LXV.—*Action of Heat on the Mixed Vapours of Benzene and Toluene.
Two New Methylene-diphenylenes.*

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IN a former communication (this Journal, 1876, i, 13) it has been shown that the hydrocarbon, paratolylphenyl, may be obtained by the action of sodium on a mixture of bromobenzene and parabromotoluene. The yield, however, was so small that the amount of pure compound obtained rendered it impossible to give more than a general description of the hydrocarbon and a few of its derivatives. With the view, therefore, of making a more complete study of this hydrocarbon, as well as of the homologous hydrocarbon ditolyl, both bodies have been prepared in much larger quantity and at much less cost, by the action of heat on a mixture of benzene and toluene, a reaction analogous to that by which diphenyl is obtained from benzene. The preparation of these hydrocarbons by this method has also induced me to make a more or less complete investigation of this reaction, which has not only given a very fair yield of both tolylphenyl and ditolyl, but has also led to the discovery of two new hydrocarbons, viz., γ - and δ -methylene-diphenylene.

The action of heat on various aromatic hydrocarbons has already formed the subject of several investigations by different chemists, especially Barbier, but it will be sufficient to refer to previous researches on the action of heat on benzene alone, toluene alone, and on a mixture of these two hydrocarbons.

Benzene.—(1.) In *Watts' Dict. of Chem.*, i, 542, it is stated that when the vapour of benzene is passed through a red-hot tube carbon is separated and a gaseous hydrocarbon formed. (2.) Berthelot (*Bull. Soc. Chim.* [2], 6, 272, 279) has shown that under these circumstances

benzene gives hydrogen, a little acetylene, diphenyl, chrysene, benzerhythrene, and a black pitchy substance, which he termed bitumene. (3.) Schultz (*Annalen*, 174, 201; this Journal, 1875, 151) states that when benzene is passed through a red-hot tube, the same bodies are obtained as mentioned by Berthelot, but finds that Berthelot's chrysene is a mixture of paradiphenylbenzene, isodiphenylbenzene, and a yellow oil, and that his benzerhythrene consists chiefly of diphenylbenzene, together with two hydrocarbons melting at 266° and 196° respectively. Schultz was unable to detect the presence of coal-tar chrysene as stated by Berthelot. (4.) Berthelot (*Bull. Soc. Chim.* [2], 22, 437; this Journal, 1875, 760) in his reply to Schultz, maintains that the chrysene which he obtained by the action of heat on benzene is an individual body identical with coal-tar chrysene, and that it is distinct from Schultz's diphenylbenzene, for it combines with picric acid, whereas the latter does not.

Toluene.—(1.) According to Berthelot (*Bull. Soc. Chim.* 1867, 1, 218), toluene, when passed through a porcelain tube heated to bright redness, gives uncondensable gases, benzene, naphthalene, dibenzyl, a hydrocarbon apparently isomeric therewith, anthracene, chrysene, and benzerhythrene. (2.) Graebe (*Ber.*, 1874, 48; this Journal, 1874, 471) finds that under these circumstances toluene gives benzene, diphenyl, anthracene, and phenanthrene, but no naphthalene or benzyltoluene. The chief product was a liquid boiling at 270 – 280° , and consisting probably of two ditolyls. (3.) Lorenz states (*Ber.*, 1874, 1097) that toluene by the action of heat in presence of lead oxide is converted into stilbene, diphenyl, phenanthrene, anthracene, and liquid hydrocarbons, probably ditolyl. Benzyltoluene and naphthalene could not be found.

Benzene and Toluene.—Barbier (*Ann. Chim. Phys.* [5], 7, 472; this Journal, 1877, i, 74) endeavoured to obtain fluorene (diphenylene-methane or methylene-diphenylene) by passing a mixture of benzene and toluene through a red-hot tube, but without any decisive result; a minute quantity of a body boiling near 301° and possessing fluorescent properties was formed, but the greater portion became converted into diphenyl and anthracene.

Judging from the above researches, the following bodies might be expected to be formed when a mixture of benzene and toluene is passed through a red-hot tube:—

		M. p.	B. p.
Hydrogen	H	—	—
Acetylene	C ₂ H ₂	—	—
Benzene	C ₆ H ₆	—	80
Naphthalene	C ₁₀ H ₈	79	218
Diphenyl	C ₁₂ H ₁₀	70	254
Two ditolyls.	C ₁₄ H ₁₄	?	?
Stilbene.	C ₁₄ H ₁₂	(115—118)	About 292
Phenanthrene.	C ₁₄ H ₁₀	100	340
Anthracene.	C ₁₄ H ₁₀	213	360
Chrysene.	C ₁₈ H ₁₂	<div style="display: inline-block; vertical-align: middle;"> <div style="display: flex; align-items: center;"> <div style="font-size: 3em; margin-right: 5px;">{</div> <div style="text-align: center;"> 200 230—235 250 275 </div> </div> </div>	Above 360
Paradiphenylbenzene	C ₁₈ H ₁₄	205	Above 360
Isodiphenylbenzene	C ₁₈ H ₁₄	85	About 360
Hydrocarbon	?	196	?
Hydrocarbon	?	266	?
Bitumene	?	—	—

In the experiments to which the present communication refers, the benzene and toluene were mixed in molecular proportion so as to give the best yield of tolylphenyl, thus:—

and the mixture dropped into a red-hot iron tube from a tap-funnel attached to the turned-up end of the tube. The latter, 3 feet long, and $1\frac{1}{2}$ inch internal diameter, was filled with fragments of pumice-stone and laid in an ordinary combustion furnace, one end of which was slightly tilted up, so that the end of the tube bearing the tap-funnel was higher than the other; to this was fixed a glass tube leading to a well-cooled flask fitted with a condenser leading to a second flask. By this means the loss of any of the condensable products was avoided. The end of the iron tube remote from the tap-funnel was kept cool by tying round it a piece of cloth moistened by a continuous jet of cold water.

