was obtained.

Anal. Calc'd for C₂₄H₄₂: C, 87.19; H, 12.81.

Found: C, 87.27; H, 12.73.

Krafft reported the melting point of octadecylbenzene as 36° . The product described above was, therefore, recrystallized twice from ether. In this state of purity it melted at $35-36^{\circ}$.

Octadecylcyclohexane [11].—Ninety grams of octadecylbenzene dissolved in 200 cc. of glacial acetic was placed in a bottle securely attached to a shaker. A half-gram of platinum oxide catalyst² was then added. The bottle was evacuated, and filled with hydrogen from an attached reservoir of the latter. Shaking was continued until the calculated amount of hydrogen had been absorbed. The product was then poured into water, extracted with ether, washed free of acetic acid and dried over sodium sulfate. The residue obtained on removal of the ether was distilled under 4 mm. pressure. The entire product passed over between 204 and 210°. Without any further purification it melted at 40°.

Anal. Calc'd for C24H48: C, 85.61; H, 14.39.

Found: C, 85.59; H, 14.46.

Heptadecyl-n-butylphenylcarbinol.—One and a half grams of dry activated mag nesium was suspended in 15 cc. of dry ether. To this was then added 4 g. of *n*-butyl chloride. When the reaction had gone to completion, the Grignard reagent was added slowly to 15 g. of stearophenone in 60 cc. of dry ether. The solution was refluxed under a return condenser for about two hours, whereupon it was poured into ice and hydrochloric acid. The carbinol was extracted with ether, washed free of hydrochloric acid, and dried over sodium sulfate. On removal of the ether, the

⁵ KRAFFT, Ber., **19**, 2982 (1886).

⁶ CLEMMENSEN, *ibid.*, 46, 1837 (1913).

residue was distilled under 2 mm. pressure. The entire product distilled between 235 and 240° .

The carbinol has a tendency to dehydrate on distillation. If a pure product is desired, only a small quantity must be distilled at a time. The yields obtained are practically quantitative.

Anal. Calc'd for C28H50O: C, 83.49; H, 12.52.

Found: C, 83.46; H, 12.49.

(1-Butyloctadecen-1-yl)benzene [5].—A mixture of 336 g. of heptadecyl-n-butylphenylcarbinol, prepared as described in the preceding experiment was dehydrated by heating with 100 g. of oxalic acid for 1.5 hours at 180° to 200° in an atmosphere of carbon dioxide. The product was then dissolved in ether and washed free of oxalic acid. On removal of the solvent, 275 g. of a product distilling at 210–220° under 1 mm. pressure was obtained. Analysis showed that the product still contained some oxygen. The product was, therefore, redissolved in dry ether and treated as before with a Grignard solution prepared from 15 g. of magnesium and 45 g. of *n*-butyl chloride. The carbinol was isolated, and was treated once more with oxalic acid at 180° to 200°. On distillation, 241 g. of a colorless oil boiling between 205° and 210° under 1 mm. pressure was obtained.

Anal. Calc'd for C₂₈H₄₈: C, 87.41; H, 12.59.

Found: C, 87.73; H, 12.61.

(1-Butyloctadecyl)benzene [4].—One hundred sixty grams of (1-butyloctadecen-1-yl)benzene and 100 cc. of glacial acetic acid contained in a thick glass bottle was treated with 0.2 g. of platinum oxide catalyst. The air in the bottle was replaced with a measured amount of hydrogen. Absorption of the hydrogen began immediately on shaking. The volume of hydrogen consumed was measured as the absorption continued. When one molecule (3200 cc. at 26° and 257 mm.) had been absorbed, the hydrogenation was discontinued.

A little alcohol was added to coagulate the platinum catalyst, which was then filtered off. The filtrate was poured into water, extracted with ether, washed, and dried over sodium sulfate. On removal of the solvent, 193 g. of product boiling at $200-201^{\circ}$ under 1 mm. pressure was obtained. On recrystallizing twice from ether, the product melted at 38° .

Anal. Calc'd for C28H50: C, 86.95; H, 13.05.

Found: C, 86.90; H, 13.05.

Heptadecyl biphenyl ketone.—One hundred grams of stearic acid was converted into stearyl chloride as described in the preparation of stearophenone. The chloride was then added to a solution of 55 g. of biphenyl in 200 cc. of carbon bisulfide. The solution was cooled to 0° , whereupon 50 g. of aluminum chloride was added little by little. The reaction mixture was then allowed to stand at room temperature overnight.

The next day the reaction solution was poured into ice and hydrochloric acid, whereupon a voluminous snow-white precipitate was obtained. The product was thoroughly washed with water to remove hydrochloric acid and inorganic salts, and finally dried in the air. The product was then washed several times with ether, in which it is insoluble, in order to remove unchanged stearic acid, and was finally recrystallized from chloroform. When pure, the ketone melted at 106-107°.

Anal. Calc'd for $C_{30}H_{44}O$: C, 85.63; H, 10.56.

Found: C, 85.55; H, 10.60.

