

XCV.—*Hexamethylene from American and Galician Petroleum.*

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THE object of the present research, undertaken at the suggestion of Professor Sydney Young, was, by means of fractional distillation, to obtain hexamethylene in a pure state from petroleum, with a view to the

accurate determination of its physical properties, and to prepare some of its derivatives, amplifying the work of Markownikoff (*Ber.*, 1895, 28, 577 ; 1897, 30, 1225) and at the same time repeating a portion of that of Baeyer (*Ber.*, 1893, 26, 229 ; *Annalen*, 1893, 278, 88) on the synthetical hydrocarbon. The presence of hexamethylene had been detected in American petroleum by Professor Young while engaged in the isolation of some of the paraffins, and that source was the one first employed, on account of the difficulty in procuring the Caucasian oil. The distillation was carried out with the aid of a fractionating column kindly made for the purpose by Professor Young, and similar to that described by him in the *Chemical News* (1895, 71, 177), but containing twelve constrictions instead of seven. The fractional distillation occupied about six months, at the expiration of which time it became evident that it would not be possible to obtain the hydrocarbon in a pure state, although the fractions obtained would serve for the preparation of its derivatives. The purest fraction boiled at 80·55—80·65°, sp. gr. 0·7722 at 0°/4°. A supply of Galician petroleum was next procured, and the distillation was recommenced, the same fractionating column being used throughout. This oil had previously been investigated by Lachowicz (*Annalen*, 1883, 220, 188), who concluded that the proportion of naphthenes present was greater than in American petroleum, although considerably less than in Caucasian naphtha; there seemed, therefore, reasonable hope that pure hexamethylene might be obtained from it by repeated fractional distillation, and this expectation has been realised. After about nine months' work, a fraction was obtained boiling constantly at 80·8° (corr.) and having the sp. gr. 0·7903 at 0°/4°; this fraction was set apart for the determination of certain physical constants, whilst the others, boiling within a range of 1° were used for the preparation of derivatives, of which the following were obtained. The monochloride, $C_6H_{11}Cl$; dichloride, $C_6H_{10}Cl_2$; trichloride, $C_6H_9Cl_3$; and tetrachloride, $C_6H_8Cl_4$; the monobromide, $C_6H_{11}Br$; dibromide, $C_6H_{10}Br_2$; and tetrabromide, $C_6H_8Br_4$; dihydrobenzene, C_6H_8 ; tetrahydrobenzene, C_6H_{10} ; chlorodihydrobenzene, C_6H_7Cl ; chlorhydroxyhexamethylene, $C_6H_{10}OH \cdot Cl$; (*Proc. Chem. Soc.*, 1897, p. 161 ; 1898, p. 103). Of these substances, the following have been prepared synthetically by Baeyer: the monobromide, dibromide, and tetrabromide, dihydrobenzene and tetrahydrobenzene. The agreement between the properties is, on the whole, satisfactory, as will be seen from the following comparison (p. 934), especially when it is remembered that the quantities of the substances obtained by the synthetical methods were very small.

It may be noted that, in an earlier paper, Baeyer gives the boiling point of dihydrobenzene as about 81·5°.

Dr. W. H. Perkin, sen., has very kindly determined the magnetic

	B. p.		M. p.	
	Baeyer.	E. C. F.	Baeyer.	E. C. F.
Hexamethylene	79—79·5°	80·8°		
Tetrahydrobenzene.....	82—84	82·3		
Dihydrobenzene	84—86	81—82		
Monobromhexamethylene	165—166	162—163		
Dibromhexamethylene	215—220	145—146		
	(713 mm.)	(100 mm.)		
Tetrabromhexamethylene			184—185°	185°

rotation of hexamethylene and of tetrahydrobenzene; unfortunately, the amount of dihydrobenzene obtained was not sufficient for the purpose. He has, however, determined the index of refraction and the specific and molecular refractions of all three hydrocarbons, and the results are tabulated on p. 946 and compared with the numbers obtained by Brühl.

The same constants have been determined by Dr. Perkin for monochlor- and dichlor-hexamethylene and for monobromhexamethylene.

Hexamethylene from American Petroleum.

Twenty-five pounds of American light petroleum having the sp. gr. 0·680 were procured and distilled in 10 successive portions from a can of about 5 litres capacity. No correction was made during the first few distillations for the barometric pressure, as it would have been negligible compared with the alteration of temperature caused by slight variations in the rate of distillation. The first drops distilled over at 16°, but all below 28° and above 95° was rejected. After nine distillations, extending over two months, the fractions were freed from aromatic hydrocarbons by nitrating the latter; they were first shaken three times in separating funnels with sulphuric acid, and then with two or three times their volume of a mixture of nitric and sulphuric acids, in the proportion of 3:10 by weight, with which they were left in contact for some hours. The mixed acids were then separated from the hydrocarbon, and poured into a large volume of water, when crystals were obtained from several of the fractions; this treatment was repeated until no turbidity was produced on diluting the mixed acids with water. The crystals, when collected and recrystallised five times from methylated spirits and water, and then once from water, melted at 89·6°, showing that they were pure metadinitrobenzene; the greatest quantity was obtained from the lowest fraction, which boiled at 68—70°, and decreasing amounts were

