By reducing a solution of the free radical with hydrogen at a temperature of about 100°, and identifying the products formed, it was hoped that it would prove possible to determine whether such a dissociation of the monomolecular diphenylnaphthylmethyl occurs. But as in the case of reduction at ordinary temperatures, the reduced solution contained only diphenylnaphthyl methane so far as the examination revealed. Consequently the explanation suggested above still remains unsupported, and yet it seems difficult to find any other explanation equally satisfactory.

5. Summary.

(1) Several new diphenyl-α-naphthylmethyl derivatives have been synthesized and described.

(2) The important chemical reactions of the free radical, diphenyl-α-naphthylmethyl, have been studied including the oxidation, the reduction, the action of iodine, the action of light, and the action of hydrochloric acid.

(3) It has been shown that diphenyl-α-naphthylmethyl, unlike triphenylmethyl, does not form additive compounds with various solvents, in spite of its high degree of dissociation, and a plausible explanation for this difference has been suggested.

(4) By means of a series of exact molecular-weight determinations of diphenyl-α-naphthylmethyl extending over a range of temperature from 6° to 80°, it has been proven that the temperature as well as the concentration has a marked influence upon the degree of dissociation of free radicals, while the nature of the solvent seems to exert but slight influence.

(5) It has been shown that at a temperature of approximately 60° diphenyl-α-naphthylmethyl is present in the monomolecular phase entirely, and that above this temperature the molecular weight suffers a further decrease, the cause of which has not been established.

ANN ARBOR, MICH.

THE SYNTHESIS OF SOME HOMOLOGS OF THE TERPENES, DERIVATIVES OF 1,4-DIISOPROPYL CYCLOHEXANE.

BY MARSTON TAYLOR BOGERT AND CLARENCE PEAVY HARRIS.[1]

Introductory Part.

An interesting fact concerning the terpenes, and one to which attention often has been called, is that the graphic formulas conventionally assigned

[1] The investigation reported in this article formed part of the work carried out by Mr. Harris as a candidate for the degree of Ph.D. under the Faculty of Pure Science, Columbia University. Its publication has been delayed by the war duties of the senior author.

to this numerous group of compounds all contain the follbwing carbon skeleton, either as an open or as a closed chain:
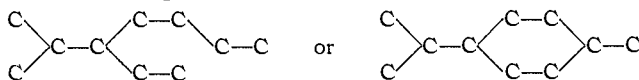
There is something peculiar about this arrangement of carbon atoms, the effect of which is to endow the compound with properties markedly divergent from the lower homologs of the same series, and this peculiarity of behavior seems to be referable to the isopropyl rather than to the methyl group.

The question presented itself therefore whether the presence of a second isopropyl group would cause any considerable change in properties as compared with homologs of the same series. The line of attack planned was to compare derivatives of the following types:

p-Xylene.	Cymene.	p-Diisopropyl benzene.
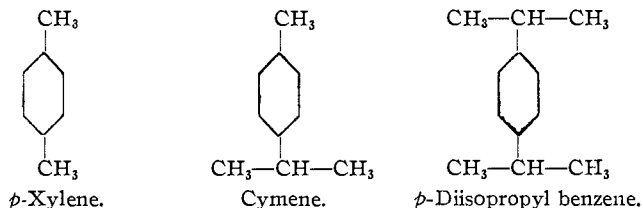
Derivatives of the first and second of these are numerous and well-known. Of the third type, very little appears to be on record.

As the hydrogenized hydrocarbons were regarded as most interesting, because of their structural relationship to the naturally occurring terpenes, the first problem was the synthesis and study of such substances, and this paper records the results so far accomplished in this direction. It is hoped to continue the investigation.

The only derivatives of 1,4-diisopropyl cyclohexane uncovered in our search of the literature were the p-diisopropyl cyclohexandiol-1,4 obtained by Wallach[1] on treating sabina ketone with methyl magnesium iodide, and the tetraphenyl p-phenylene glycol of Ullmann and Schlaepfer[2] prepared by the action of methyl magnesium iodide upon methyl terephthalate.

The new derivatives synthesized were as follows: tetramethyl p-phenylene glycol; 1,4-diisopropenyl benzene; 1,4-diisopropenyl-$\Delta^{1,4}$-dihydrobenzene; two isomeric $C_{12}H_{18}$ hydrocarbons from Δ^1-tetrahydroterephthalic acid; and certain bromine addition products of these hydrocarbons.