The furnace was maintained at a low red heat, and the mixed hydrocarbons passed through at the rate of about 80 grams per hour. When the whole had been passed through, the product obtained was distilled, and the portion boiling below 120° again passed through, the process being repeated ten times.

The benzene employed boiled at 80—85°, and the toluene at 105—115°, the total weight of the mixture taken for the experiment being 4,587 grams. The amount of action which occurred each time the mixture was passed through was as follows:—

	Per cent.	Mean. Per cent.
Unchanged hydrocarbons, b. p. 80—120°	84·4—91·9	89
Changed do. boiling above 120°..	3·9— 7·4	6
Loss and uncondensable gases	3·3— 8·2	5
		<hr/> 100

After passing through ten times (the changed portion being separated by distillation after each passage), the final result was as follows:—

	Grams.	Per cent.
Unchanged hydrocarbons, b. p. 80—120°	1769	39·1
Changed do. boiling above 120°....	1453	32·1
Loss and uncondensable gases	1365	28·8
	<hr/> 4587	<hr/> 100·0

Though what is termed above “unchanged hydrocarbon,” consisted of benzene and toluene, it must not be supposed that the whole of it had absolutely undergone no change at all, for a certain portion of the benzene had really been produced from the toluene by the action of heat, Berthelot and Graebe (*loc. cit.*) having shown that toluene, under these circumstances, is partially converted into benzene.

In order to ascertain the relative proportion of benzene and toluene in this “unchanged hydrocarbon” remaining at the end of the experiment, it was subjected to fractionation, with the following results:—

		After action. Per cent.	Before action. Per cent.
Benzene, b. p. 80—87°	1088	24	18
Toluene, b. p. 105—115°	681	15	21
	<hr/> 1769	<hr/> 39	<hr/> 39

so that after the action of heat the hydrocarbons were present in the proportion of 24 to 15, whilst before the action the proportion was 18 to 21. This is due partly to the toluene being more easily acted on than benzene, and partly to the fact that toluene gives benzene as well as other products when exposed to a red heat.

The “loss” is chiefly due to the formation of uncondensable gases, hydrogen, acetylene, &c.

The total changed hydrocarbons, amounting to 1,453 grams, were then submitted to a systematic fractionation, as follows. For the measurement of temperatures above 300° the method described by Mr. Williams and myself (this Journal, 1878, **33**, 281) was employed, which consisted in placing capillary tubes containing metallic

salts of known melting point in the vapour of the boiling hydrocarbon.

Fraction.	Weight of fraction.	Remarks.
120—190.....	29	Liquid.
190—245.....	1	Solid.
{ 245—258.....	499	Solid. }
{ 245—258.....	5	Liquid. }
258—263.....	25	Liquid, with very little solid.
263—269.....	231	Liquid.
269—272.....	55	Liquid.
272—280.....	104	Liquid, nearly all at 272—276.
280—293.....	31	Liquid, with a little solid.
293—305.....	36	Nearly all solid.
305—316.....	10·5	All solid.
316—339.....	24·5	
339—359.....	22·5	
359—383.....	15·5	
383—404.....	12·0	
404—427.....	65·0	
427—439.....	19·0	
Above 439	71·0	
Loss and small portion below 120°.....	197·0	
	<hr/> 1453·0	

From the above it is seen that the products formed in largest quantity are those boiling at 245—258° (diphenyl, b. p. 254°), at 263—269° (paratolylphenyl, b. p. 263—267°), at 272—280° (ditolyl, b. p. 270—280°), at 404—427° (paradiphenyl-benzene, b. p. 404—427°), and bituminous bodies boiling above 439°

Each of the above fractions was then examined separately, and the constituent hydrocarbons isolated as far as possible in the pure state by the combined assistance of fractionation, crystallisation of the solid from the liquid portions in a freezing mixture of salt and ice, and recrystallisation from alcohol, benzene, &c. The more important fractions gave the following results:—

Fraction 120—190 consisted of toluene.

Fraction 190—245 gave naphthalene.

Fraction 245—258 gave diphenyl.

Fraction 263—269 gave paratolylphenyl.

Fraction 272—280 gave orthoparaditolyl.

Fraction 293—305 gave the new hydrocarbon γ -methylene diphenylene, a little phenanthrene, and an oil.

Fraction 305—316 gave the new hydrocarbon δ -methylene diphenylene, phenanthrene, and an oil.

Fraction 316—339 gave δ -methylene diphenylene, a very little diphenylbenzene, phenanthrene, and an oil.

Fraction 339—359 consisted chiefly of an oil with a little diphenylbenzene.

Fraction 359—383 gave anthracene, diphenylbenzene, and an oil.

Fraction 383—404 gave anthracene, diphenylbenzene, and an oil.

Fraction 404—427 consisted of diphenylbenzene, an oil, a hydrocarbon having the composition $C_{32}H_{28}$, and a semi-solid portion which on oxidation with chromic and glacial acetic acids gave a small quantity of paradiphenyl-carboxylic acid, and a quinone which blackens at 260° , but does not completely melt at 310° .