obtained from successive fractions up to 74—77·5°. From the higher fractions, no crystals were obtained, showing that benzene was apparently the only aromatic hydrocarbon present. The fact that this substance, when mixed with the paraffins, distils over far below its true boiling point had already been observed by Dr. Young. The fractions were next treated three times with about twice their volume of sulphuric acid, the operation lasting about an hour, and after washing twice with water, they were shaken twice with a strong solution of caustic potash. They were again washed three times with water, and then dehydrated with phosphoric anhydride. Each fraction was then distilled separately into its old flask from a distilling flask containing roughly powdered caustic potash; the operation was repeated with fresh potash, and the fractional distillation was then continued. After the tenth distillation, the specific gravity of some of the fractions was taken, the highest being 0·7513 at 0°/4° for fraction 80—83°. After 15 distillations, the sp. gr. of the purest fraction was 0·7621, and after 33, the highest sp. gr. was 0·7722, namely, that of the fraction 80·55—80·65°. This fraction gave, on analysis, the following numbers, which agree fairly well with those required for hexamethylene.

0·0716 gave 0·2239 CO₂ and 0·0931 H₂O. C = 85·22; H = 14·44.

C₆H₁₂ requires C = 85·71; H = 14·29 per cent.

As a proof that the substance was hexamethylene itself, and not one of its isomerides, it was oxidised with fuming nitric acid, when it yielded adipic acid, as had been previously shown by Markownikoff (*Ber.*, 1897, 30, 975) in the case of hexanaphthene from Caucasian petroleum.

Although the specimen of hexamethylene obtained was not entirely free from paraffins, it was necessary to stop the distillation at the above stage, as the quantities were so small as to render further purification of the substance impossible; the fractions boiling between 80·25° and 80·65° were used in the following experiments.

Action of Chlorine.

The hydrocarbon (10 grams) was placed in a reflux apparatus, together with iron filings (0·5 gram), and exposed to sunlight while a current of dry chlorine was passed through the liquid; in less than half an hour, chemical action began, the liquid became hot, and hydrogen chloride was evolved in abundance. After about 4 hours, the action was interrupted, the product washed successively with sodium carbonate solution and water, and dried over calcium chloride. When about

70 grams of hexamethylene had been chlorinated in this way, the dried product was distilled under reduced pressure; no monochlorhexamethylene was obtained, but after repeated fractional distillation under a pressure of 30 mm. a fraction boiling at 110—115° (30 mm.) was obtained, consisting chiefly of *dichlorhexamethylene*, $C_6H_{10}Cl_2$ a substance which is described in greater detail on p. 943.

0.1242 gave 0.2094 CO_2 and 0.0634 H_2O . C = 45.98; H = 5.67.

0.2881 „ 0.5642 AgCl. Cl = 48.34.

$C_6H_{10}Cl_2$ requires C = 47.12; H = 6.54. Cl = 46.34 per cent.

The oils boiling above 115° (at 30 mm.) were subjected to repeated careful fractionation under reduced pressure, when two fractions of fairly constant boiling point were obtained, one boiling at 135—140° (at 30 mm.) and the other at 160—165° (at 30 mm.). The former consisted chiefly of *trichlorhexamethylene*, $C_6H_9Cl_3$, and gave the following numbers on analysis.

0.1240 gave 0.1706 CO_2 and 0.0585 H_2O . C = 37.52; H = 5.24.

0.2512 „ 0.5930 AgCl. Cl = 58.27.

$C_6H_9Cl_3$ requires C = 38.46; H = 4.81; Cl = 56.73 per cent.

The higher boiling fraction was chiefly composed of *tetrachlorhexamethylene* $C_6H_8Cl_4$, an analysis giving the following results.

0.1213 gave 0.1406 CO_2 and 0.0377 H_2O . C = 31.61; H = 3.45.

0.2669 „ 0.7029 AgCl. Cl = 65.01.

$C_6H_8Cl_4$ requires C = 32.49; H = 3.61; Cl = 63.90 per cent.

Both the above fractions were heavy, pale yellow oils, which distilled without decomposition under a pressure of 30 mm., and on long standing deposited crystals, but not in sufficient quantity for analysis. The fraction consisting chiefly of trichlorhexamethylene was heated with alcoholic potash on the water bath for some hours in a reflux apparatus. Potassium chloride separated, and the product was extracted with ether, washed, dried, and fractionated after distilling off the ether. As it seemed probable that the small quantity of liquid boiling below 90° might contain benzene, formed from trichlorhexamethylene by the removal of 3HCl, it was treated with a mixture of nitric and sulphuric acids. The product had the odour of nitrobenzene, and on extracting with ether, reducing, &c., aniline was detected by its odour, and by the purple coloration produced by bleaching powder.