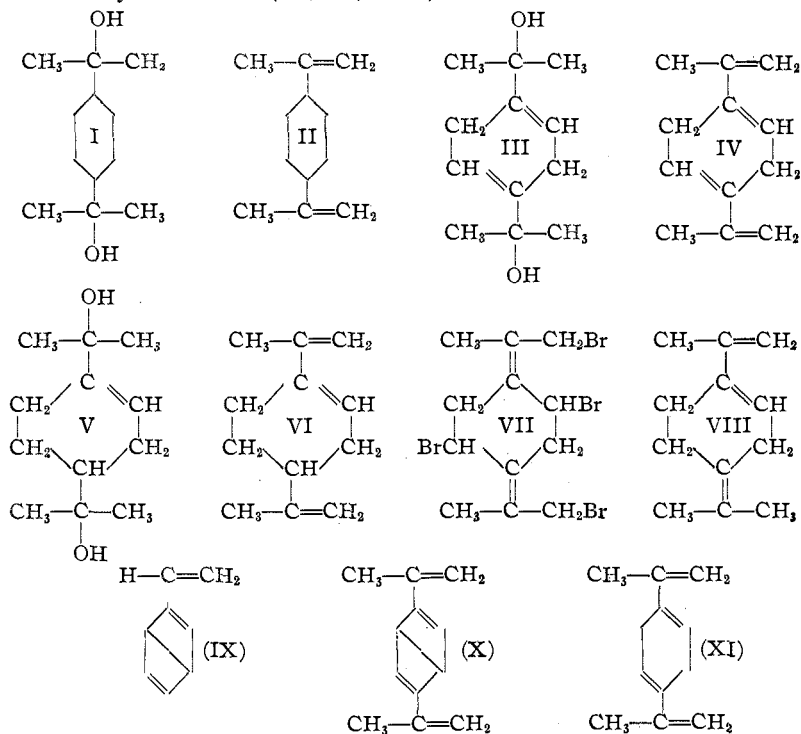The synthesis of these compounds was carried out briefly as follows:

Cymene was oxidized to terephthalic acid by the action of sodium

[1] Ann., 263, 149 (1891); 302, 362 (1898).
[2] Ber., 37, 2001 (1904).

dichromate in presence of sulfuric acid, the terephthalic acid esterified, and the ester treated in anhydrous ether solution with methyl magnesium iodide, giving the glycol (I). This was then dehydrated by heating it with potassium hydrogen sulfate, yielding the diisopropenyl benzene (II).

In the case of the di- and tetra-hydrogenated compounds, obtained in similar manner from the hydrogenated terephthalic acids, the intermediate glycols (III and V) could not be isolated, as they lost water under the conditions of the experiment, passing immediately to the unsaturated hydrocarbons (IV, VI, VIII).

$$
\begin{array}{cccc}
\text{OH} & & \text{OH} & \\
| & & | & \\
CH_3{-}\overset{|}{C}{-}CH_2 & CH_3{-}C{=}CH_2 & CH_3{-}\overset{|}{C}{-}CH_3 & CH_3{-}C{=}CH_2 \\
\text{(I)} & \text{(II)} & \text{(III)} & \text{(IV)} \\
& & CH_3{-}\overset{|}{C}{-}CH_3 & CH_3{-}C{=}CH_2 \\
CH_3{-}\overset{|}{C}{-}CH_3 & CH_3{-}C{=}CH_2 & | & \\
| & & \text{OH} & \\
\text{OH} & & &
\end{array}
$$

(I) (II) (III) (IV)

OH
|
CH₃—C—CH₃ (V)   CH₃—C=CH₂ (VI)   CH₃—C—CH₂Br (VII)   CH₃—C=CH₂ (VIII)

(V): CH₃—C—CH₃ with ring; CH₂ C CH; CH₂ CH₂; CH₃—C—CH₃, OH

(VI): CH₃—C=CH₂; CH₂ C CH; CH₂ CH₂; CH₃—C=CH₂

(VII): CH₃—C—CH₂Br; CH₂ C CHBr; BrCH CH₂; CH₃—C—CH₂Br

(VIII): CH₃—C=CH₂; CH₂ C CH; CH₂ CH₂; CH₃—C—CH₃

H—C=CH₂ (IX)   CH₃—C=CH₂ (X)   CH₃—C=CH₂ (XI)

(X): CH₃—C=CH₂

(XI): CH₃—C=CH₂

Derivatives of II in general proved more stable and hence more readily isolated and purified than the corresponding derivatives of IV, VI or VIII.

Titration of II with a standardized solution of bromine in chloroform, and analysis of the product, both showed that 4 atoms of bromine had been added. Excess of the halogen caused no further addition nor any evolution of hydrogen bromide.

Hydrocarbon IV possesses a constitution resembling the $\Delta^{1,4}$-terpadienes, and, like the terpenes, gives a deep green coloration with acetic anhydride and sulfuric acid. It reduces permanganate in the cold, adds

bromine and hydrogen bromide, and forms both a solid and a liquid tetra-bromide like limonene, to which latter it is also related structurally. Treated with bromine in excess, it appears to take up but 4 atoms of bromine, after which substitution sets in, as evidenced by the evolution of hydrogen bromide. This corresponds with the results observed by Perkin in the case of the analogously constituted $\Delta^{3,8(9)}$-p-menthadiene, and was ascribed by him to the presence of a true conjugated system of double bonds. The structure of the tetrabromide of IV therefore is probably that pictured in Formula VII; the solid and liquid forms being the *cis* and *trans* isomers.

Hydrocarbon VI (or VIII), obtained from tetrahydro terephthalic acid in two isomeric forms, was much more sensitive to the action of bromine than either II or IV. Although these isomers decolorized the bromine solution instantly when first added, elimination of hydrogen bromide began very soon and we were unable to control it or to separate any pure bromo derivative from the products, the latter being oily, viscous and intractable.