Fraction 427—439 on exhaustion with boiling alcohol gave an insoluble black bitumen, becoming solid and brittle on cooling, a small quantity of nearly insoluble diphenylbenzene, and a difficultly soluble reddish oil, which formed the chief portion.

Fractions above 439, and which remained behind in the still, consisted of a solid black bitumen.

The several hydrocarbons isolated from the above fractions were identified as follows:—

Naphthalene, $C_{10}H_8$, obtained from the solid fraction 190—245, was recrystallised from alcohol, when the m. p. = $72-76^\circ$, and b. p. = 213° uncorr., 217° cor.; after sublimation the m. p. = 79.5° . It sublimed in beautiful plates, and had the characteristic smell of naphthalene, which melts at 79.5° , and boils at $217-218^\circ$ (Vohl, *J. pr. Chem.*, **102**, 29).

Diphenyl, $C_{12}H_{10}$, after recrystallisation twice from alcohol melted at 70° , and boiled at $245-258^\circ$: pure diphenyl melts at 70° , and boils at 254° (Schultz, *Annalen*, **174**, 205; according to Christomanos, *Gazzetta*, 1875, 402, it melts at 69.6° and boils at 238.5°). The dibromide was prepared, and on analysis gave the following numbers:—

- (1.) 0.1985 gram of substance gave 0.2305 gram AgBr, and 0.0048 gram Ag = 51.2 per cent. Br.
- (2.) 0.2346 gram of substance gave 0.2700 gram AgBr, and 0.0077 gram Ag = 51.4 per cent. Br.

	Calculated.	Found.		Mean.
		(1.)	(2.)	
$C_{12}H_8Br_2$	51.28	51.20	51.40	51.30

The melting point of this dibromide = 162° (164° , "Schorlemmer's Chemistry of the Carbon Compounds").

(1.4) *Paratolylphenyl*, $Me.C_6H_4.Ph$.—This hydrocarbon, after distil-

lation over sodium, formed a colourless refractive liquid boiling at 263—268° (paratolylphenyl from the action of sodium on mixed bromobenzene and parabromtoluene boils at 263—267°, Carnelley, this Journal, 1876, **29**, 16), and on analysis gave the following:—

Weight taken.....	0.1764	
H ₂ O obtained	0.1129 = 7.11 per cent. H.	
CO ₂ „	0.5955 = 92.07 per cent. C.	
	Calculated.	Found.
C ₁₃	92.86	92.07
H ₁₂	7.14	7.11

Two vapour-density determinations by Victor Meyer's method gave—

	(1.)	(2.)
Weight taken.....	0.030 gram.	0.0415 gram.
Volume of gas	4.4 c.c.	5.6 c.c.
t	14° C.	14° C.
Barometer	757 mm. at 13° C.	757 mm. at 12.2° C.

	Calculated for C ₁₃ H ₁₂ .	Found.		
		(1.)	(2.)	Mean.
Vapour-density (H = 1)....	84	82	89	85.5

The hydrocarbon on oxidation with chromic and glacial acetic acids gave first paradiphenyl-benzoic acid, C₆H₄.Ph.COOH, melting at 216—220° (216—217°, Schultz, *Annalen*, **174**, 213; 218—219°, Doebner, *ibid.*, **172**, 112), and then terephthalic acid.

The *monobromide*, C₁₃H₁₁Br, obtained by the action of the calculated quantity of bromine on the hydrocarbon, crystallises from alcohol in pearly plates (m. p. 127—129°, resolidifies at 123°) exactly resembling those (m. p. 130—131°, resolidifies at 121°) obtained from the tolylphenyl resulting from the action of sodium on the mixed bromides of benzene and toluene.

The analysis of the hydrocarbon b. p. 263—268°, its vapour-density, the products of its oxidation, and the formation of the monobromide, together with its general properties, prove it to be (1.4) paratolylphenyl, identical with that obtained from the mixed bromides by the action of sodium.

(1.2, 1.4) *Orthoparaditolyl*, Me.C₆H₄.C₆H₄.Me, boils at 272—280°, and on oxidation with chromic and glacial acetic acids gives first (1.2 1.4) orthoparatolylphenyl carbonic acid, Me.C₆H₄.C₆H₄.COOH (m. p. 179—180°), and finally terephthalic acid. On analysis the following numbers were obtained:—

	(1.)	(2.)
Weight taken....	0.0202 gram.	0.1865 gram.
CO ₂ obtained	0.6780 „	An accident to the potash bulbs prevented the determination of the C in this case.
H ₂ O obtained....	0.1370 „	0.1300 gram.

	Calculated.	Found.		Mean.
		(1.)	(2.)	
C ₁₄	92.31	91.54	—	91.54
H ₁₄	7.69	7.54	7.74	7.62

Two vapour-density determinations gave as follows:—

	(1.)	(2.)
Weight taken ..	0.0385 gram.	0.0400 gram.
Volume of gas..	4.81 c.c.	5.3 c.c.
<i>t</i>	11° C.	13° C.
Barometer.....	755.6 mm. at 10°	757 mm. at 11.7°.

