

flux condenser using a half atmosphere of excess pressure. The reaction mixture was poured into 150 cc. of hot water, boiled and filtered from a slight residue. The reddish filtrate upon cooling gave a large crop of reddish yellow needles which after twice recrystallizing from hot water gradually melted between 115 and 140°.

0.1659 g. subst. gave 0.4976 g. CO<sub>2</sub> and 0.0784 g. H<sub>2</sub>O. Calc. for C<sub>11</sub>H<sub>10</sub>O<sub>4</sub>: C, 64.08; H, 4.85. Found: 64.05, 5.32.

The analysis indicates a monomethyl ether but we believe the reaction will bear further study.

**Metallic Salts.**—Attempts were made to prepare metallic salts of the tetrahydroxynaphthalene. Water and alcohol solutions were used but no salts of barium, lead or silver could be obtained.

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[CONTRIBUTION FROM THE UNIVERSITY OF PITTSBURG, DEPARTMENT OF CHEMICAL ENGINEERING.]

## THE PRESENCE OF BENZENE HOMOLOGS IN THE HIGH BOILING DISTILLATES OF PETROLEUM.

BY BENJAMIN T. BROOKS AND IRWIN W. HUMPHREY.

Received December 14, 1915.

In studying the properties of the substances which cause fluorescence in petroleum distillates,<sup>1</sup> the conclusion was drawn that the substances in question were probably related to benzene and the essential facts advanced in support of this hypothesis were the following:

(1) Oils distilled *in vacuo* are much less fluorescent than when distilled slowly at ordinary pressure and accompanied by cracking and formation of relatively large quantities of coke. There is an unmistakable parallelism between the distillation of coal *in vacuo* and at atmospheric pressure and the distillation of oil under similar conditions. In general, destructive distillation of organic material containing little oxygen is conducive to the formation of aromatic hydrocarbons. The coal-tar distillates produced by distillation *in vacuo* are relatively very low in aromatic hydrocarbons and are only very slightly fluorescent.<sup>2</sup>

(2) No fluorescent organic substances are known which belong strictly to the paraffin or naphthene series of hydrocarbons. The vast majority of fluorescent organic compounds, whose constitution is known, possess condensed ring structures such as the derivatives of benzene, naphthalene, anthracene, fluorene, pyrone, acridine, azine, oxazine, thiazine, and the like. The character of the fluorescence of petroleum distillates is affected by such solvents as carbon bisulfide, aniline, nitrobenzene, amyl alcohol,

<sup>1</sup> Brooks and Bacon, *J. Ind. Eng. Chem.*, 6, 623 (1914).

<sup>2</sup> A. Pictet, *Ber.*, 46, 3342 (1913); Jones and Wheeler, *J. Chem. Soc.*, 105, 2562 (1914); 107, 1318 (1915).

pyridine, ether, acetone, etc., in a manner strictly parallel to the effect of these solvents on the fluorescence of the esters of terephthalic acid studied by Kauffman.<sup>1</sup>

(3) Suspensoids of colloidal degree of dispersion were found to be totally absent in strongly fluorescent petroleum oils.

(4) The fluorescent substances are readily sulfonated by strong sulfuric acid, forming water-soluble compounds whose aqueous solutions are strongly fluorescent.

Before considering the matter further it should be recalled that all petroleums which have been thoroughly examined have been shown to contain benzene and its simpler homologs. Even gasoline distilled from light Pennsylvania crude oil contains small percentages of them. The isolation and identification of the higher benzene homologs has apparently not been attempted, probably owing to the much greater experimental difficulties encountered, although Markownikow<sup>2</sup> isolated 3,5-diethyltoluene and isoamylbenzene,  $C_6H_5.C_5H_{11}$ , from the light kerosene distillate of Baku oil and H. O. Jones and H. A. Wootton<sup>3</sup> isolated  $\beta$ -dimethylnaphthalene from a Borneo petroleum.

#### Some Conditions under which Benzene Hydrocarbons are Formed.

It is known that in the manufacture of oil gas at a temperature of about  $950^\circ$  profound decomposition of the oil occurs, with the formation of hydrogen, methane, acetylene, olefines and a series of benzene hydrocarbons. The assumption is probably warranted that whenever the temperature is sufficiently high for the formation of acetylene, aromatic compounds will be found among the reaction products. The lowest temperature at which acetylene can be formed from petroleum oils has apparently not been determined, but no references exist in the literature noting its presence in oil gas made at temperatures lower than  $750^\circ$ .<sup>4</sup> It is known that under certain conditions naphthenes may form benzene hydrocarbons, accompanied by the splitting off of hydrogen, and the work of Nikiforoff and Ogloblin<sup>5</sup> shows that by employing heat alone temperatures of at least  $525$ – $550^\circ$  are necessary.<sup>6</sup> Engler<sup>7</sup> obtained no free hydrogen whatever by heating kerosene to temperatures below  $470^\circ$ . Although cyclohexane and methyl cyclohexane have been con-

<sup>1</sup> *Ann.*, **393**, 1 (1912).