The behavior of the 4 hydrocarbons (II, IV, VI and VIII) towards bromine is thus quite different and obviously reflects some difference in their constitution. The smooth addition of 4 bromine atoms to II, the absence of any hydrogen bromide evolution even when excess of the halogen was employed, and the stability of the final product, all indicate side-chain and not nuclear addition. It is analogous to the addition of bromine to p-isopropenyl toluene[1] or to isopropenyl benzene.[2] On the other hand, Wallach[3] noted many years ago the evolution of hydrogen bromide during the formation of terpene tetrabromides, and Perkin[4] made a similar observation in the addition of bromine to certain p-menthadienes. Other investigators have had like experiences, and it is a well established fact that where bromine is attached to the carbon of a hydroaromatic nucleus hydrogen bromide splits out very easily. The indications therefore are that in the other unsaturated hydrocarbons (IV, VI and VIII) bromine adds to nuclear carbon and hydrogen bromide then splits out with formation of various as yet unidentified derivatives.

In the case of the $C_{12}H_{18}$ hydrocarbons prepared from tetrahydro tere-phthalic acid, it has not been determined as yet whether they represent the two possible structural isomers (VI and VIII) which can be formed from the dicarbinol by loss of water, or whether they are only geometrical isomers of one of these two (VI).

A discussion of the refractivities and magnetic rotatory powers of the new hydrocarbons will be found in the Experimental Part.

[1] Perkin, *J. Chem. Soc.*, **87,** 654 (1905).
[2] Perkin, *Ibid.*, **87,** 672 (1905).
[3] *Ann.*, **279,** 389 (1894).
[4] *J. Chem. Soc.*, **87,** 667, 1101, 1102 (1905).

In the course of this study, an improved process for the production of terephthalic acid from cymene was developed; and the methods of Baeyer for the preparation of $\Delta^{1,4}$-dihydro- and Δ^1-tetrahydroterephthalic acids were modified as so to improve the yields considerably.

Experimental Part.

p-Di(hydroxyisopropyl) Benzene (1,4-Di(isopropanol-2) Benzene) (Formula I).—The raw material was crude cymene from the paper mills, which was washed with alkali, steam distilled and then fractioned under diminished pressure. In most cases, the distillation under reduced pressure could be dispensed with, the yields of terephthalic acid being just about as good when the dried steam-distilled product was used direct.

This cymene was oxidized by boiling it, under a return condenser, with a mixture of sodium dichromate and sulfuric acid. To a solution of 560 cc. of conc. (sp. gr. 1.84) sulfuric acid in 1500 cc. of water, 440 g. of technical sodium dichromate was added, and then 50 g. of cymene, and the whole boiled gently until the oxidation was completed, which was usually after about 48 hours boiling. It was found necessary to use resistance glass flasks, and to protect the corks with tinfoil against the solvent action of the cymene.

Upon completion of the oxidation, the mixture was diluted with an equal volume of water, the crude acid filtered out, washed thoroughly with water, dried at 110° to remove traces of cymene, and then washed again with water to remove small amounts of chromium salts not easily eliminated so long as any cymene is present. The product thus obtained was micro-crystalline and nearly colorless. This method of purification was found more satisfactory than solution in alkali and reprecipitation by acid. Final purification was always accomplished through the methyl ester. Yield of terephthalic acid by the above process, 25–28 g., or approximately 45% of the theoretical amount.

In spite of the slight solubility of both terephthalic acid and of its methyl ester in methyl alcohol, the acid when suspended in this solvent can be esterified in two or three hours by the action of dry hydrogen chloride. The course of the reaction can be followed by the change in the appearance of the suspended solid from the granular condition of the free acid to the needles or plates characteristic of the methyl ester. The ester so prepared was crystallized once from ethyl alcohol and was then quite pure, m. p. 140.8° (corr.). Yield, 80 g. of pure ester from 100 g. of crude acid, or about 70% of the theoretical amount.

By the action of methyl magnesium iodide upon methyl terephthalate, the desired dicarbinol was obtained.

This step presented something of a problem, owing to the very slight solubility of the ester in anhydrous ether. After experimenting with various methods and different forms of apparatus, the one described

below, using the apparatus depicted in Fig. 1, was devised and proved the most satisfactory.
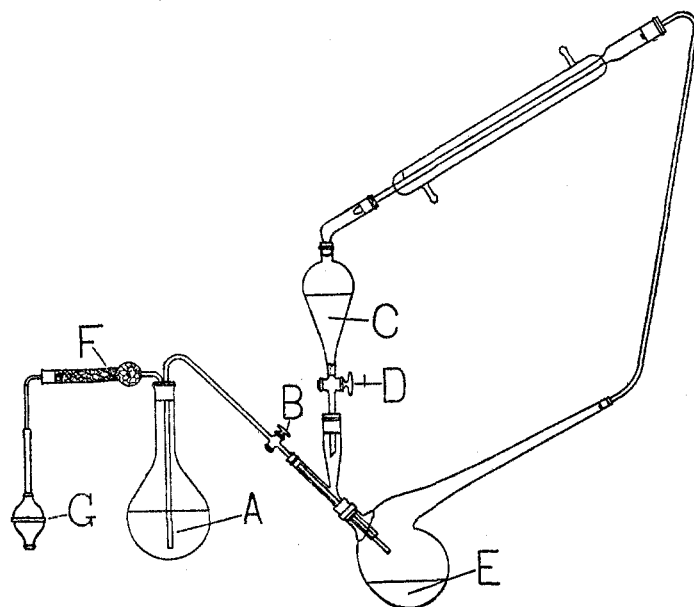
Fig. 1.