Besides benzene, a considerable quantity of a substance boiling at 135—140° was isolated from the product of the action of alcoholic potash on trichlorhexamethylene; this consisted of *chlorodihydrobenzene*, C_6H_7Cl , formed by the removal of 2HCl from trichlorhexamethylene.

0.0970 gave 0.2228 CO_2 and 0.0516 H_2O . $\text{C} = 63.20$; $\text{H} = 5.91$.

0.1684 „ 0.2065 AgCl . $\text{Cl} = 30.36$.

$\text{C}_6\text{H}_7\text{Cl}$ requires $\text{C} = 62.93$; $\text{H} = 6.12$; $\text{Cl} = 30.95$ per cent.

The action of alcoholic potash on dichlorhexamethylene and tetrachlorhexamethylene was also investigated, but in both cases the action was a complicated one, and the amount of material at my disposal was, unfortunately, too small to allow of a separation being effected.

In view of the statements of both Markownikoff (*Ber.*, 1897, 30, 1222) and Zelinsky (*Ber.*, 1897, 30, 1532) that methylpentamethylene is obtained by heating derivatives of hexamethylene with concentrated hydriodic acid, it seemed to be of interest to ascertain whether the hydrocarbon itself would undergo isomeric change under these conditions. It was therefore heated in a sealed tube, with five times the volume of hydriodic acid and a little amorphous phosphorus for 3 hours at temperatures ranging from 160° to 270° . The product, after being washed and dried, boiled almost constantly at 80° , whereas methylpentamethylene boils at $70-71^\circ$. Hexamethylene, therefore, remains unchanged under these conditions, being apparently more stable in this respect than some of its derivatives.

Hexamethylene from Galician Petroleum.

Twenty-five kilograms of Galician oil of low boiling point were procured from Kahlbaum and distilled in 14 portions from a tin of about one gallon capacity, using the same fractionating column as before. As one distillation alone of this quantity extended over nearly three months, all the liquid boiling below 65° and above 96° was discarded ; after 12 distillations of the fractions retained, they were treated with a mixture of nitric and sulphuric acids to remove the benzene, which was found in all the fractions up to and including $79.7-80.7^\circ$, but not in the higher fractions, the treatment with the acids being repeated until all traces of benzene were removed. The fractions were then washed and dried as before, and distilled over potash into their old flasks, after which the fractional distillation was continued. After the fourteenth distillation, the specific gravity of the fractions was taken and the results are given in the table on page 938. The column headed $\Delta w/\Delta T$ represents the weight in grams of each fraction divided by its temperature range, and thus gives a measure of the relative purity of the fractions.*

A fractional distillation of the portion boiling at $80.7-81^\circ$ was then carried out separately, as the time required to go through the

* See S. Young, *Phil. Mag.*, Jan., 1894, p. 25.

Fraction.	Weight Δw	$\frac{\Delta w}{\Delta T}$	Sp. gr. at 0°/4°.
71·5—74°	134	53·6	—
74 —76	75	37·5	0·7529
76 —78·5	166	66·4	0·7648
78·5—79·5	75	75	0·7720
79·5—80·2	176	251·4	0·7756
80·2—80·7	211	422	0·7817
80·7—81·0	322	1073·3	0·7834
81·0—81·5	219	538	0·7819
81·5—83·2	171	100·5	0·7764
83·2—87·2	119	31·3	0·7549

whole fractionation until a pure substance was obtained would have been too great. Four of the remaining fractions, namely, the two boiling nearest on each side of the fraction 80·7—81° were subsequently used in the preparation of derivatives.

After 11 distillations, a fraction boiling apparently constantly at 80·7° was obtained, and the specific gravity of this fraction and those on either side of it were taken.

Fraction.	Sp. gr. at 0°/4°.
80·65—80·7°	0·7846
80·7	0·7878
80·7—80·75	0·7899

The higher specific gravity of the last fraction showed that pure hexamethylene had not yet been obtained, and the distillation was therefore continued. In addition to the difficulty of reading accurately to within a twentieth of a degree, considerable trouble was experienced, owing to the fact that the constant of the variation of the boiling point with the pressure was not known for hexamethylene, and a slight error in this constant would make an appreciable difference in determining the true boiling point. It was found that the most concordant results were obtained by assuming that a change of pressure of 1 mm. corresponded with a difference of 0·04° in the boiling point. Three more distillations were carried out, and then a fraction consisting of 37 grams was obtained which boiled constantly at 80·8° and had a higher specific gravity than those on either side of it.

Fraction.	Sp. gr. at 0°/4°.
80·75—80·8	0·7881
80·8	0·7903
80·8—80·85	0·7896

The liquid boiling constantly at 80·8° was analysed and the results obtained indicate that it was pure hexamethylene.

0.1311 gave 0.4110 CO₂ and 0.1691 H₂O. C = 85.50; H = 14.34.
C₆H₁₂ requires C = 85.71; H = 14.29 per cent.

Hexamethylene is a colourless, volatile oil with a pleasant odour resembling that of light petroleum. It is not attacked by bromine in the cold, and is not oxidised by potassium permanganate solution. The specific gravities at different temperatures, the magnetic rotation, and the refraction constants of this specimen were determined by Dr. W. H. Perkin, sen., with the following results.

