

point, 264°, yield, 4 g. or 85%. The compound contains no bromine, is slightly soluble in hot alcohol, acetone and chloroform, and is insoluble in benzene, water and ether.

Anal. (Modified Kjeldahl). Calcd. for $C_{14}H_{10}N_3O_4$: N, 19.85. Found: N, 19.06.

The product formed in the same way from dichlorobarbituric acid and α -naphthylhydrazine was identical, melting at 264°. A melting point of mixtures of the two products was also 264°.

Dibromobarbituric Acid and 4,4-Diphenyl Semicarbazide.—A hot alcohol solution of 4 g. of dibromobarbituric acid was added to 3.2 g. of 4,4-diphenyl semicarbazide dissolved in alcohol. After warming the solution for a few minutes, 4 g. of a fine yellow powder separated, which after recrystallizing melted at 267°, with decomposition. It contained no bromine.

Anal. (Dumas) Calcd. for $C_{17}H_{13}N_3O_4$: N, 19.93. Found: N, 19.95.

This semicarbazone of alloxan is soluble in hot alcohol and insoluble in the other usual organic solvents.

Dichlorobarbituric acid reacted slowly with 4,4-diphenyl semicarbazide under the same conditions, but was expected to give the same semicarbazone of alloxan. However, the orange-yellow product, insoluble in alcohol and containing chlorine, was apparently a mixture which could not be purified. It contained 20.17% of nitrogen (Dumas) and 8.25% chlorine.

Summary

1. Further evidence is presented showing that one halogen in the 5,5-dihalogen barbituric acids is more reactive than the other.
2. Dibromobarbituric acid reacts readily with primary and secondary amines with the loss of one molecule of hydrogen bromide.
3. Dichlorobarbituric acid is much less reactive than the dibromo compound, reacting readily only with benzylamines.

COLUMBIA, MISSOURI

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE OF THE PETROGRAD ACADEMY OF SCIENCE]

FORMATION OF NAPHTHENIC ACIDS¹

BY A. D. PETROV AND I. Z. IVANOV

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The mechanism of the formation of naphthenic acids present in petroleum is explained by two theories. According to C. Engler² naphthenic acids could have been formed² by cracking and cyclization of unsaturated fatty acids, which are considered as one of the original substances from which petroleum was formed, or³ by oxidation of naphthenes and polynaphthenes with air. G. Kraemer and Weger³ are in favor of the first theory from their experiments with acids from montan wax, while Kharichkov⁴ prefers the

¹ Translated from the manuscript, by K. T. Steik.

² Engler, "Das Erdoel," Vol. I, 1911, p. 452.

³ Kraemer and Weger, *Chem.-Ztg.*, **31**, 675-77, 734 (1907); *Chem. Zentr.*, II, 734 (1907).

⁴ Kharichkov, *J. Russ. Phys.-Chem. Soc.*, **40**, 1757 (1908); *Chem. Abstracts*, **3**, 1761 (1909).

oxidation theory on the basis of his laboratory experiments in which he oxidized petroleum with air. In neither case were indisputable proofs produced for the formation of naphthenic acids analogous to natural acids. This was due mainly to shortage of material. According to Kobayashi⁵ naphthenic acids are formed when fish fats are distilled at atmospheric pressure. We⁶ observed that naphthenic acids are formed when linoleic acid is cracked under pressure.

We had at our disposal a considerable amount of synthetic acids from two sources, namely, from cracking of oleic acid under pressure and from oxidation of gas oil distillate from Emba crude oil with air on a semi-manufacturing scale. Thus, it was possible for us to make closer investigation for determining whether the acids from cracking and those from oxidation belong to the group of saturated fatty acids or the group of naphthenic acids. We used a method similar to that of N. D. Zelinskii⁷ for natural naphthenic acids, namely, we converted the acids into esters, alcohols, iodides and finally into the corresponding hydrocarbons. The amount of acids available was not sufficient for determining their structures and we worked therefore with wider fractions than those used by Zelinskii.