20 g. of methyl terephthalate was placed in the separatory funnel C. The Grignard reagent was prepared in the flask A from 10 g. of magnesium, 60 g. of methyl iodide and 800 cc. of anhydrous ether. 200 cc. of anhydrous ether was introduced into the retort E and heated gently so that the ether distilled over into C at the rate of about 10 cc. per minute, there dissolving the crystalline ester and carrying it down into E. As soon as this saturated solution of the ester began to enter the retort, a small amount of the Grignard reagent was blown over into the retort by compressing the bulb G. Instead of a rubber bulb, in later experiments there was employed a source of constant pressure, controlling the flow by the stopcock B. F contained soda-lime and calcium chloride. By this manner of operating, there was never any large excess of Grignard reagent in the reaction vessel E, and less danger of splitting water out of the tertiary alcohol formed.

The ester was dissolved completely in 3 or 4 hours, after which the contents of E were boiled gently for another hour, and then left over night at laboratory temperature. The ether was decanted from the insoluble addition product, the latter decomposed by ice and dil. hydrochloric acid, and the mixture warmed on the water bath to remove ether. The dicarbinol was then filtered off and washed with water to free it from

magnesium salts. The somewhat sticky solid was heated at 100° for half an hour with 200 cc. of 5% aqueous caustic alkali solution, to eliminate traces of iodine and to saponify any unchanged methyl terephthalate, filtered, washed free from alkali, and crystallized twice from 50% ethyl alcohol. The dicarbinol was thus produced in colorless, short, lustreless needles; m. p. 142.4–142.9° (corr.); it was insoluble in water, but moderately soluble in alcohol or in glacial acetic acid. The yield of crude product was 15 g., or 85% of the theoretical amount; of pure substance, 10 g., or 50% of the theoretical amount.

Calc. for $C_{12}H_{18}O_2$: C, 74.23; H, 9.28. Found: C, 74.0, 73.8; H, 9.5, 9.4.

1,4-Diisopropenyl Benzene (Formula II).—This diolefin was prepared from the above carbinol by heating it with dry powdered potassium hydrogen sulfate. As it polymerizes very readily, some investigation was necessary to ascertain the conditions requisite for good yields. The following procedure gave the best results:

8 g. of the dicarbinol was mixed intimately with 4 g. of powdered potassium hydrogen sulfate and distilled under reduced pressure, maintaining the temperature of the bath at 150° to 160°. At a pressure of 20 mm., the diolefin distilled over at 110 to 123°, condensing to a colorless highly refractive liquid which soon changed to a white solid. Yield, 4.5 g., or 68.4% of the theoretical amount.

This hydrocarbon crystallized from dil. ethyl alcohol in micaceous plates with high nacreous lustre, and possessed a very pleasant odor. It was easily soluble in the ordinary organic solvents at their boiling points. Recrystallized to constant m. p., it melted at 63.6–64° (corr.).

Calc. for $C_{12}H_{14}$: C, 91.13; H, 8.87. Found: C, 90.8, 90.2; H, 8.7, 8.8.
M. W. calc., 158. Found: 153.

Tetrabromide.—Diisopropenyl benzene dissolved in chloroform was titrated with a standardized solution of bromine in the same solvent, determining the end-point with starch-iodide paper. The addition proceeded rapidly at first, but slowed up toward the close, making the exact reading of the end-point a matter of considerable difficulty. No evolution of hydrogen bromide was observed at any time during the reaction. The amount of standard solution consumed showed that the hydrocarbon had taken up 4 atoms of bromine.

Evaporation of the chloroform solution yielded a solid, together with a small amount of a liquid product. Recrystallization of the solid gave pale yellowish, cubical crystals, m. p. 130.3–131.3° (corr.), of impure tetrabromide. In spite of 3 further recrystallizations from ethyl acetate, the product remained impure; but the amount of bromine found on analysis indicated that it was evidently a tetra- and not a dibromide. Insufficient material prevented further work in this direction.

1,4-Diisopropenyl- $\Delta^{1,4}$**-dihydrobenzene** (Formula IV).—Baeyer[1] found that when terephthalic acid was reduced by sodium amalgam, the first product of the reduction was the $\Delta^{2,5}$-dihydro acid. Upon boiling this with water, the $\Delta^{1,5}$-dihydro acid was formed, whereas heating with alkali gave the $\Delta^{1,4}$-dihydro acid. The latter is therefore the most stable of the three and by carrying out the reduction at slightly elevated temperatures without neutralizing the alkali, the $\Delta^{1,4}$ acid was the main product.