<sup>2</sup> *Ibid.*, **234**, 89 (1886).

<sup>3</sup> *J. Chem. Soc.*, **91**, 1146 (1907); *Chem. Zent.*, **1907**, II, 1029.

<sup>4</sup> W. A. Noyes, *THIS JOURNAL*, **16**, 688 (1894).

<sup>5</sup> *Z. angew. Chem.*, **18**, 546 (1905).

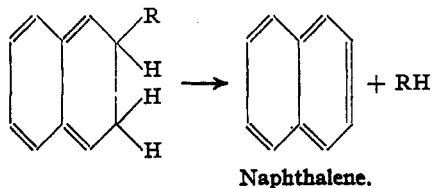
<sup>6</sup> Since the outbreak of the war in Europe, benzene and toluene have been made from petroleum on a commercial scale in several plants using the Hall process, which method employs a temperature of about  $650^\circ$  and pressures of 50 to 75 pounds per square inch and by the Rittman process employing slightly higher temperatures and pressures.

<sup>7</sup> "Das Erdol," Vol. I, p. 574.

verted into benzene and toluene, respectively, by splitting off hydrogen in the presence of metallic catalysts, such as nickel, platinum and palladium at temperatures below  $300^{\circ}$ , these conditions are widely removed from the conditions of the experiments described in this paper.

We have found that the heavier portion of Jennings and Oklahoma crude petroleums, *i. e.*, that part remaining after removing by distillation those fractions boiling below  $275^{\circ}$ , and hereinafter designated as reduced oil, yields benzene, toluene and xylene by "cracking" at temperatures not exceeding  $420^{\circ}$  and under 100 pounds' pressure; that these aromatic hydrocarbons are also obtained by cracking Jennings and Oklahoma reduced oils by heating with anhydrous aluminum chloride; that pure paraffin wax on cracking under either of these conditions does not yield benzene or its homologs, nor does it yield fluorescent distillates; that synthetic phenyl-paraffin, made by condensing chloroparaffin with pure benzene, is readily cracked by heating to  $420^{\circ}$  under 100 pounds' pressure or by merely heating with aluminum chloride to  $230^{\circ}$  yielding benzene and toluene among the reaction products. It is noteworthy, too, as agreeing with the above noted theory of the nature of the fluorescent compounds in petroleum, that, while the decomposition products of pure paraffin are not fluorescent, the introduction of a benzene nucleus leads to decomposition products which are highly fluorescent.

Jones and Wheeler<sup>1</sup> have shown that certain aromatic hydrocarbons are produced in the distillation of coal *in vacuo* at  $350^{\circ}$  and point out that this is below the temperature at which hydrogen is split off. They suggest that a reaction of the following type may take place:



In view of the facts recorded in this paper, we believe that the formation of free naphthalene at  $350^{\circ}$ , as noted by Jones<sup>2</sup> and Wheeler, is better accounted for by the decomposition of a complex molecule containing

<sup>1</sup> *J. Chem. Soc.*, 105, 2562 (1914).

<sup>2</sup> In a recent paper [*J. Chem. Soc.*, 107, 1582 (1915)], Jones states that cyclohexane, methyl cyclohexane and tetrahydronaphthalene began to decompose at approximately the same temperature namely, between  $490^{\circ}$  and  $510^{\circ}$ . The gas evolved contained approximately 40% hydrogen. Dihydronaphthalene decomposed at  $390^{\circ}$  and the gas evolved contained 80% hydrogen. The important bearing of Jones' work upon the matter here presented is the confirmation of the earlier work that a temperature of  $500^{\circ}$  is necessary to form benzene or toluene from cyclohexane and methyl cyclohexane, respectively, and that this decomposition of cyclohexane occurs relatively much easier than in the case of the normal paraffines.

the naphthalene radical, in the same way as we have shown phenyl-paraffin to be broken down into benzene, toluene and unsaturated hydrocarbons. For example,  $C_{10}H_7.C_nH_{2n+1} \longrightarrow C_{10}H_8$  (naphthalene) +  $C_nH_{2n}$  (olefine of naphthene).