Specific gravity. $d\ 4^{\circ}/4^{\circ} = 0.7865$; $d\ 10^{\circ}/10^{\circ} = 0.7812$.
 $d\ 15^{\circ}/15^{\circ} = 0.7771$; $d\ 20^{\circ}/20^{\circ} = 0.7731$; $d\ 25^{\circ}/25^{\circ} = 0.7694$.
Magnetic rotation (mean of two determinations).

t	Sp. rot.	Mol. rot.
16.1°	0.9752	5.754

This rotation is very much lower than was to be expected. In ring compounds, the value for CH₂ is usually nearly normal, namely, 1.023. Hexamethylene would therefore be expected to have a molecular rotation of about $1.023 \times 6 = 6.128$ or 0.374 higher than that given by the product examined.

* *Refraction*, $t = 17.4^{\circ}$; $d\ 17.4^{\circ}/4^{\circ} = 0.7742$.

	Index of re- fraction	Sp. refraction		Mol. refraction.	
	μ .	$\frac{\mu-1}{d}$	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{1}{d}$	$\frac{\mu-1}{d} \cdot P$.	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{P}{d}$.
A.....	1.41977	0.54217	0.32671	45.542	27.444
Li	1.4218	0.54480	0.32810	45.762	27.560
H _a	1.42211	0.54520	0.32831	45.797	27.578
Na	1.42446	0.54823	0.32991	46.051	27.713
H _s	1.42960	0.55488	0.33340	46.610	28.003
H _y	1.43391	0.56044	0.33631	47.077	28.292

The calculated molecular refraction for H_a is 45.653, the above being 45.797; the difference is not very large, but is in the opposite direction to the rotation.

The agreement with the numbers obtained by Brühl is very good; a table of comparison is given on p. 946.

* In this and all other cases, the specific and molecular refractions have been calculated according to the formulæ $\frac{\mu^2-1}{\mu^2+2} \cdot \frac{1}{d}$ and $\frac{\mu^2-1}{\mu^2+2} \cdot \frac{P}{d}$ from Dr. Perkin's determinations of μ and d , for the sake of comparison with the numbers obtained by Brühl.

Derivatives of Hexamethylene from Galician Petroleum.

Monochlorhexamethylene, $C_6H_{11}Cl$, and its conversion into *Tetrahydrobenzene*, C_6H_{10} .—Monochlorhexamethylene was obtained together with dichlorhexamethylene by passing a current of dry chlorine into hexamethylene in the cold, in diffused daylight. An attempt to chlorinate in the dark was made in order to see whether in this way the action of the chlorine would stop after the formation of a monochloro-derivative, but it proved unsuccessful, hexamethylene remaining almost unchanged. It had already been found (p. 935) that application of heat or the addition of chlorine carriers gave rise to the formation almost exclusively of higher substitution products such as di-, tri-, and tetrachlorhexamethylene. When chlorine is passed into hexamethylene in the cold, it dissolves, in the first instance forming a yellow solution, then, at a certain point, combination begins, heat is developed and hydrogen chloride is evolved. If from this point the gas is passed slowly for about 3 hours, a good yield of the monochloride is obtained. Similar observations were made by Schorlemmer (*Annalen*, 1877, 188, 250) in the case of the chlorination of isoheptane, the action indeed taking place in the same way. The product was washed with sodium carbonate solution, and then with water and dried over calcium chloride.

After repeated fractional distillations with a Glinsky column, a sample of monochlorhexamethylene was obtained boiling at $141.3\text{--}141.6^\circ$ (768 mm.) and having a sp. gr. = 0.9991 at $0^\circ/0^\circ$.

0.1758 gave 0.2130 AgCl. Cl = 29.85.

$C_6H_{11}Cl$ requires Cl = 29.86 per cent.

Monochlorhexamethylene is a colourless oil with a characteristic odour; it is an unstable substance readily losing a molecule of hydrogen chloride and yielding tetrahydrobenzene. It distills, however, unchanged when pure. It dissolves in strong sulphuric acid with evolution of heat, giving a deep red solution. The sp. gr., magnetic rotation, and refraction experiments gave the following results.

Specific gravity. $d\ 4^\circ/4^\circ = 0.9897$; $d\ 10^\circ/10^\circ = 0.9842$;
 $d\ 15^\circ/15^\circ = 0.9800$; $d\ 20^\circ/20^\circ = 0.9762$; $d\ 25^\circ/25^\circ = 0.9725$.

Magnetic rotation (twice determined).

	<i>t</i> .	Sp. rot.	Mol. rot.
Average	15.8	1.1125	7.478

This molecular rotation, like that of hexamethylene, is somewhat lower than the calculated, if the value of chlorine replacing hydrogen

is taken as 1.558, namely, that which it has in the paraffin series, thus,

$$6\text{CH}_2 = 6 \times 1.023 = 6.138$$

$$\text{Cl replacing H} = 1.558$$

Calculated rotation of monochlorohexamethylene = 7.696

Refraction, $t = 18^\circ$; $d \ 18^\circ/4^\circ = 0.9765$.