Analyses of hydrocarbons showed that in the first instance (cracking of oleic acid) at least part of them belongs to the naphthene series, while the hydrocarbons from acids from the other source are completely naphthenes. When considering the fact that products analogous with each other and with those from natural acids were obtained from two different starting materials and by different processes, it is reasonable to assume that in nature naphthenic acids were formed in both ways. Such a conclusion explains an observation made by L. Gurwitsch⁸ that petroleum from deep layers of Bibi-Eibat and Balakhanui contains more naphthenic acids than petroleum from Surakhanui, which is located much nearer to the surface. Such a case would be impossible if naphthenic acids were formed by air-oxidation of naphthenes only.

Experimental Part

Oleic acid was cracked in a two-liter autoclave in the presence of water and alumina at 380–390° and during three to four hours; 300 cc. of acid, 100 cc. of water and 10 g. of alumina were taken for each experiment. The highest pressure reached was 210–220 atmospheres, which dropped to 25–30 atmospheres on cooling. About four kilograms of oleic acid was treated in that way.

The cracked products were distilled into two fractions, the gasoline fraction up to 200° and the kerosene fraction from 200–280°. Ten per cent. of acids were isolated

⁵ Kobayashi, *J. Chem. Ind. Japan*, **24**, 1–26 (1921); *Chem. Abstracts*, **15**, 2542 (1921).

⁶ Petrov, *Ber.*, **63B**, 75–84 (1930); *J. Russ. Phys.-Chem. Soc.*, **61**, 1849–1859 (1929); *Chem. Abstracts*, **24**, 2696 (1930).

⁷ Zelinskii, *Ber.*, **57B**, 42–51 (1924); *Chem. Abstracts*, **18**, 2148 (1924).

⁸ Gurwitsch, "Scientific Foundation of Petroleum Technology," London, 1926.

from the kerosene fraction by the Spitzer-Hoenig⁹ method. After two fractionations 130 g. of acids was obtained. They distilled over between 211–250° and had a specific gravity of 0.9220 and an iodine number of 11.0.

Thus unsaturated acids were present only in small quantities.

Methyl esters were prepared from the mixture of these acids. They had a pleasant fruity odor. The crude esters distilled over at 150–220°. They were fractionated and the fraction boiling between 180–220° was used in further operations. The redistilled esters had a refractive index of 1.4239 (at 15°) and their ultimate analysis showed 69.05% carbon and 11.33% hydrogen.

The esters were converted into alcohols by the Bouveault method.¹⁰ They distilled between 170–220°, had a refractive index of 1.4419 (at 15°) and contained 76.75% carbon and 13.22% hydrogen.

The alcohols were converted into iodides by means of iodine and phosphorus and these in turn were converted into the corresponding hydrocarbons by reduction with zinc dust in an alcoholic medium. Due to losses during these operations, only about two grams of hydrocarbons was obtained.

The hydrocarbons were treated with sulfuric acid to remove the unsaturates and they were subsequently distilled over metallic sodium. They distilled between 100–170°, had a specific gravity of 0.780, refractive index of 1.417. Their ultimate analysis was: C, 85.89; H, 14.62; calculated for C_nH_{2n} : C, 85.60; H, 14.40.

The analytical data correspond quite closely to values for octonaphthene carboxylic acid, nonanaphthene alcohol and nonanaphthene, which would approximately represent the average of the investigated wide fractions of esters, alcohols and hydrocarbons.

The presence of acids of the methane series in the cracked acids is indicated by the somewhat low specific gravity of these acids and by the high hydrogen content of the ester and alcohol fractions.

Naphthenic Acids Obtained by Oxidation of Emba Gas Oil.—The products of oxidation of Emba gas oil were obtained on a semi-manufacturing scale by G. S. Petrov. The gas oil, previous to oxidation, was treated with fuming sulfuric acid. The distillate was oxidized for the purpose of obtaining acids suitable for soap making. The oxidation was effected by air-blowing at 90–100° in the presence of catalysts. Oxy acids and carboxylic acids were obtained. The oxy acids decomposed into hydrocarbons during distillation at atmospheric pressure, while the carboxylic acids, which distilled without decomposition, were soluble in benzene and had a specific gravity below one.

The carboxylic acids were separated from the oxy acids by dissolving them in benzene and by repeated fractionation. The fraction distilling between 290–360° (at atmospheric pressure) was used in further investigations.