### Experimental Part.

The Oklahoma reduced oil employed in the following experiments had the specific gravity 0.877,  $20^\circ/4^\circ$ , all material boiling below  $275^\circ$  having been distilled from the mixture. Three liters of the oil were cracked by slowly distilling under 100 pounds' pressure in a small iron still, capacity about 5.5 liters, the temperature gradually rising during the distillation through the range  $375-415^\circ$ . After three hours the distillate, 75% of the charge, was redistilled at atmospheric pressure and the fraction boiling below  $150^\circ$ , amounting to 22% of the charge was collected separately.<sup>1</sup> This low boiling portion was extracted at  $-15^\circ$  with liquid sulfur dioxide. This extraction was carried out by shaking in a large Dewar flask with an equal volume of liquid  $SO_2$  divided into three portions which were added successively after siphoning off the heavy layer from the preceding treatment. From the sulfur dioxide solution there were recovered about 10% by volume of the gasoline fraction, or 2.2% of the original charge of reduced oil. This was fractioned three times and the fractions boiling at  $75-85^\circ$ ,  $105-115^\circ$  and  $135-145^\circ$  were nitrated first in the cold and finally on a steam bath with an excess of ordinary sulfuric and nitric acids. The crude crystalline masses obtained by pouring into water were recrystallized and pure 1,3-dinitrobenzene, m. p.  $90^\circ$ , also 2,4-dinitrotoluene, m. p.  $70^\circ$ , and 2,4,6-trinitrometaxylene, m. p.  $182^\circ$ , were isolated.

We then examined the gasoline obtained by heating heavy high boiling oils with anhydrous aluminum chloride. Twenty liters of Oklahoma reduced oil were heated with 6% anhydrous aluminum chloride until four liters of light distillate were collected. When this was extracted with  $\frac{1}{2}$  volume liquid sulfur dioxide 0.40 liter extract was obtained. On fractionating and nitrating the proper fractions as before, pure 1,3-dinitrobenzene, 2,4-dinitrotoluene and 2,4,6-trinitro-*m*-xylene were isolated.

In order to determine quantitatively the amounts of aromatic compounds present in cracked gasolines, and in order to compare these results with those given by several natural gasolines distilled from crudes, we extracted a series of gasolines by using a total of 1.5 volumes of liquid sulfur dioxide in three successive extractions at  $-15^\circ$  in Dewar flasks. The following tabulated results include a sample of gasoline made by cracking Texas Solar oil with aluminum chloride:

<sup>1</sup> Cf. Brooks, Bacon, Padgett and Humphrey, *J. Ind. Eng. Chem.*, **6**, 180 (1914); Brooks, *J. Franklin Inst.*, **1915**, p. 653 (December).

TABLE I.—COMPARISON OF NATURAL GASOLINE AND THAT OBTAINED BY CRACKING WITH RESPECT TO AROMATIC COMPOUNDS.

Gasoline source.	Volume of sample treated, cc.	Per cent. soluble in SO <sub>2</sub> .	Fractionation of SO <sub>2</sub> Soluble portion, per cent.			Grams dinitrotoluene.	Grams trinitroxylyene.
			to 90° C.	90°–120°.	120°–145°.		
Bristow crude.....	1000	4.5	9.0	48.8	17.7	1.6	..
Muskogee crude <sup>1</sup> ....	1000	13.0	6.1	42.3	23.0	4.1	17.4
Mexican crude.....	1000	14.0	31.4	27.1	17.1	0.9	..
California crude....	750	13.0	20.0	58.0	19.0	4.4	..
Texas solar oil by AlCl <sub>3</sub> .....	1000	32.5	23.0	26.1	16.9	13.8	39.6

### Relative Stability of Paraffins and Naphthenes.

In cracking commercial paraffin, we were surprised to find that this material is more difficult to decompose than light lubricating oil which is composed almost exclusively of naphthenes and polynaphthenes. While the simpler naphthenes whose constitutions are known, such as cyclohexane and methyl cyclopentane, are apparently more stable to heat than normal paraffins, and have been found among the products resulting from heating simple paraffin hydrocarbons under pressure,<sup>2</sup> the instability of the three- and four-membered rings in the terpene series is well established. The properties of cycloheptane, cyclooctane, cyclononane and their derivatives are not so well known, but their tendency to rearrange to five- and six-ring systems has been frequently observed. It is probable that the relatively greater ease of cracking petroleum naphthenes, such as constitute much the greater part of light lubricating oil, as compared with the cracking of commercial paraffin wax of substantially the same average molecular weight and boiling point range, is to be interpreted as indicating that these high boiling naphthenes belong to series other than of five- or six-membered rings. The behavior on heat decomposition of naphthenes of known constitution such as cyclooctane, cyclononane, or their derivatives is not known.