	Index of refraction.	Sp. refraction.		Mol. refraction.	
	μ .	$\frac{\mu-1}{d}$.	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{1}{d}$.	$\frac{\mu-1}{d} \cdot P$.	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{P}{d}$.
A.....	1.45053	0.46138	0.27549	54.673	32.563
Li	1.45267	0.46358	0.27661	54.934	32.695
H _a	1.45313	0.46404	0.27686	54.989	32.725
N _a	1.45552	0.46649	0.27812	55.279	32.874
H _s	1.46153	0.47264	0.28128	56.008	33.248
H _y	1.46644	0.47767	0.28286	56.604	33.552

This result is a good deal higher than the calculated, thus,

Molecular refraction for H_a found = 54.989

Calculated 54.170

Difference = 0.819

Tetrahydrobenzene, C₆H₁₀, is very readily prepared from monochlorohexamethylene, being formed when the latter is heated with quinoline or alcoholic potash, and in smaller quantity when heated with moist silver oxide or even with silver acetate or silver nitrite, the best yield being obtained by heating with quinoline for 7 or 8 hours in a reflux apparatus. On subjecting the product to careful fractional distillation without previous washing with acid, a fraction was finally obtained boiling constantly at 82.3° (764 mm.).

An analysis of the freshly distilled substance gave the following numbers.

0.1230 gave 0.3947 CO₂ and 0.1503 H₂O. C = 87.50; H = 12.22.

C₆H₁₀ requires C = 87.80; H = 12.20 per cent.

It yielded a liquid dibromide (p. 948) and a crystalline nitrosochloride, and its alcoholic solution was coloured yellow on warming with concentrated sulphuric acid as stated by Baeyer (*Ber.*, 1893, 26, 230).

Determinations of the specific gravity, magnetic rotation, and refraction were made by Dr. Perkin. The specimen sent him distilled in

the first instance constantly at 82.3° (764 mm.), but after standing for some days, it was found that it did not evaporate completely when placed on bibulous paper, but left an oily stain.

Specific gravity. $d\ 4^{\circ}/4^{\circ}=0.8244$; $d\ 10^{\circ}/10^{\circ}=0.8188$;
 $d\ 15^{\circ}/15^{\circ}=0.8149$; $d\ 20^{\circ}/20^{\circ}=0.8110$; $d\ 25^{\circ}/25^{\circ}=0.8072$.

	<i>t.</i>	Sp. rot.	Mol. rot.
<i>Magnetic rotation.</i>	15°	1.1439	6.395

The specimen was then redistilled, when the chief fraction came over at 82.3° ; the temperature then gradually rose, until a gummy product was left in the retort, and this, on further heating, seemed to undergo decomposition, some drops of water condensing in the neck of the distilling flask, a fact which seems to indicate that the gummy product contained a product of the oxidation of the hydrocarbon. The tendency of unsaturated cyclic hydrocarbons to become oxidised to thick gummy substances in presence of air has been noted by Markownikoff (*Annalen*, 1898, 301, 158).

The fraction boiling at 82.3° was then examined.

Specific gravity. $d\ 20^{\circ}/20^{\circ}=0.7995$; $d\ 25^{\circ}/25^{\circ}=0.7956$.

The expansions given by these density determinations are practically the same as for the undistilled product, but the densities are about 0.0154 lower.

Magnetic rotation of recently distilled product.

<i>t.</i>	Sp. rot.	Mol. rot.
16.8°	1.1198	6.392

It will be seen that the specific rotation is much lower than in the original product, but owing to the change in density, this is counter-balanced in the calculation for the molecular rotation, which comes out much the same as before.

The molecular rotation of this compound is very low. If compared with that of hexamethylene, it will be seen that the difference is not much greater than it should be for the difference in composition of H_2 , namely, 0.508, whereas it would be expected to be this *plus* the difference for unsaturation, which is generally about 1.112.

Tetrahydrobenzene	= 6.392
Hexamethylene	= 5.754
	<hr/>
	0.638

It is certainly very remarkable that the magnetic rotation of hexamethylene and tetrahydrobenzene should be so low, unlike that of any other hydrocarbons which Dr. Perkin has as yet examined.

Refraction of redistilled specimen. $t = 14.4$; $d_{14.4}^{14.4}/4^\circ = 0.79934$.