	Calculated for C ₁₄ H ₁₄ .	Found.		Mean.
		(1.)	(2.)	
Vapour-density (H = 1)..	91	95	90	92.5

This hydrocarbon is therefore identical with the orthoparatolyl-phenyl (b. p. = 270—280°) which is obtained by the action of sodium on bromtoluene, and on oxidation gives first orthoparatolylphenyl-carboxylic acid (m. p. 176°), and finally terephthalic acid (Carnelley, this Journal, 1877, ii, 655). No solid (dipara-) ditolyl was produced by the action of heat on the mixed vapours of benzene and toluene. Only a very small quantity is obtained by the action of sodium on bromtoluene (Zincke, *Ber.*, 4, 396).

γ-Methylene-diphenylene, $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{CH}_2$.—This new hydrocarbon was

obtained from the fraction boiling at 293—305° by pressing out the oily portion between filter-paper, and crystallising the solid portion repeatedly from alcohol. It crystallises in small pearly plates, which melt at 118°, resolidify at 116°, and boil at 295° (uncorr). It is moderately soluble in hot alcohol and hot glacial acetic acid, but only sparingly soluble in cold alcohol, or in cold glacial acetic acid; it is easily soluble in ether. Its alcoholic and acetic acid solutions possess a faint blue fluorescence. In one case it was obtained crystallised in small needle-shaped prisms. It gave the following on analysis:—

	(1.)	(2.)
Weight taken....	0.2450 gram.	0.1932 gram.
CO ₂ obtained....	0.8433 „	An accident to the potash bulbs prevented the determination of the C in this case.
H ₂ O obtained....	0.1346 „	0.1100 gram.

	Calculated.	Found.		Mean.
		(1.)	(2.)	
C ₁₃	93.99	93.87	—	93.87
H ₁₀	6.01	6.10	6.33	6.21

The vapour-density was determined as follows:—

	(1.)	(2.)
Weight taken ..	0.0355 gram.	0.0355 gram.
Volume of gas ..	5.1 c.c.	5.0 c.c.
<i>t</i>	14° C.	14° C.
Barometer	755.6 mm. at 11.7°	758.9 mm. at 12.2°.

	Calculated for C ₁₃ H ₁₀ .	Found.		Mean.
		(1.)	(2.)	
Vapour-density (H = 1)..	83	83.8	85.0	84.4

The *picrate*, C₁₃H₁₀.C₆H₃(NO₂)₃O, was prepared by dissolving the calculated quantities of the two compounds separately in ether, mixing, and leaving the mixture to evaporate spontaneously. It crystallises in splendid blood-red needles, melting at 79—81°, to a dark blood-red liquid.

γ-Methylene-diphenylene quinone, C₁₃H₈O₂, was obtained by oxidising the hydrocarbon with chromic and glacial acetic acids. The white curdy precipitate produced on dilution with water was filtered off and treated with warm ammonia to separate any acid, and filtered. The ammoniacal filtrate did not give the least precipitate on addition of hydrochloric acid, showing the absence of any insoluble acid as the product of oxidation. The yellow body insoluble in ammonia was crystallised from alcohol in the form of long golden-yellow needles (m. p. 280—281°, corr.), which were scarcely soluble in cold, and only sparingly soluble in hot alcohol. It sublimes when heated on a watch-glass without previous melting. An analysis gave the following:—

Weight taken	0.0840 gram.	
CO ₂ obtained.....	0.2435 „	= 79.06 per cent. C.
H ₂ O „	0.0340 „	= 4.49 per cent. H.

	Calculated.	Found.
C ₁₃	79.59	79.06
H ₈	4.08	4.49
O ₂	16.33	16.45
	<hr/> 100.00	<hr/> 100.00

The hydrocarbon when treated with a large excess of chromic acid was oxidised entirely to carbonic anhydride and water, but in no case was any diphenylene ketone obtained.

Dibromo-γ-methylene-diphenylene, C₁₃H₈Br₂, was obtained by adding gradually an excess of bromine to an ethereal solution of the hydrocarbon. The liquid became warm, but no precipitate separated (in this respect differing from stilbene). After slight evaporation and standing it became a mass of white crystals; these (A) were filtered off from the solution (B), washed with ether and dried; under the microscope they appeared to consist of octohedrons mixed with a few needles. They were boiled with ether and then consisted entirely of octohedrons (m. p. 157°, s. p. 149°); the ethereal solution on evaporation gave crystals consisting at first entirely of needles, but these on standing and drying changed to octohedrons (m. p. 162°, s. p. 149°). The original ethereal mother-liquor (B) on evaporation gave crystals consisting entirely of octohedrons (m. p. 162°, s. p. 149°). Dibrom-γ-methylene-diphenylene crystallises therefore either in needles or octohedrons, the latter being the more stable form, the acicular always changing into the octohedral form in course of time. It melts at 162° and resolidifies at 149°; it is but very sparingly soluble in alcohol or ether whether hot or cold. On analysis it gave:—

0.2255 gram of substance, gave 0.202 gram AgBr, and 0.0354 gram Ag = 49.74 per cent. Br.

	Calculated for C ₁₃ H ₈ Br ₂ .	Found.
Br ₂	49.38	49.74

δ-Methylene-diphenylene, $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{CH}_2$. This new hydrocarbon occurred

in the fractions boiling at 305—339°. It formed the portion of those fractions least soluble in alcohol, and was therefore obtained pure by repeated crystallisation from that solvent. It crystallises in small pearly plates, which are only sparingly soluble in cold, but more easily in hot alcohol. It melts at 205° uncorr., 208° corr., and boils at about 320°. An analysis gave the following results:—

Weight taken	0.135 gram.		
CO ₂ obtained	0.464	„	= 93.74 per cent. C.
H ₂ O „	0.074	„	= 6.09 per cent. H.