That the heavy residues of certain crudes are more easily cracked than others is known to refiners. Heavy Mexican crude, particularly, is readily decomposed by heat and is conspicuous for its extremely high coke residue. (By slow direct fire distillation we have noted coke residues from this crude as high as 42%.) That higher temperatures are required for the cracking of paraffin than for reduced Jennings oil, made up of naphthenes and polynaphthenes and free from paraffin and from which all constituents boiling below 275° had been removed, was shown in two parallel distillations made under 100 pounds' pressure, the temperature being taken about

<sup>1</sup> That the extraction of aromatic hydrocarbons by the SO<sub>2</sub> method, as carried out above, was incomplete was shown by the isolation of 5 grams of dinitrotoluene after nitrating the 100–120° fraction of the portion insoluble in the sulfur dioxide.

<sup>2</sup> Engler.

ten minutes after distillation had commenced and afterwards at intervals of one hour.

TABLE II.—DISTILLATION OF PARAFFIN AND JENNINGS REDUCED OIL UNDER PRESSURE.

Material distilled.	Time required for distillation. Hours.	Temperature at 1-hour intervals.	Per cent. of charge distilled at last temperature reading.	Product distilling below 150°—per centage of original charge.	Volume of gas evolved per 1 liter oil.
Jennings reduced oil....	3.5	370-415-422°	69.0	19.0	31.36
Paraffin.....	3.5	417-432-437°	71.0	20.5	9.33 liters

The following summarized results show that when anhydrous aluminum chloride is used, commercial paraffin wax decomposes much less readily than the other hydrocarbons studied.

TABLE III.—DECOMPOSITION OF PARAFFIN AND NAPHTHENES WITH ALUMINUM CHLORIDE.

Material treated.	Temperature when first drop distilled and at 1-hour intervals.				Time heated. Hours.	Yield of product, %.	
						Bkg. to -150°.	% $\text{Al}_2\text{Cl}_6$ .
Jennings reduced oil.....	200°	226°	244°	255°	4.5	22.2	7.0
Texas solar oil.....	175°	190°	194°	210°	4.5	24.5	7.0
Paraffin.....	205°	235°	276°	282°	4.5	4.5	7.0
Phenyl paraffin.....	185°	220°	255°	265°	4.5	15.0	7.0

### The Cracking of Synthetic Phenyl Paraffin.

A mixture of phenyl paraffins was made by condensing pure benzene with chlorinated paraffin in the presence of anhydrous aluminum chloride at moderate temperatures, not exceeding 90°. In making up this material the commercial paraffin wax, m. p. 53°, was considered as a mixture of hydrocarbons of the mean molecular formula  $\text{C}_{24}\text{H}_{50}$ . Two kilos of melted paraffin were chlorinated until the gain in weight was 251 g., theoretical for  $\text{C}_{24}\text{H}_{49}\text{Cl}$ , being 201 g. This was treated with 2 liters of pure benzene, a large excess, and 0.5 liter of carbon bisulfide. Anhydrous aluminum chloride was then added in small portions until 150 g. had been added. The evolution of hydrogen chloride was very rapid at first, but after standing at room temperature for 14 hours had nearly ceased. The reaction mixture was then gently warmed for six hours on a steam bath, after which time it was washed several times with hot water to remove aluminum chloride and then distilled with steam until liquid ceased to distil, the  $\text{CS}_2$  and excess benzene being thus completely removed. After separating from water, the product was heated several hours in a large porcelain dish until all emulsified water had been driven off and then finally heated to 250° to insure the complete removal of free benzene. The dried material was then divided into two portions, one portion of 500 g. being heated with 35 g. anhydrous  $\text{Al}_2\text{Cl}_6$  to temperatures within the range 200-240°, the distillate being partially refluxed through a fractionating column. In

3 hours 78 cc. of distillate were collected. This was redistilled and 55 cc. of benzene, b. p. 79–85°, and 11 cc. toluene, b. p. 105–115° were obtained.

The identity of the benzene and toluene was further proved by conversion into the corresponding dinitro derivatives. The dinitrobenzene obtained, after recrystallizing, melted at 90° and the dinitrotoluene at 70°. Since pure benzene of tested purity and free from toluene was employed for the synthesis, the presence of toluene can be accounted for only by the splitting of the phenyl paraffin,  $C_6H_5CH_2 | CH_2R$ . In this reaction the higher boiling portion of the material was converted into a mixture of naphthenes. After pouring off the warm residue from the aluminum chloride and pitch, the oil was chilled and about 32 g. of crystalline paraffin were filtered from it. The filtered oil was then a viscous material resembling light lubricating oil but possessing an *intense green fluorescence*, resembling very closely the highly fluorescent oil obtained by treating Mexican crude petroleum with a small amount of aluminum chloride.