	Index of refraction.	Sp. refraction.		Mol. refraction.	
	μ .	$\frac{\mu-1}{d}$.	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{1}{d}$.	$\frac{\mu-1}{d} \cdot P$.	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{P}{d}$.
H ₂	1.43998	0.55043	0.32970	45.135	27.035
H ₈	1.44943	0.56224	0.33583	46.104	27.538
H ₇	1.45507	0.56930	0.33947	46.688	27.837

The molecular refraction of the redistilled specimen is not far from that calculated for C₆H₁₀ with one ethylene linking, but is rather low.

$$\begin{array}{r}
 \text{C}_6 = 30.000 \\
 \text{H}_{10} = 13.000 \\
 \text{Ethylene linking} = 2.300 \\
 \hline
 45.300 \\
 \text{Found } 45.135 \\
 \hline
 \text{Difference} = 0.165
 \end{array}$$

Dichlorhexamethylene, C₆H₁₀Cl₂, and its conversion into *Dihydrobenzene*, C₆H₈.—In the course of the preparation of monochlorhexamethylene, a considerable quantity of a substance of higher boiling point was obtained; this was submitted to fractional distillation, when the largest quantity boiled at 190—195°. On exposure to air, it became rapidly coloured, but on further fractionation, about 15 grams of a colourless liquid was obtained boiling at 193—194°. This fraction gave the following numbers on analysis.

0.2251 gave 0.4204 AgCl. Cl = 46.04.

C₆H₁₀Cl₂ requires Cl = 46.30 per cent.

Dichlorhexamethylene is a heavy, colourless oil with a penetrating odour, and, like monochlorhexamethylene, dissolves in strong sulphuric acid, forming a deep red solution. Determinations were made by Dr. Perkin of its specific gravity, magnetic rotation, and refraction.

Specific gravity. $d_{4^\circ}^{14^\circ} = 1.1777$; $d_{10^\circ}^{10^\circ} = 1.1720$;
 $d_{15^\circ}^{15^\circ} = 1.1678$; $d_{20^\circ}^{20^\circ} = 1.1638$; $d_{25^\circ}^{25^\circ} = 1.1603$.

	t .	Sp. rot.	Mol. rot.
<i>Magnetic rotation.</i>	16.6°	1.2224	8.906

The calculated value of dichlorhexamethylene may be obtained as follows.

$$6\text{CH}_2 = 6 \times 1.023 = 6.138$$

$$2\text{Cl replacing } 2\text{H} = 2 \times 1.558 = 3.116$$

$$\text{Calc. rotation of dichlorhexamethylene} = 9.254$$

$$\text{Refraction. } t = 16.6^\circ; d \ 16.6^\circ/4^\circ = 1.670.$$

	Index of refraction.	Sp. refraction.		Mol. refraction.	
	μ .	$\frac{\mu-1}{d}$.	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{1}{d}$.	$\frac{\mu-1}{d} \cdot P$.	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{P}{d}$.
A.....	1.48274	0.41365	0.17094	63.288	26.050
Li.....	1.48517	0.41574	0.17167	63.608	26.162
H _a	1.48556	0.41607	0.17179	63.659	26.180
Na.....	1.48862	0.41692	0.17271	64.060	26.321
H _s	1.49467	0.42388	0.17452	64.853	26.598
H _y	1.50189	0.43006	0.17668	64.800	26.926

On comparing the value obtained with that calculated for H_a, we have the following result.

$$\text{Found } 63.659$$

$$\text{Calc. } 62.740$$

$$\text{Difference} = 0.919$$

This compound, then, gives higher refraction values than were to be expected.

The oil boiling above 194° was submitted to careful fractional distillation, and a considerable quantity of liquid was obtained boiling very constantly between 201° and 202° and giving the following numbers on analysis.

$$0.1990 \text{ gave } 0.3823 \text{ AgCl. Cl} = 47.28.$$

$$\text{C}_6\text{H}_{10}\text{Cl}_2 \text{ requires Cl} = 46.30.$$

Possibly this oil may contain a dichlorhexamethylene which is isomeric with the dichlorhexamethylene boiling at 193 — 194° , but the quantity of material at my disposal was not sufficient to decide this point.

Dihydrobenzene, C₆H₈, was obtained by distilling dichlorhexamethylene with quinoline; in this case, it was found that the yield was not increased by prolonged heating of the mixture before distillation. The product, after repeated fractional distillation, yielded a fraction boiling

at 81—82°; this was redistilled just before the analysis, when the following result was obtained.

0.2806 gave 0.9274 CO₂ and 0.2527 H₂O. C = 90.14; H = 10.00.

C₆H₈ requires C = 90.00; H = 10.00 per cent.

Dihydrobenzene is a light, colourless oil with a peculiar odour resembling that of tetrahydrobenzene, and very readily undergoes oxidation. The vapour turns potassium permanganate solution brown (Baeyer, *Ber.*, 1893, 26, 230), and on standing it takes up oxygen from the air and is converted into a thick, syrupy liquid. At first, a heavy layer is formed at the bottom of the tube, and this gradually spreads up through the liquid until, finally, the tube may be inverted without spilling its contents. The liquid boiling at 81—82° was sent to Dr. W. H. Perkin, sen., and he determined the specific gravity and the refraction constants. The specimen sent him, like that of tetrahydrobenzene, had undergone some change by keeping, as it did not evaporate regularly on blotting paper. Unfortunately, there was not enough to allow of the determination of the magnetic rotation, so that in this respect its relationship to benzene and tetrahydrobenzene could not be ascertained.