Octadecylbiphenyl [40].—Two hundred fifty grams of heptadecyl biphenyl ketone was reduced with zinc-mercury amalgam exactly as described for octadecylbenzene.

After the second reduction the product was isolated, and was distilled under 5 mm. pressure, under which conditions it boiled at 270-275°. A yield of 178 g. was obtained. On recrystallization from chloroform, the hydrocarbon melted at 79-81°.

Anal. Calc'd for CzoH46: C, 88.60; H, 11.40.

Found: C, 88.40; H, 11.38.

(1-Butyloctadecen-1-yl)biphenyl [41].—n-Butylmagnesium chloride solution was prepared in the usual manner from 40.7 g. of dry magnesium, 122 g. of n-butyl chloride and 400 cc. of dry ether. This was added slowly to a suspension of 326 g. of heptadecyl biphenyl ketone in 1200 cc. of dry ether. The product, which was isolated in the usual way, consisted of 464 g. of semi-crystalline material. Without any further purification, the product was dehydrated with oxalic acid as described in previous experiments. On distillation under 7 mm. pressure, 312 g. of distillate boiling at 300-310° was obtained.

The distillate was re-treated with *n*-butylmagnesium chloride, with subsequent dehydration by means of oxalic acid. The product was isolated as usual, and was finally heated to 150° under 7 mm. pressure to insure the removal of the last traces of solvents. The residue, of which 297 g. was obtained, consisted of a practically colorless viscous oil which solidified partially on prolonged standing at room temperature.

Anal. Calc'd for C24H52: C, 88.62; H, 11.38.

Found: C, 88.49; H, 11.31.

(1-Butyloctadecyl)biphenyl [42].—The reduction of (1-butyloctadecen-1-yl)biphenyl was carried out in every respect as described for the reduction of (1-butyloctadecen-1-yl)benzene. After distillation, the product was recrystallized from ether. When pure, it melted at 41.5-43°C.

Anal. Calc'd for C₃₄H₅₄: C, 88.24; H, 11.76.

Found: C, 88.45; H, 11.82.

(1-Butyloctadecyl)bicyclohexyl [46].— The procedure employed in the preparation of the bicyclohexyl derivative was in every respect similar to the procedure used in the preparation of octadecylcyclohexane. The product, consisting of a colorless oil, distilled at 255-260° under a pressure of 1 mm.

Anal. Calc'd for C₃₄H₆₆: C, 85.97; H, 14.03.

Found: C, 86.38; H, 13.97.

Heptadecyl naphthyl ketone.—Heptadecyl α -naphthyl ketone was first prepared by Ryan and Nolan' by the action of α -naphthylmagnesium bromide on the nitrile of stearic acid. Our product was prepared by the action of stearyl chloride on naphthalene in the presence of aluminum chloride, in carbon bisulfide solution.

Our method of procedure was essentially the same as that recently reported by Seidel and Engelfried⁸ except in so far as the final stages of purification are concerned.

Six hundred grams of pure stearic acid was converted into stearyl chloride by treatment with 150 g. of phosphorus trichloride. The stearyl chloride was decanted from the phosphorous acid formed into a solution of 290 g. of naphthalene in 800 cc. of carbon bisulfide. The mixture was cooled to 0° , whereupon 300 g. of aluminum chloride was added with cooling and occasional shaking. When all the chloride had been added, the flask was taken out of the ice bath and the mixture was allowed to stand at room temperature overnight. The next day the solution was decomposed with ice and hydrochloric acid. The ketone was extracted with ether, washed, dried, and the solvent was removed. The residue was taken up with fresh ether and

⁷ RYAN AND NOLAN, Proc. Roy. Irish Acad., B30, 1 (1912).

⁸ SEIDEL AND ENGELFRIED, Ber., 69, 2584 (1936).

saturated with ammonia to remove unchanged stearic acid. Ammonium stearate was then removed by filtration, the ether was removed by evaporation and the residue was distilled under 3 mm. pressure. The entire product, 690 g., distilled at $240-260^{\circ}$.

The product was then dissolved in 1200 cc. of ether. On addition of 1200 cc. of methyl alcohol the product crystallized in a snow-white form, and melted at 54.5-56°. No attempt was made to separate the two isomers.

Anal. Calc'd for C₂₈H₄₂O: C, 85.21; H, 10.73.

Found: C, 85.46; H, 10.58.

(1-Butyloctadecen-1-yl)naphthalene [18].—Two hundred eighty-six grams of heptadecyl naphthyl ketone was dissolved in 900 cc. of dry ether. This was then heated for four hours with n-butylmagnesium chloride prepared from 20 g. of magnesium and 70 g. of n-butyl chloride.

The carbinol was then isolated in the usual way by decomposition with dilute hydrochloric acid. On removal of the solvent, 295 g. of crystalline material was obtained.