Two and one-half kilos of phenyl paraffin, prepared as above, were subjected to distillation under 75 pounds' pressure for three hours. The 1510 cc. of distillate were redistilled giving the following:

TABLE IV.—RESULTS OF DISTILLING PHENYL PARAFFIN UNDER 75 POUNDS' PRESSURE.

Fraction of product.	Quantity, cc.	Result on nitration
70–100°	112	25 g. crude dinitrobenzene
100–115°	150	41 g. crude dinitrotoluene
115–145°	272	

The isolation of dinitrotoluene, melting point of recrystallized product 69.2°, from the products of the distillation of phenyl paraffin under pressure shows, as in the case of decomposition by aluminum chloride, that the phenyl paraffin can break down so as to give not only benzene but toluene and possibly other homologs.

As regards the character of the fluorescent hydrocarbons in petroleum it was noted that the residue from the distillation of pure paraffin was not fluorescent, although if the distillation had been carried further so as to form considerable coke, the oil residue would undoubtedly have been fluorescent.

### Summary.

(1) Benzene and toluene and *m*-xylene have been found among the products from the cracking of heavy petroleum oils by (a) distillation at temperatures not exceeding 420° and pressures not exceeding 100 pounds, and (b) heating with anhydrous aluminum chloride to temperatures not exceeding 300°.

(2) Commercial paraffin wax does not yield benzene, toluene or xylene under the conditions just named.

(3) Synthetic phenyl paraffin, made from pure benzene and chlorinated paraffin, yields benzene and toluene among the reaction products under the conditions named in (1).

(4) From the above facts the conclusion is drawn that the heavy high boiling fractions of petroleum contain homologs of benzene, or hydrocarbons containing the benzene nucleus.

(5) The high boiling residues from the decomposition of phenyl paraffin are highly fluorescent, which supports the theory advanced in an earlier paper that the fluorescence of petroleum oils is due to the presence of complex hydrocarbons related to benzene.

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## THE STRUCTURE OF THE DIHYDRO- $\beta$ -NAPHTHOIC ACIDS.

By C. G. DERICK AND OLIVER KAMM.<sup>1</sup>

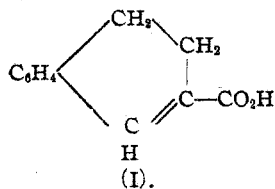
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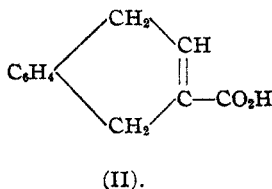
I. Introduction. II. The Third Isomeric Dihydro- $\beta$ -naphthoic Acid. III. Proof of the Atomic Linking Structures of the Three Dihydro- $\beta$ -naphthoic Acids from the Chemical Behavior of Their Respective Dibromides. IV. Proof of the Atomic Linking Structure of the Third Dihydro- $\beta$ -naphthoic Acid by Oxidation. V. A Correlation of Structure and Odor. VI. Experimental Part.

### I. Introduction.

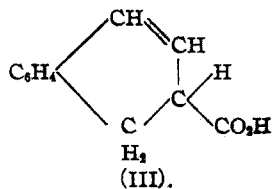
Three dihydro- $\beta$ -naphthoic acids which have an unsaturated linkage in the ring carrying the carboxyl group are theoretically possible, their structures being represented as follows:



$\Delta^1$ -Dihydronaphthoic acid-2.<sup>2</sup>



$\Delta^2$ -Dihydronaphthoic acid-2.



$\Delta^3$ -Dihydronaphthoic acid-2.

Of the above acids, two have previously been prepared and the structure of one of them has been definitely demonstrated. In the present work, which was carried out in connection with a study of the correlation of ionization and structure, the third isomeric acid has been prepared and demonstrations of the structures of the three isomers have been developed.

By the reduction of  $\beta$ -naphthoic acid with sodium amalgam, Sowinski<sup>3</sup> obtained two of the isomeric acids represented above. This work is also

<sup>1</sup> Presented at the Cincinnati meeting (1914) of the American Chemical Society. From a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Illinois (Kamm, 1915).

<sup>2</sup> The nomenclature used is that given in Meyer and Jacobson's "Lehrbuch der Organischen Chemie," 1903, Vol. 2, Pt. 2, p. 446.

<sup>3</sup> *Ber.*, 24, 2354-2363 (1891).