On repeating this work, we found that the yield of $\Delta^{1,4}$-dihydro acid could be materially increased by various modifications of Baeyer's original process, and the method finally adopted was as follows:

10 g. of methyl terephthalate was saponified by boiling with 500 cc. of water containing 5 g. of sodium hydroxide, the solution was cooled to 50°, diluted to a liter and reduced by successive additions of 100 g. portions of 3% sodium amalgam, with vigorous stirring, until the permanganate test[2] showed a faint cloud only. It is essential that all of the terephthalic acid be reduced at this point and before taking the next step in the process, since the solubilities of its ester are much the same as those of the methyl ester of the dihydro acid and the complete separation of the two is therefore a matter of no little difficulty. The mixture was heated an hour longer on the water bath, to complete the conversion of all $\Delta^{2,5}$ and $\Delta^{1,5}$ acids into the $\Delta^{1,4}$ isomer, the aqueous layer decanted from the mercury, nearly neutralized and filtered. The filtrate was made strongly acid with hydrochloric acid, the $\Delta^{1,4}$-dihydro acid filtered out, washed and dried. Yield, 6.3 g. of crude acid, or 73% of the theoretical amount.

10 g. of this crude $\Delta^{1,4}$-dihydro acid was converted into the acid chloride by heating with excess of phosphorus pentachloride. The crude chloride was cooled in a freezing mixture and, without further purification, cold methyl alcohol was added to it slowly. The ester separated almost immediately in small, white prisms. These were filtered out, washed with methyl alcohol, and recrystallized from ethyl alcohol, giving short, thick, lustreless prisms. From ethyl acetate, it crystallized in rhombs resembling calcium oxalate in appearance. Yield, 4.8 g., or 41% of the theoretical amount. M. p. 128.4–129.4° (corr.). Baeyer gives the m. p. as 130° uncorrected.

This dimethyl ester was treated with methyl magnesium iodide, in anhydrous ether solution, in exactly the same way as already described for methyl terephthalate, but no carbinol was isolated, dehydration occurring under the conditions of the experiments and the diolefin being the sole product recovered.

From 12 g. of the ester, 6.5 g. of magnesium and 38 g. of methyl iodide,

[1] *Ann.*, **245**, 103 (1887); **251**, 272, 292 (1889); **256**, 1 (1890); **258**, 1, 145 (1890); **266**, 169 (1892); **269**, 169 (1892); see also Perkin, *J. Chem. Soc.*, **87**, 1083 (1906).

[2] Baeyer, *Ann.*, **245**, 147 (1888).

9.5 g. crude product, or 79% of the theoretical amount was obtained. Direct crystallization of this crude product from alcohol, or distillation under diminished pressure, followed by crystallization from alcohol, gave only the unsaturated hydrocarbon and no dicarbinol. The hydrocarbon separated from alcohol in plates, with faint nacreous lustre, difficultly soluble in water, but soluble in most of the ordinary organic solvents on heating. M. p. 117–117.5° (corr.).

Calc. for $C_{12}H_{16}$: C, 90.0; H, 10. Found: C, 90.0; H, 10.1.

M. W. calc., 160. Found: 161.5.

Tetrabromide.—When this hydrocarbon was dissolved in chloroform and titrated with a standardized solution of bromine in the same solvent, the bromine solution was decolorized until 1.93 moles, or approximately 4 atoms of the halogen had been taken up. At this point the yellow color of the solution remained and a small amount of hydrogen bromide was evolved. Evaporation of the chloroform solution yielded an oil which could not be handled.

By carrying out the addition of the calculated amount of bromine in glacial acetic solution, a small amount of cubical crystals was secured, which melted at 107 to 109° (corr.) after recrystallization from ethyl acetate. Only 0.13 g. of these crystals was recovered.

Calc. for $C_{12}H_{16}Br_4$: Br, 66.7. Found: 67.4.

Hydrocarbons from Δ^1-Tetrahydro Terephthalic Acid (Formulas VI and VIII).—Δ^1-Tetrahydro terephthalic acid was produced from terephthalic acid according to the method of Baeyer,[1] with a few modifications introduced to increase the yield. The amount of crude tetrahydro acid recovered averaged 96% of the theoretical quantity. The crude acid was converted into the acid chloride by the action of phosphorus pentachloride, and the chloride then changed to the methyl ester by the action of methyl alcohol at low temperature. The methyl alcohol solution of the ester so obtained was poured slowly into a saturated aqueous solution of sodium hydrogen carbonate, which caused the ester to separate on top of the solution as an oily layer which quickly solidified. This was collected with ether, the ethereal solution dried with calcium chloride and fractioned under reduced pressure, the ester coming over at 153.3 to 154.5° (corr.) at 20 mm. Yield, 45% of the theoretical amount. From water, it crystallized in colorless needles, m. p. 35.2–36.2° (corr.), soluble in most of the ordinary organic solvents.

When this ester was subjected to the action of methyl magnesium iodide, in dry ether solution, in the manner described above for the other esters, the dicarbinol was probably the main product of the reaction, because when it was distilled under diminished pressure, both water and unsaturated hydrocarbon were recovered. Attempts to isolate the car-

[1] *Loc. cit.*

binol from the crude product however proved fruitless, so it was heated for 15 minutes at 180 to 190° with excess of potassium hydrogen sulfate, water added, the mass extracted with ether, the ethereal solution separated, dried over solid sodium hydroxide, decanted, the ether removed by distillation, and the residue fractioned at 20 mm. pressure.