	Calculated.	Found.
C ₁₃	93·99	93·74
H ₁₀	6·01	6·09

Two vapour-density determinations gave as follows:—

	(1.)	(2.)
Weight taken....	0·0185 gram.	0·0250 gram.
Volume of gas....	2·65 c.c.	3·7 c.c.
<i>t</i>	20° C.	20° C.
Barometer	746·8 mm. at 19°	746·8 mm. at 19°.

	Calculated. for C ₁₃ H ₁₀ .	Found.		Mean.
Vapour-density (H = 1).	83	(1.) 87·7	(2.) 84·8	86·2

This hydrocarbon is probably identical with Linnemann's (*Annalen*, **133**, 1) benzhydrolene (C₁₃H₁₀), which he obtained by the distillation of the succinate or benzoate of benzhydrol. Benzhydrol has the constitution C₆H₅.CHOH.C₆H₅, being obtained from benzophenone by the action of nascent hydrogen. Benzhydrolene melted at 209—210°, was nearly insoluble in alcohol even on boiling, from which it crystallised in small needles, sparingly soluble in ether, but easily in hot benzene. It did not appear to combine with picric acid.

δ-Methylene-diphenylene quinone, C₁₃H₈O₂, was obtained by oxidising the hydrocarbon with chromic and glacial acetic acids. On addition of water the quinone was thrown down as a white precipitate, which was perfectly insoluble in ammonia. It is a pure white powder, which sublimes in needles and melts at 276—277° uncorr., 288° corr. (another sample melted at 277—278° uncorr.), to a yellowish-green fluorescent liquid, resembling uranium glass, except that the green is rather more decided. It is insoluble in water, but moderately soluble in glacial acetic acid. An analysis gave the following numbers:—

0·0672 gram substance gave 0·1970 gram CO₂, and 0·0272 gram H₂O = 79·95 per cent. C and 4·49 per cent. H.

	Calculated.	Found.
C ₁₃	79·59	79·95
H ₈	4·08	4·49
O ₂	16·33	15·56
	<hr/> 100·00	<hr/> 100·00

The formation of a diphenylene ketone was not observed.

Phenanthrene, C₁₄H₁₀, was found in those solid portions of the fractions 293—339°, which were most easily soluble in alcohol. It was recognised as follows:—It fused at 101° (100°, Graebe, *Ber.*, **5**, 861;

99–100°, Fittig and Ostmeyer, *ibid.*, 5, 933) and resolidified at 92°. It crystallised in small pearly white plates, which were easily soluble in hot and moderately soluble in cold alcohol. On oxidation with chromic and glacial acetic acids it gave phenanthraquinone, $C_{14}H_8O_2$, which crystallised from alcohol in orange-yellow needles, melting in one case at 203–205° and in another at 201° (205°, “Schorlemmer’s Chemistry of the Carbon Compounds;” 202°, Limpricht, *Ber.*, 6, 533; 198°, Graebe, *Ber.*, 5, 861; 198, Fittig and Ostmeyer, *Ber.*, 5, 933). The quinone combined with acid sodium sulphite, from which it was precipitated by hydrochloric acid; the solution in acid sodium sulphite, on standing in contact with sulphurous acid, was converted into the dark-brown quinhydrone.

Anthracene, $C_{14}H_{10}$, occurred in the fractions 359–404°, and was separated from the admixed diphenylbenzene by boiling repeatedly with alcohol, in which the latter is insoluble. On oxidation with chromic and glacial acetic acids it gave anthraquinone, $C_{14}H_8O_2$, crystallising from hot alcohol in pale-yellow needles, which melt at 273–274° (273°, *Watts’ Dict. Chem.*, 6, 180), and are only very sparingly soluble in hot alcohol.

(1.4) *Paradiphenylbenzene*, $C_6H_4Ph_2$, was found in the fractions 316–439°, but chiefly in that boiling at 404–439°. It is isolated by exhausting the several fractions with boiling alcohol, when it remains behind insoluble. It was further purified by crystallising several times from benzene. It crystallised in needles and sublimed in iridescent laminae, which melted at 205–207° uncorr., 212–213° corr. (another sample gave 206–208° uncorr.), and boiled* at 404–427° (m. p. 206°, Barth and Schreder, this Journal, 1879, xxxvi, 66; m. p. 201° uncorr., 205° corr., boils in the vapour of boiling sulphur at 440°, Riese, *Zeits. f. Chem.* [2], 6, 192, 735; m. p. 205°, b. p. above 360°. Schultz, *Ber.*, 6, 415; b. p. about 400°, “Schorlemmer’s Chemistry of Carbon Compounds”). It was insoluble in water and almost perfectly insoluble in alcohol; very sparingly soluble even in boiling glacial acetic acid, and separated therefrom in small iridescent laminae. It was moderately soluble in benzene, the solution possessing a blue fluorescence, and crystallised therefrom in pearly plates, which adhered together and exhibited a greenish reflection, but became white on drying at 120°. It was easily soluble in carbon bisulphide, and in this solvent was not perceptibly attacked by bromine. An analysis of the hydrocarbon dried at 120° gave as follows:—

Weight taken	0.237	gram.	
CO ₂ obtained	0.811	„	= 93.33 per cent. C.
H ₂ O „	0.1335	„	= 6.26 per cent. H.