No attempt was made to purify the carbinol. The product was dehydrated by heating with 50 g. of oxalic acid for 1.5 hours at $180-200^{\circ}$ in an atmosphere of carbon dioxide. On recovery of the olefin the product was retreated with *n*-butylmagnesium chloride and finally with oxalic acid as before. The olefin was finally distilled under 3 mm. pressure; 215 g. of the product boiling between 232° and 240° was obtained. It consisted of a practically colorless viscous oil.

Anal. Calc'd for C32H50: C, 88.39; H, 11.61.

Found: C, 88.41; H, 11.52.

(1-Butyloctadecyl)naphthalene [19].—Fifty grams of (1-butyloctadecen-1-yl)naphthalene was treated with hydrogen in glacial acetic acid in the presence of platinum oxide catalyst² until one mole of hydrogen had been absorbed. The catalyst was then removed by filtration, the product was dissolved in ether, washed free of acetic acid, and dried over sodium sulfate. On removal of the solvent, the residue distilled at 200-201° under 2 mm. pressure. On recrystallization from ether, the product melted at 38°.

Anal. Calc'd for C₃₂H₅₂: C, 86.95; H, 13.05.

Found: C, 86.90; H, 13.03.

Heptadecyl tetrahydronaphthyl ketone.—The ketone was prepared by the action of molecular proportions of stearyl chloride on tetralin in carbon bisulfide solution in the presence of aluminum chloride exactly as described for the corresponding naph-thalene derivative. On removal of the unchanged stearic acid the product was distilled under 2 mm. pressure; 333 g. of ketone boiling between 255-263° was obtained from 300 g. of stearic acid and 145 g. tetralin.

On crystallization from acetone, the ketone melted at 49.5-50°.

Anal. Calc'd for C₂₈H₄₆O: C, 84.38; H, 11.62.

Found: C, 84.41; H, 11.64.

Octadecyltetrahydronaphthalene [S1].—One hundred grams of heptadecyl tetrahydronaphthyl ketone was reduced with zinc-mercury amalgam exactly as described for octadecylbenzene. After the reduction, the product was isolated and distilled under 4 mm. pressure; 66 g. of product distilling at 237-275° was obtained. The product was analyzed without any further purification.

Anal. Calc'd for C₂₈H₄₈: C, 87.41; H, 12.59.

Found: C, 87.41; H, 12.58.

Octadecyldecahydronaphthalene [37].-Fifty grams of octadecyltetrahydronaph-

thalene was treated with hydrogen at room temperature in glacial acetic acid in the presence of platinum oxide. When three moles of hydrogen had been absorbed the reaction was interrupted, and the catalyst was removed by filtration. The filtrate was dissolved in ether, washed free of acetic acid, and dried over sodium sulfate. On addition of methyl alcohol to the filtrate the product crystallized. It was recrystallized from a mixture of methyl alcohol and ether. A colorless crystalline product which melted at $43-47^{\circ}$ was obtained.

Anal. Calc'd for C28H54: C, 86.07; H, 13.93.

Found: C, 85.94; G, 13.94.

(1-Butyloctadecen-1-yl)tetrahydronaphthalene [34].—Four hundred grams of heptadecyl tetrahydronaphthyl ketone was converted into the ethylene derivative in a manner in every respect analogous to the preparation of (1-butyloctadecen-1-yl)naphthalene. After the second treatment with *n*-butylmagnesium chloride and oxalic acid, the product was isolated in the usual way, and was distilled under 4 mm. pressure; 405 g. of the olefin, a viscous colorless oil boiling at 263-264°, was obtained.

Anal. Calc'd for C₃₂H₅₄: C, 87.59; H, 12.41.

Found: C, 87.63; H, 12.39.

(1-Butyloctadecyl)tetrahydronaphthalene [33].—The saturation of the ethylenic product was carried out exactly as described in the preparation of (1-butyloctadecyl)naphthalene. When the required volume of hydrogen had been absorbed, the catalyst was removed by filtration, the filtrate was dissolved in ether, washed free of acetic acid and dried over sodium sulfate. On removal of the sodium sulfate and ether, the residual oil was distilled under 2 mm. pressure. The entire product distilled at 235-245°.

Anal. Calc'd for C₃₂H₅₅: C, 87.19; H, 12.81.

Found: C, 87.22; H, 12.72.

(1-Butyloctadecyl)decahydronaphthalene [39].—The procedure employed in the preparation of (1-butyloctadecyl)decahydronaphthalene was in every respect analogous to the procedure used in the preparation of octadecyldecahydronaphthalene. When the required amount of hydrogen had been absorbed, the product was isolated and distilled under 3 mm. pressure. The entire product, consisting of a viscous colorless oil, distilled at 240–245°.

Anal. Calc'd for C₃₂H₆₂: C, 86.00; H, 14.00. Found: C, 85.88; H, 14.18.

SUMMARY

The preparation of fifteen hydrocarbons of high molecular weight, and of their intermediates is described. Inasmuch as the physical properties usually given for hydrocarbons have been recorded in a previous publication, they are not included in this paper. The melting points of products melting above room temperature as well as the approximate boiling points of most of the compounds described are given.