From 9 g. of crude carbinol, there were obtained 5 g. of a fraction (A), b. p. 95–98° at 20 mm., and 3 g. of a fraction (B), b. p. 105–108° at the same pressure. Both were colorless oils, and on analysis proved to be isomeric $C_{12}H_{18}$ hydrocarbons.

Analysis of A. Calc. for $C_{12}H_{18}$: C, 88.9; H, 11.1. Found: C, 88.5; H, 10.98. M. W. calc., 162. Found: 164.

Analysis of B. Calc. for $C_{12}H_{18}$: C, 88.9; H, 11.1. Found: C, 88.8; H, 10.95. M. W. calc., 162. Found: 154.

Upon long standing in the air, both isomers became viscous and slightly yellow.

Towards bromine, the behavior of the two isomers was much the same. Various solvents were tried. The bromine was absorbed quickly at the outset, but very soon evolution of hydrogen bromide began and the yellow color of the solution disappeared but slowly. Addition of bromine therefore was continued as long as any reaction was evident, but the products were thick oils, from which no pure bromine dervatives could be separated.

Specific Gravities, Refractivities, and Magnetic Rotatory Powers of the New Hydrocarbons.

Specific Gravity.—The density of the liquid hydrocarbons ($C_{12}H_{18}$) was ascertained by use of a 1 cc. pycnometer. In the case of the solids ($C_{12}H_{14}$ and $C_{12}H_{16}$), the specific gravity was determined by the "free-swimming" method regarded by Nernst[1] as the most accurate for small quantities of material. We employed the modification recommended

TABLE I.
Specific Gravities.

Liquid.	Substance.	Per cent.	Solvent.	Specific gravity.	Temp. T_4.
1........	(a)	..	....	1.0649	22.3
2........	(a)	5.11	Benzene	0.8843	16.0
3........	(a)	4.27	Chloroform	1.4547	19.0
4........	(b)	..	....	1.0669	20.0
5........	(b)	3.76	Benzene	0.8836	16.0
6........	(b)	4.79	Chloroform	1.4447	16.0
7........	(c)[95]	..	....	0.8715	20.0
8........	(c)[105]	..	....	0.8706	20.0
9........	..	..	Benzene	0.8832	17.5
10........	..	..	Chloroform	1.4939	15.8
11........	(b)	3.19	Benzene	0.8853	15.0
12........	(a)	4.57	Benzene	0.8872	15.0

[1] *Theoretical Chemistry*, from 6th German ed., 1911, p. 305.

by Andrae.[1] The density of solutions of these solids was determined with a Westphal balance, and chloroform and benzene were used as the solvents.

Table I gives the results of these determinations, the concentration of solute, density of solvent, and temperature (referred to water at $4°$).

In this and the following tables, (a) $= C_{12}H_{14}$, (b) $= C_{12}H_{16}$, and (c) $= C_{12}H_{18}$; (c)[95] being the fraction boiling at $95–98°$ at 20 mm., and (c)[105] being the fraction boiling at 105 to $108°$ at same pressure.

Refractivity.—The determination of the refractive powers of these hydrocarbons was found somewhat troublesome, because of their slight solubility at the temperature employed, and the relatively high m. p. of the $C_{12}H_{16}$ compound. It was necessary therefore to use quite dilute (3% to 5%) solutions.

The coefficients of refractivity were determined by means of the Pulfrich refractometer, using a Geissler hydrogen tube as the source of illumination. The indices of refraction were found in all cases for the α hydrogen or C line, and where chloroform solutions were used were determined also for the γ hydrogen or G line.

Molecular refractivities (M) were calculated by both the Gladstone-Dale (Table III) and the Lorentz-Lorenz (Table II) formulas. The admixture formulas, as given by Eisenlohr[2] were employed. According to Smiles[3] the admixture formula is accurate "if the solvent and solute have nearly the same refractive index; but if these differ much from one another" the results are not so reliable. Two solvents, benzene and chloroform, therefore were employed and the average result taken as the nearest approximation to the truth.

In Tables II and IV (Lorentz-Lorenz formula), and III (Gladstone-Dale formula), the liquids listed in the first column are the same as those given in Table I. Not much reliance should be placed upon Table IV, as the violet hydrogen line was indistinct in the instrument used; and for this reason the dispersivities were not calculated.

Molecular refractivities were calculated from the atomic values recently revised by Eisenlohr;[4] figuring, for compound II, 12 C, 14 H and 5 double bonds; for compound IV, 12 C, 16 H and 4 double bonds; and for compounds VI and VIII, 12 C, 18 H and 3 double bonds.

To reduce the errors and inaccuracies arising from the determination of molecular refractivities in such dilute solutions, and to get a nearer approach to the truth, the average values obtained by the use of two solvents, benzene and chloroform, differing considerably from each other

[1] *Z. physik. Chem.*, **76**, 491 (1911).

[2] *Spektrochemie organischer Verbindungen*, Stuttgart, **1912**, p. 189.