* Between the melting points of $Tl_{12}V_{10}O_{31}$ (m. p. 404°) and $TlCl$ (m. p. 427°)
See this Journal, 1878, 33, 277.

	Calculated.	Found.
C ₁₈	93·91	93·33
H ₁₄	6·09	6·26

A vapour-density determination gave:—

Weight taken	0·034 gram.
Volume of gas.....	3·7 c.c.
<i>t</i>	16° C.
Barometer.....	757 mm. at 16·9°.

	Calculated for C ₁₈ H ₁₄ .	Found.
Vapour-density (H = 1).....	115	111·6*

This hydrocarbon did not combine with picric acid, and dissolved in strong sulphuric acid on warming, first with a dirty green colour, changing to a dirty blue, and finally on boiling to purple. On oxidation with a deficit of chromic and glacial acetic acids it gave a white acid which fused at 216° uncorr., and formed a white silver salt, an analysis of which gave:—

0·080 gram of substance gave 0·0283 gram Ag = 35·37 per cent. Ag.

	Calculated for C ₁₃ H ₉ O ₂ Ag.	Found.
Ag	35·41	35·37

The acid was therefore paradiphenylcarboxylic acid, which, according to Doebner (*Annalen*, **172**, 112), melts at 218—219°, and according to Schultz (*Annalen*, **174**, 213) at 216—217°. On oxidation with excess of chromic acid the hydrocarbon gave terephthalic acid. The above facts prove that this hydrocarbon is paradiphenylbenzene, and identical with that obtained by Riese (*Zeits. f. Chem.* [2], **6**, 192) from the action of sodium on an ethereal solution of solid dibromobenzene and monobromobenzene, and also with that obtained by Schultz (*Ber.*, **7**, 1365), by passing benzene through a red-hot tube.

I was unable to detect the presence of the isodiphenylbenzene (m. p. 85°) said by Schultz to be produced at the same time as the above isomer (m. p. 205—207°), though it is very probable that its isolation in the present case was prevented by its mixture with other hydrocarbons of nearly equal solubility.

The Hydrocarbon, C₃₂H₂₈, which apparently occurred in fraction 404—427°, could not be isolated in the pure state. It was more soluble in alcohol than paradiphenylbenzene, and on oxidation with chromic and glacial acetic acids it gave a quinone, which crystallised

* Barth and Schreder also found 111·5 (H = 1) by Meyer's method; this *Journal*, 1879; xxxvi, 66.

from alcohol in orange-red needles (m. p. 180°). This quinone is insoluble in water, but moderately soluble in alcohol, forming a dark red-brown liquid. It dissolves in strong sulphuric acid with a brown colour, which did not change on boiling. An analysis gave:—

Weight taken.....	0.071 gram.		
CO ₂ obtained.....	0.226	,,	= 86.81 per cent. C.
H ₂ O obtained.....	0.038	,,	= 5.94 per cent. H.
	Calculated.		Found.
C ₃₂	86.88		86.81
H ₂₆	5.88		5.94
O ₂	7.24		7.25
	<hr/> 100.00		<hr/> 100.00

The bitumene from fraction 427—439° consisted of a solid black mass with a conchoidal fracture. It was insoluble in alcohol and glacial acetic acid, but easily soluble in carbon bisulphide and in benzene, and moderately soluble in ether. No definite compound could be isolated from it either by the use of solvents or by combination with picric acid. On oxidation with chromic and glacial acetic acids, to which a little benzene had been added to increase the solvent power, it was burnt almost completely to carbonic anhydride and water, the liquid on dilution with water giving only a very small precipitate. This precipitate, by treatment with ammonia, was separated into a small quantity of an acid and a quinone. The acid after crystallisation from alcohol melted about 280° , but the quantity was so small that it could not be obtained in the pure state. The yellow quinone, which melted only partially at 340° , dissolved in alcohol, forming a yellow liquid, with a beautiful green fluorescence. The quantity obtained, however, was too small to work with.

The bitumene boiling above 439° was a solid black mass with conchoidal fracture. It was scarcely at all soluble in benzene, but much more easily in carbon bisulphide; very sparingly soluble in glacial acetic acid with a yellowish-green fluorescence. It first showed signs of melting at 190° , began really to melt at about 220° , but was not completely fused even at 320° . It melted completely when heated in capillary tubes directly over the lamp. It burnt with a smoky flame, but was at once extinguished on removing from the lamp flame. On oxidation with chromic and glacial acetic acids (with addition of a little benzene) the portion attacked was burnt completely to carbonic anhydride and water.

The oils from the several fractions 293—439° were cooled in a freezing mixture to separate solid hydrocarbons and submitted to a

systematic fractionation, when they distilled almost completely in three different portions, viz. :—

(A) 293—316° (B) 359—383° (C) 404—427°.

These are still under investigation. The fraction (A) appears to be a nearly pure compound; after distillation over sodium it forms a pale yellow oil, which solidifies at -10° and melts at about $+13^{\circ}$.

From the above we may conclude, therefore, that when the mixed vapours of benzene and toluene are passed through a red-hot tube, the following hydrocarbons are formed:—Benzene, naphthalene, diphenyl, paratolylphenyl, orthoparaditolyl, γ -methylene-diphenylene, δ -methylene-diphenylene, phenanthrene, anthracene, paradiphenylbenzene, a hydrocarbon having the formula $C_{32}H_{28}$, a liquid hydrocarbon boiling at 293—316°, and melting at 13° , two other liquid hydrocarbons or mixtures of hydrocarbons boiling at 359—383° and 404—427° respectively, and a solid black bitumene.