Acids of this fraction were purified according to the Spitzer and Hoenig⁹ method and were then converted into their esters. For this purpose a mixture of 200 g. of acids, 400 g. of methyl alcohol and 50 g. of sulfuric acid (1.84 specific gravity) was heated on a water-bath for twenty hours. The excess of alcohol was then distilled off and the esters were washed with alkali and water. These esters had a pleasant fruity odor and distilled between 100–230° (at 1–3 mm. pressure). A portion of the 100 g. of esters obtained was saponified and converted into acids. These acids had a neutralization value of 135 and an iodine number of 0.7, while the saponification number of esters was 185.

The esters were converted into alcohols by the Bouveault-Blanc method. The following proportions of reagents were used: esters 80 g., absolute alcohol 240 g. and metallic sodium 25 g. The alcohols distilled between 100–212° (at 3–5 mm. pressure).

⁹ Spitzer and Hoenig, *Monatsh.*, **39**, 1–14 (1918); *Chem. Abstracts*, **13**, 131 (1919).

¹⁰ Bouveault, *Compt. rend.*, **136**, 1676 (1903); *Brit. Chem. Abstracts*, **84**, [I] 597 (1903).

They were a mobile straw-colored liquid with an odor similar to that of coriander oil. A portion of the alcohols was converted into acetates. The following proportions were used for this conversion: alcohols 10 g., fused sodium acetate 10 g. and acetic anhydride 40 g. Eight grams of acetates, with an acetyl number of 131, was obtained.

In the next step alcohols were converted into iodides. From 10 g. of alcohols, 1 g. of red phosphorus and 10 g. of iodine, 10 g. of iodides was obtained. The iodides were reduced to hydrocarbons by the Zelinskii method with zinc dust in an aqueous alcoholic medium; 5 g. of hydrocarbons was obtained. The distillation range of these hydrocarbons at 45 mm. pressure was 160–260°. The hydrocarbons did not dissolve in sulfuric acid and did not discolor bromine.

Anal. Calcd. for C_nH_{2n} : H, 14.38; C, 85.62. Found: H, 14.04; C, 85.84.

The hydrocarbons were dehydrogenated with sulfur and brominated with aluminum bromide according to Gustavson's method. Hydrogen sulfide evolved during the dehydrogenation and an oil was obtained as the reaction product. The bromination was accompanied by evolution of hydrogen bromide and resulted in a salve-like product. The hydrocarbon radical of these carboxylic acids is therefore of the naphthene type, mostly of the monocyclic type judging by the analytical data.

Summary

Oleic acid was cracked in presence of water and alumina. Esters, alcohols and iodides were prepared and the latter finally converted to hydrocarbons. These corresponded to structures of octonaphthene and nonanaphthene type.

Emba gas oil was oxidized by air blowing at 90 to 100° in presence of catalysts, giving oxy and carboxy acids of monocyclic naphthene type.

[CONTRIBUTION FROM THE LABORATORY FOR PURE RESEARCH OF MERCK AND CO., INC.]

PREPARATION AND PROPERTIES OF ALPHA- AND BETA-METHYLCHOLINE AND GAMMA-HOMOCHOLINE¹

BY RANDOLPH T. MAJOR AND JOSEPH K. CLINE

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A good deal of work has been devoted to the study of choline, its homologs and derivatives because of their interesting physiological properties.² Among the more important of the homologs of choline that have been investigated are those in which the hydroxyethyl group of choline has been replaced by the hydroxypropyl or hydroxyisopropyl group. Thus, α -methylcholine, $(CH_3)_3N(OH)CH(CH_3)CH_2OH$, β -methylcholine, $(CH_3)_3N(OH)CH_2CH(OH)CH_3$, and γ -homocholine, $(CH_3)_3N(OH)CH_2CH_2CH_2OH$, have been synthesized. A search through the literature has shown that there is considerable disagreement as to the properties of each of these compounds. Also, various investigators have

¹ Presented at the Indianapolis Meeting of the American Chemical Society April, 1931.

² Fraenkel, "Arzneimittel-Synthese," Julius Springer, Berlin, 1927, p. 336.