[3] *Chemical Constitution and Physical Properties*, London, **1912**, p. 244.

[4] *Z. physik. Chem.*, **75**, 585 (1910).

in refractive index, were calculated and appear in Table V. These were figured from Table II, since the Lorentz-Lorenz formula is believed to give results more nearly correct than the Gladstone-Dale expression.

TABLE II.

Liquid.	Index H_α or C.	n^2-Form. Spec. ref.	n_2-Form. M(calc.).	M(obs.).	Exaltation.
2.......	1.49755	0.35868	52.674	56.687	4.013
3.......	1.44985	0.35660	52.674	56.343	3.669
5.......	1.49593	0.35167	53.171	56.267	3.095
6.......	1.45005	0.36475	53.172	57.629	4.458
7.......	1.48717	0.33013	53.670	53.481	—0.189
8.......	1.48650	0.33080	53.670	53.473	—0.197
9.......	1.49421	...	..	...	...
10.......	1.44172	...	..	...	...

TABLE III.

Liquid.	Index H_α or C.	n-Form. Spec. ref.	n-Formula. M(calc.).	M(obs.).	Exaltation.
2.......	1.49755	0.61985	90.2	98.01	7.81
3.......	1.44985	0.61320	90.2	96.95	6.75
5.......	1.49593	0.60398	90.4	96.71	6.31
6.......	1.45005	0.62642	90.4	100.31	9.91
7.........1.48717		0.55902	90.6	90.64	0.04
8.......	1.48650	0.55883	90.6	90.61	0.01

TABLE IV.

Liquid.	Index H_γ or G'.	n^2-Form. Spec. ref.	n^2-Formula. M(calc.).	M(obs.).	Exaltation.
3.......	1.46620	0.36192	54.765	57.184	2.419
6.......	1.46570	0.36591	55.112	58.546	3.434
7.......	1.50902	0.34264	55.457	55.508	0.051
9.......	1.52082	...	..	...	...
10.......	1.45852	...	..	...	...

TABLE V.

Substance.	M(calc.).	M(observed).	Exaltation.
(a).....................	52.674	56.515	3.841
(b).....................	53.172	56.948	3.776
(c)[95]...................	53.670	53.481	—0.189
(c)[105]..................	53.670	53.473	—0.197

Examination of Table V discloses the fact that the difference in exaltation between compounds (a) and (b) is within experimental error. If the structures assigned to these two hydrocarbons are correct, they differ only in that one contains a true benzene nucleus and the other a dihydrobenzene nucleus. The exaltation observed in the case of compound (b) is assumed to be due to the presence of two systems of conjugated double bonds. The exaltation recorded for compound (a) therefore would indicate the existence in it also of two such systems of double bonds, an assumption which is in line with the exaltation characteristic

of styrene and of other benzenoid compounds having an unsaturation adjacent to the nucleus, a fact which has been explained on the hypothesis that the external double bond becomes conjugated with an adjoining unsaturation of the nucleus. The third unsaturation occurring in the nucleus of (a) must bear a somewhat different relation to the molecule, or there would be 5 sets of conjugated double bonds present and a corre--spondingly higher refractivity.

It is perhaps of interest to point out here that the Dewar formula for styrene (IX) contains but one system of conjugated double bonds and should therefore exhibit a smaller exaltation than hexatriene, and this has been found to be the fact. On the same formulation, diisopropenyl benzene (X) shows but two such systems and the same is true of its dihydro derivative (XI). The difference in refractive power between the two therefore would be that due solely to the *para* bond. If we regard the centric formula for benzene as nearest the truth, we may look upon the Dewar formulation as the phase in which this centric formula preferably presents itself in the case of styrene and related compounds. The fact that the first reduction product of terephthalic acid is the $\Delta^{2,5}$-dihydro acid apparently links it up with this *para* bond relation also.

That the $C_{12}H_{18}$ hydrocarbons gave a slight depression instead of an exaltation in molecular refractivity seems at first sight rather puzzling, in view of the assumed presence in their molecules of a conjugated system of double bonds; but the case is not unique, as it falls exactly into line with $\Delta^{1,3}$-dihydrobenzene, which both Harries[1] and Willstätter[2] found to give normal and not exalted values for refractivity.

Magnetic Rotatory Power.—The apparatus employed consisted of an electromagnet having a hollow core to permit the passage of light, and with a polariscope attached to the same frame. The compound to be examined was placed in a 5 cm. tube between the poles, and the same tube was used in all the experiments, so as to avoid errors due to variations in the thickness of the liquid. The angle was read to hundredths of a degree, and conductivity water was taken as the standard.

Table VI gives the angle readings with direct and reversed currents, the total rotation, specific rotation, calculated and observed molecular rotation, and magneto-rotatory exaltation. The molecular rotatory power was calculated by the usual formulas for a pure liquid and for a solution.

Table VII shows the average of the results with two different solvents, benzene and chloroform. The liquids used in Tables VI and VII, appearing in the first column, are the same as those given in Table I.

[1] *Ber.*, **45**, 809 (1912).
[2] *Ibid.*, **45**, 1468 (1912).

TABLE VI.