The more important changes occurring during this reaction may be represented as follows :—

The γ - and δ -methylene-diphenylenes described above are isomeric, and not identical, with the methylene-diphenylene $\ddagger$ obtained by Graebe (*Annalen*, **174**, 194) by passing diphenylmethane through a red-hot tube; and by Fittig (*Ber.*, **6**, 187) by the reduction of diphenylene ketone with zinc-dust, or with hydriodic acid and amorphous phosphorus; or with the fluorene§ discovered by Berthelot (*Ann. Chim. Phys.* [4], **12**, 222) in the portion of coal-tar boiling at 300—

* Compare Barbier (*Ann. Chim. Phys.* [5], **7**, 472; this Journal, 1877, **1**, 74.

† Compare Barbier (*Compt. rend.*, **79**, 121; this Journal, 1874, 1091.

‡ This may be distinguished as α -methylene-diphenylene; Graebe called his compound *diphenylene-methane*.

§ This may be called β -methylene-diphenylene.

400°, and more fully examined by Barbier (*ibid.* [5], 7, 472). More recently the methylene-diphenylene from diphenylene ketone has been re-examined by Fittig and Schmitz (*Annalen*, 193, 134), who have obtained it in large quantity, and consider that they have shown it to be identical in all respects with coal-tar fluorene. The following table (p. 717) exhibits the more important properties of the several diphenylene methanes.

This table shows: (1) that the δ -compound is undoubtedly different from the other three. (2) That the γ -compound is also distinct from Graebe's and Berthelot's hydrocarbons, as is proved by its higher melting point, by the fact that it does not give the least trace of diphenylene ketone, but a quinone (melting at 280°) on oxidation, and by the melting point of its dibromide. It also differs from the α -compound in the very sparing solubility of its dibromo-derivative in ether, that of the former compound being very easily soluble in this solvent.

The only question that remains is the identity or non-identity of coal-tar fluorene and the methylene-diphenylene from diphenylene ketone. As already mentioned, Fittig and Schmitz believe that the two are identical, and that the difference in properties is due to the fluorene examined by Barbier being contaminated with small quantities of other hydrocarbons. Watts (*Dict. of Chem.*, 8, 797) suggests that Barbier's fluorene was a mixture of two isomeric methylene-diphenylenes, one of which was identical with Graebe's hydrocarbon. If this supposition be correct the admixed hydrocarbon cannot be either the γ - or the δ -compound described above, as Barbier's quinone melted at 181–182°, whilst the quinones from the latter hydrocarbons fused at 280° and 288° respectively. In view of the formation of the two new methylene-diphenylenes, both of which give a quinone on oxidation, it is thought to be more probable that coal-tar fluorene is isomeric and not identical with Graebe's methylene-diphenylene from diphenylene ketone, the chief points of distinction between the two being (1) the much stronger fluorescence of coal-tar fluorene; (2) the colour and melting points of the dinitro-compounds, the one being colourless and melting at 200°, and the other reddish-yellow and melting above 260°; (3) on oxidation the one gives a ketone only, and the other a ketone (m. p. 81–82°) and a quinone; (4) the dibromide of the one melts at 153° (Graebe), at 162–167° (Fittig and Schmitz), and is easily soluble in ether, whilst that of the other melts at 166–167°, and is nearly insoluble in ether.

The compound, $C_{13}H_8O_2$, obtained by Behr and v. Dorp (*Ber.*, 7, 398), together with diphenylene oxide, by the action of lead oxide on phenol is probably identical with Barbier's methylene-diphenylene quinone. It melts at 173–174°.

If then all these four methylene-diphenylenes are distinct, what is

	α -Methylene-diphenylene from diphenylmethane and diphenylene ketone (Graebe, Fittig, and Schmitz).	β -Methylene-diphenylene or coal-tar fluorene (Berthelot; Barbier).	γ -Methylene-diphenylene. From benzene and toluene (Carnelley).	δ -Methylene-diphenylene.
Melting point .. {	113–114° (Graebe), 112–113° (Fittig and Schmitz)	113°.	118° (uncorr.).	205° (uncorr.), 208° (corr.).
Boiling point .. {	300–305° (Graebe); 294–295° (Fittig and Schmitz).	About 305° (corr.).	295° (uncorr.).	About 320°.
Crystalline form {	Colourless laminae with faint blue fluorescence.	Sublimes in plates with strong violet fluorescence.	Colourless pearly plates or small needle-shaped prisms, with very faint blue fluorescence.	Small colourless pearly plates.
Solubility	Easily in hot alcohol. Less soluble in cold alcohol, very easily in carbon bisulphide, ether, and benzene.	Very soluble in ether, benzene, carbon bisulphide, and hot alcohol, but only sparingly soluble in cold alcohol.	Moderately soluble in hot alcohol or hot glacial acetic acid, but only sparingly soluble in cold alcohol or cold glacial acetic. Easily in ether.	Sparingly soluble in cold, but more easily in hot alcohol.
Picrate	Yellow-red or red needles, m.p. = 80–82°, very easily soluble in alcohol, but decomposed at same time (Graebe). Red - brown prisms, m. p. = 79–80° (Fittig and Schmitz).	Red needles, m. p. 80–82°.	Blood-red needles, m. p. = 79–81°.	—