Specific gravity of redistilled specimen. $d_{15^\circ/15^\circ} = 0.84987$.

Refraction of redistilled specimen. $t = 15.5^\circ$; $d_{15.5^\circ/4^\circ} = 0.84785$.

	Index of refraction.	Sp. refraction.		Mol. refraction.	
	μ .	$\frac{\mu - 1}{d}$	$\frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{1}{d}$	$\frac{\mu - 1}{d} \cdot P$	$\frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{P}{d}$
H _a	1.47254	0.55734	0.32681	44.587	26.145
H _b	1.48687	0.57424	0.33711	45.939	26.969
H _v	1.49589	0.58488	0.34389	46.790	27.511

The refraction of this compound does not differ largely from the calculated value with two ethylene linkings, although it is somewhat lower.

$$\begin{array}{r}
 \text{C}_6 = 30.000 \\
 \text{H}_8 = 10.400 \\
 \text{Two ethylene linkings} = 4.600 \\
 \hline
 45.000 \\
 \text{Found} = 44.587 \\
 \hline
 \text{Difference} = 0.413
 \end{array}$$

It may be interesting here to give a table comparing the refraction constants of hexamethylene, tetrahydrobenzene, and dihydrobenzene, as determined by Dr. Perkin from the author's specimens with those of the same hydrocarbons determined by Brühl from specimens obtained synthetically by Baeyer.

	Sp. gr. d.		Index of refraction, μ .		Sp. refraction. $\frac{\mu_a^2 - 1}{\mu_a^2 + 2} \cdot \frac{1}{d}$		Mol. refraction. $\frac{\mu_a^2 - 1}{\mu_a^2 + 2} \cdot \frac{P}{d}$	
	Brühl.	Perkin.	Brühl.	Perkin.	Brühl.	Perkin.	Brühl.	Perkin.
Benzene, C_6H_6	0.8799 (20°/4°)		1.4967		0.3324		25.93	
Dihydrobenzene, C_6H_8	0.8478 (20°/4°)	0.84785 (15.5°/4°)	1.4699	1.47254	0.3291	0.32681	26.33	26.145
Tetrahydrobenzene, C_6H_{10} ...	0.8102 (20°/4°)	0.79934 (14.4°/4°)	1.4435	1.43998	0.3277	0.32970	26.87	27.035
Hexamethylene, C_6H_{12}	0.790 (20°/4°)	0.7742 (17.4°/4°)	1.426	1.42211	0.3255	0.32831	27.56	27.578

The specific gravity of the hexamethylene prepared by Baeyer is considerably higher than that of the specimen obtained during the present research, but the agreement between the refraction determinations is very good in the case of all three hydrocarbons. The constants for benzene are appended for the sake of comparison.

Dispersion of the hydrocarbons.

	Mol. refraction for $H_\gamma - H_\alpha$.	Dispersion.
Hexamethylene	= 28.292 - 27.578	= 0.714
Tetrahydrobenzene	= 27.837 - 27.035	= 0.802
Dihydrobenzene	= 27.511 - 26.145	= 1.366

Monobromhexamethylene, $C_6H_{11}Br$.—Many attempts were made in the first instance to prepare this substance by the direct bromination of hexamethylene both with and without the aid of a bromine carrier, but the results proved unsatisfactory, as the products on distillation always decomposed at a comparatively low temperature, so that purification by fractionation was impossible. The behaviour of the hydrocarbon in this respect is very similar to that of normal hexane and isoheptane, as Schorlemmer was only able to obtain an exceedingly poor yield of the secondary bromide from these hydrocarbons by direct bromination, much loss being caused by decomposition (*Annalen*, 1877, 188, 250). Ultimately, monobromhexamethylene was obtained in a pure state by the addition of hydrogen bromide to tetrahydrobenzene. In the first experiments, the hydrocarbon was dissolved in an acetic acid solution of hydrogen bromide, and after standing all night and then warming for a short time on the water bath at 60°, it was mixed with water and the heavy oil extracted with ether, washed with sodium carbonate solution, and dried over calcium chloride. On distilling the product, it was found that, although most of the oil dis-

tilled fairly constantly at 163—164°, a small quantity of a substance of higher boiling point was present which smelt like pear-drops and was evidently the corresponding acetate. Different specimens of the monobromide prepared in this way, when analysed, gave the bromine always 3 to 4 per cent. too low. Tetrahydrobenzene was then placed in a reflux apparatus with 4 or 5 times its volume of aqueous hydrobromic acid saturated at 0°; no action took place in the cold, but on warming on a water bath, the colour of the hydrocarbon changed to deep violet and after about 4 hours the action was complete. On pouring the product into water, the heavy monobromide sank to the bottom as a brown oil which was extracted with ether, washed, dried, and distilled; the greater part of the liquid boiled with slight decomposition at 162—163°, and a bromine determination gave the following result.

0.1665 gave 0.1917 AgBr. Br = 49.00.

$C_6H_{11}Br$ requires Br = 49.08 per cent.