Liquid.	Rotation.		Total.	Spec. rot.	M(calc.).	M(obs.).	Exalta-tion.
	Direct.	Reversed.					
Water................	4.40	—1.19	5.59	...	..	..	..
3................	5.11	—1.81	6.92	2.962	13.501	24.404	10.903
12................	7.16	—3.86	11.02	2.671	13.501	22.003	8.502
6................	4.88	—1.73	6.61	2.028	13.256	16.753	3.497
11................	7.09	—3.86	10.95	2.019	13.256	16.649	3.393
7................	5.79	—2.79	8.58	1.535	13.011	15.852	2.841
8................	5.82	—3.06	8.88	1.588	13.011	16.423	3.412
9................	4.86	—1.54	6.40	...	..	..	..
10................	7.16	—3.77	10.93	...	..	..	..

TABLE VII.

Substance.	Spec. rot.	M(calc.).	M(obs.).	Exaltation.
(a)................	2.817	13.501	23.204	9.703
(b)................	2.024	13.256	16.701	3.445
(c)................	1.562	13.011	16.137	3.126

In considering the results obtained by magnetic rotation, it may be recalled that Perkin[1] found the difference in magnetic rotation between cyclohexane and benzene, 5.62, to be almost identical with that observed between hexane and hexatriene, 5.55, and concluded that benzene contained 3 conjugated systems of double bonds. By a comparison of the rotations of limonene and the isomeric $\Delta^{3,8(9)}$-p-menthadiene, he deduced the value of the conjugation as 1.82.

A glance at Table VII shows a value of 9.7 for p-diisopropenyl benzene, or the equivalent of 5 conjugated systems of double bonds ($5 \times 1.82 = 9.1$), a result which must be explained on the assumption that, in the magnetic field at least, this hydrocarbon possesses a nucleus corresponding to a Kekulé and not to a Dewar formula.

Diisopropenyl dihydrobenzene contains two conjugated systems of double bonds and should accordingly show a rotation of $2 \times 1.82 = 3.64$, which is very close to the value of 3.45 actually found.

The behavior of the tetrahydro derivatives (c) is analogous to that of $\Delta^{1,3}$-dihydrobenzene, which shows a normal refractivity but a magnetic rotatory exaltation,[2] although the figure actually found, 3.1, is somewhat higher than it should be for the structures assigned.

Recapitulating the observations noted in the foregoing concerning these new hydrocarbons:

Compound a (Formula II, $C_{12}H_{14}$) towards bromine gives no evidence of the presence of any conjugated systems of double bonds, but adds 4 bromines like a simple diolefin. Its molecular refractivity, on the other hand, indicates the presence of two such systems; and, in the magnetic field, it behaves as though possessing 5 such systems.

[1] *J. Chem. Soc.*, **69**, 1025 (1896); **91**, 810 (1907).
[2] Perkin, *J. Chem. Soc.*, **89**, 854 (1906); **91**, 806 (1907).

Compound b (Formula IV, $C_{12}H_{16}$), in its behavior with bromine, its molecular refractivity and its magnetic rotatory power, acts consistently as though containing two systems of conjugated double bonds.

Compounds c (Formulas VI and VIII, $C_{12}H_{18}$) act towards bromine like substances containing conjugated double bonds such as to cause nuclear addition and not simple addition to side chains, although no pure bromine derivatives could be isolated. In their molecular refractivities and magnetic rotatory powers, they resemble $\Delta^{1,3}$-dihydrobenzene.

A dynamic representation of benzenoid structure, similar to that proposed by Collie,[1] which includes different static formulas as phases of its vibration, lends itself best to the interpretation of the behavior of the hydrocarbons described above.

Summary.

1. Unsaturated hydrocarbons, related to the terpenes, have been prepared by the action of methyl magnesium iodide upon methyl terephthalate and its di- and tetrahydro derivatives.

2. The new compounds prepared were the 1,4-diisopropenyl benzene $(C_{12}H_{14})$; 1,4-diisopropenyl-$\Delta^{1,4}$-dihydrobenzene $(C_{12}H_{16})$; 1,4-diisopropenyl-Δ^1-tetrahydrobenzene $(C_{12}H_{18})$, or an isomer thereof; tetramethyl p-phenylene glycol; and certain bromine addition products of the new hydrocarbons.

3. The refractivities and magnetic rotatory powers of the new hydrocarbons, as well as their densities, have been determined and are discussed with reference to their bearing upon the structures assigned to these compounds.

NEW YORK CITY.

THE GENESIS OF PETROLEUM AS REVEALED BY ITS NITROGEN CONSTITUENTS.

BY CHARLES F. MABERY.

From what is known concerning natural processes of building up complex nitrogen organic compounds they are limited to the agency of vegetable or animal life. The circuitous laboratory methods leading through many changes to intricate structure have no counterpart in nature except through the influence of the life principle. If, therefore, such nitrogen derivatives are universally present in petroleum it is difficult to avoid the conviction that these bodies had their origin as evolution products of organic life, and that the hydrocarbons with which they are associated were evolved from the same source. The universal presence of nitrogen

[1] *J. Chem. Soc.,* **71,** 1013 (1897).