	α -Methylene-diphenylene from diphenylmethene and diphenylene ketone (Graebe, Fittig, and Schmitz).	β -Methylene-diphenylene or coal-tar fluorine (Bar- thelot; Barbier).	γ -Methylene-diphenylene. From benzene and toluene (Carnelley).	<i>o</i> -Methylene-diphenylene.
Dibromo-com- pound	Colourless tabular mono- clinic prisms, different in form from those of Barbier; m. p. = 162–167° (Fittig and Schmitz). Needles, m. p. 153–154° (Graebe), very sparingly soluble in alcohol, very easily in ether, benzene, carbon bisulphide and chloroform.	Monoclinic crystals, m. p. = 166–167°. Nearly insolu- ble in ether and alcohol, but readily soluble in car- bon bisulphide and chloro- form. They change on repeated crystallisation from carbon bisulphide into the same form as those of Fittig and Schmitz.	Minute octohedrons or needles, the latter changing into the former. M. p. = 162°. Very sparingly solu- ble in alcohol or ether, whether hot or cold.	—
Dinitro-com- pound	Colourless needles, m. p. 199 —201°, very slightly soluble in hot alcohol.	Reddish-yellow needles, m. p. = above 260° with decom- position, very slightly solu- ble in ordinary solvents.	—	—
Oxidation pro- ducts	Is oxidised with difficulty, and gives only diphenylene ketone.	Is slowly oxidised, giving di- phenylene ketone and a quinone, $C_{13}H_9O_2$, m. p. = 181–182°.	Gives only a quinone and no ketone. The quinone, $C_{13}H_9O_2$, crystallises in golden-yellow needles, m. p. = 280–281°. Scarcely soluble in cold, and only sparingly soluble in hot alcohol.	Gives only a quinone and no ketone. The quinone, $C_{13}H_9O_2$, is a pure white powder, subliming in needles (m. p. 288°). Insoluble in water, but moderately solu- ble in glacial acetic acid.

their constitution? According to theory six modifications of the

formula, $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{CH}_2$, are possible, viz. :—

Though the data at hand are far from conclusive, yet it is most probable that the α -, β -, γ -, and δ -methylene-diphenylenes have the constitutions I, IV or V, II, and III respectively, and for the following reasons :—

α -Methylene-diphenylene is obtained from diphenylene ketone, and α -methylene-diphenylene likewise forms diphenylene ketone on oxidation. Now diphenylene ketone is a diortho-compound, because it is produced by heating diphenic acid with lime, and diphenic acid is a diortho-compound, being derived from phenanthrene. α -Methylene-diphenylene is therefore almost certainly the diortho-modification. This is further confirmed by the fact that phenanthraquinone on heating with pure soda lime gives methylene-diphenylene (Anschütz and Schultz, *Ber.*, 9, 140). Anschütz and Japp (*Ber.*, 11, have also shown that diphenylene ketone gives phthalic acid on oxidation, and therefore that the CO-group in diphenylene ketone is in the diortho-position.

δ -Methylene-diphenylene obtained by the action of heat on benzene and toluene is almost certainly the dipara-derivative, for not only does it melt and boil above any of the other three modifications, but it melts very much higher, viz., at 205°, the next highest being the γ -modification, which melts at 118°. Now it is a general rule that the melting points of those compounds, the atoms of which are symmetrically arranged, are higher than in the case of isomeric compounds in which the atomic arrangement is less symmetrical (compare *Watts' Dict. Chem.*, 8, 221; Carnelley, *Phil. Mag.*, 1879, 378). Of the six possible constitutions for methylene-diphenylene, the dipara is the most symmetrical, and therefore the δ -modification with the highest melting point has most probably that constitution.

γ-Methylene-diphenylene.—Since this modification melts (118°) higher than the (α -) diortho-compound (113°), it is improbable that it would have a less symmetrical constitution, in which case it must be the dimeta-derivative.

β-Methylene-diphenylene.—Data are almost altogether wanting in order to decide which of the three remaining constitutions belongs to this compound (if it be really different from the α -modification), but as it forms a ketone as well as a quinone, it is not unlikely that one of the attachments is in the ortho-position, in which case it would be either the ortho-meta- or the ortho-para-compound.

General Results.

1. When the mixed vapours of benzene and toluene are passed through a red-hot tube, there are obtained benzene, naphthalene, diphenyl, paratolylphenyl, orthoparaditolyl, γ -methylene-diphenylene, δ -methylene-diphenylene, phenanthrene, anthracene, paradiphenyl benzene, a hydrocarbon having the composition $C_{32}H_{28}$, a liquid hydrocarbon boiling at 293 – 316° and melting at 13° , two other liquid hydrocarbons or mixtures of hydrocarbons boiling at 359 – 383° and 404 – 427° respectively, and a solid black bitumene.

2. Two new methylene-diphenylenes and some few of their derivatives are described.

3. Of the six possible methylene-diphenylenes three, and probably four are known.

4. Graebe and Fittig's methylene-diphenylene obtained from diphenylmethane and from diphenylene ketone is a diortho-compound; of the two modifications obtained by the action of heat on mixed benzene and toluene vapours, the one melting at 205° is the dipara-, and that melting at 118° is possibly the dimeta-modification; whilst Berthelot's coal-tar fluorene is probably either the ortho-meta- or the ortho-para-compound.