Monobromhexamethylene is a heavy, colourless oil which readily turns brown on exposure to air; the odour is penetrating, and its vapour has a slightly irritating effect on the eyes. It is very readily acted on by alcoholic potash, tetrahydrobenzene being obtained. The specimen sent to Dr. W. H. Perkin, sen., was too dark in colour for the determination of the magnetic rotation, and when distilled it gave off a little hydrobromic acid and soon became coloured again.

Specific gravity. $d\ 4^\circ/4^\circ = 1.3406$; $d\ 10^\circ/10^\circ = 1.33415$.

$d\ 15^\circ/15^\circ = 1.3290$; $d\ 20^\circ/20^\circ = 1.3240$; $d\ 25^\circ/25^\circ = 1.3188$.

The refraction of the sample was determined for three lines only, as it was too dark to allow of others being measured.

Refraction, $t = 14.6^\circ$; $d\ 14.6^\circ/4^\circ = 1.3264$.

	Index of re- fraction.	Sp. refraction.		Mol. refraction.	
	μ .	$\frac{\mu-1}{d}$.	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{1}{d}$.	$\frac{\mu-1}{d} \cdot P$.	$\frac{\mu^2-1}{\mu^2+2} \cdot \frac{P}{d}$.
Li	1.49177	0.37077	0.21864	60.435	35.638
H _a	1.49255	0.37135	0.21894	60.530	35.686
Na	1.49564	0.37368	0.22010	60.910	35.876

This compound, like the corresponding chlorine derivative, gives higher numbers than the calculated, thus,

Molecular refraction for H_a found = 60.530

Calculated = 59.690

 Difference = 0.840

Dibromhexamethylene, $C_6H_{10}Br_2$, was obtained by the action of bromine on tetrahydrobenzene in ethereal solution. The flask was cooled with water and the bromine added drop by drop, when rapid decolorisation took place, heat being evolved; as soon as a drop of bromine produced a permanent coloration in the solution, it was washed with dilute caustic soda solution and dried, the ether was distilled off, and the dibromide distilled under reduced pressure. It boiled at $145-146^\circ$ under a pressure of 100 mm.

0.3228 gave 0.5028 AgBr. Br = 66.22.

 $C_6H_{10}Br_2$ requires Br = 66.12 per cent.

Dibromhexamethylene, when pure, is a heavy, colourless oil, but it rapidly decomposes on exposure to air, becoming very dark.* It is readily acted on by alcoholic potash, yielding dihydrobenzene.

Tetrabromhexamethylene, $C_6H_8Br_4$, was obtained in a crystalline form by the action of bromine on dihydrobenzene in ethereal solution; on adding a drop of bromine to the solution, it was instantly decolorised, and white crystals separated. These were washed with ether and dried, when they melted at 184° (Baeyer $184-185^\circ$).

0.1317 gave 0.2572 AgBr. Br = 79.83.

 $C_6H_8Br_4$ requires Br = 80.00 per cent.

Chlorhydroxyhexamethylene, $C_6H_{10}Cl.OH$.—A solution of hypochlorous acid, obtained by passing chlorine into a mixture of ice and water containing freshly precipitated mercuric oxide in suspension, was shaken with tetrahydrobenzene. Heat was evolved, and the oil which formed and settled at the bottom of the flask was distilled with steam, separated from the aqueous layer, and dehydrated with calcium chloride.

0.1417 gave 0.1542 Cl. Cl = 26.86.

 $C_6H_{10}Cl.OH$ requires Cl = 26.34 per cent.

The liquid was pale yellow, had a characteristic odour, and decomposed on distillation. On treating it with zinc dust and acetic acid, much heat was evolved, but the final product still contained chlorine, and the quantity of substance was insufficient to repeat the reduction so as to obtain the corresponding alcohol.

A fractional distillation of the portion of Galician petroleum boiling below 70° was undertaken, in order, if possible, to isolate pure penta-

methylene from the oil. It appears, however, not to be present in quantity sufficient to enable this to be done without a very large expenditure of time, and if any further attempts in this direction are made, the source used must be Caucasian naphtha.

I wish to express my sincere thanks to Dr. W. H. Perkin, sen., for his courtesy in permitting me to include in this paper his determinations of the specific gravity, magnetic rotation, and optical constants of the substances obtained; to Professor S. Young for the use of the fractionating column, without which the isolation of pure hexamethylene would have been impossible, and particularly to Professor W. H. Perkin for his kind advice and help during the course of this research, which has been carried out under his guidance at Owens College. I am also greatly indebted to him for the analyses of hexamethylene, tetrahydrobenzene, and dihydrobenzene which he carried out after I left Manchester.

NOTE.—Since the above was written, a paper by Markownikoff has appeared (*Annalen*, 1898, 302, 1) giving a detailed account of the preparation of derivatives of hexanaphthene from Caucasian naphtha, and his results, taken in conjunction with those in the present paper, conclusively show that the hydrocarbon, C_6H_{12} , boiling about 80° from Caucasian, from Galician, and from American petroleum is identical with synthetical hexamethylene.

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