

XXIII.—*Note on some Derivatives of Fluorene, C<sub>13</sub>H<sub>10</sub>.*

By W. R. HODGKINSON and F. E. MATTHEWS.

THE hydrocarbon, isolated from coal-oil by Berthelot (*Ann. Chim. Phys.* [4], **12**, 222), and termed *fluorene* from its supposed fluorescent property, has been investigated by several chemists, and its constitution as *o*-diphenylenemethane determined by its production from diphenylmethane by passing through a red-hot tube (Graebe, *Annalen*,

174, 194), and the reduction of diphenylene-ketone by zinc-dust or phosphonium iodide (Fittig, *Ber.*, **6**, 187; Graebe, *Ber.*, **7**, 1625).

Its constitution would therefore be expressed by—



More recently, however, Carnelley (*C. J.*, **37**, 708) has discussed the constitution of coal-tar fluorene, and the fluorene from diphenylene-ketone, and notices that of the six possible isomerides of this body several occur in coal-oil, and several are also formed when the vapours of benzene and toluene are passed through a heated tube.

The object we had in view in commencing this investigation was in the first place to obtain the phenol or hydroxy-derivative, fluorol,  $C_{13}H_{10}O$ , as a starting point for further work.

As diphenylene ketone is somewhat difficult to obtain in quantity, and the yield of the hydrocarbon from it is by no means a quantitative one, we have employed coal-tar fluorene obtained from Kahlbaum in a state of approximate purity. For further purification it was distilled, and the fraction between  $300-310^{\circ}$  crystallised five or six times from alcohol, reserving only the crystals falling out between  $25^{\circ}$  and  $30^{\circ}$ . Thus purified, it melts constantly at  $113^{\circ}$ , and the slight fluorescence may be almost entirely removed by one or two crystallisations from glacial acetic acid, or by sublimation over potassium carbonate.

Glacial acetic acid is by far the best solvent from which to crystallise fluorene. By means of this solvent, it is possible to separate from fluorene boiling between  $300-310^{\circ}$ , hydrocarbons melting at  $112-113^{\circ}$ ;  $124^{\circ}$ ;  $118^{\circ}$ ; and, in small quantity only, at about  $200^{\circ}$ .

The one melting at  $118^{\circ}$ , and occurring in pretty large quantity in coal-tar fluorene, is most probably the  $\gamma$ -methylene-diphenylene of Carnelley. It certainly gave another body in addition to diphenylene-ketone on oxidation; we have not, however, examined these substances further, as we desired only the ortho-modification.

The product we have employed oxidises in glacial acetic solution completely with chromic acid to diphenylene ketone, no quinone being produced.

On analysis 0.1106 gram gave 0.3796 gram  $CO_2$  and 0.0645 gram  $OH_2$ .

		Found.
$C_{13} = C \dots$	93.97	C. . . . 93.60 per cent.
$H_{10} = H \dots$	6.03	H . . . . 6.47 ,,

The  $\alpha$ -dibromofluorene,  $C_{13}H_8Br_2$ , was made by dissolving the hydrocarbon in chloroform, adding a slight excess of bromine, and leaving the chloroform to evaporate spontaneously. The compound is almost

insoluble in cold alcohol, but dissolves easily in boiling alcohol, from which solution it separates in *almost* colourless tabular crystals. From hot glacial acetic solution it forms perfectly colourless crystals melting at  $165^{\circ}$ . Light causes the crystals to become slightly yellow.

A bromine determination by heating with Iceland spar gave—

$$49\cdot71 \text{ per cent. Br. Theory } \frac{C_{13}}{Br_2} = \text{Br } 49\cdot38.$$

We did not notice any formation of the  $\beta$ - and  $\delta$ -dibromofluorenes as noticed by Lehmann and Azruni; also by Fittig and Schmitz. Their formation may depend on the solvent employed.

*Monobromofluorene,  $C_{13}H_9Br$ .*

This substance is formed when bromine is very carefully added to a solution of the hydrocarbon in chloroform, care being taken to keep the temperature as low as possible. The product, even when the fluorene is maintained in excess, still contains the dibromo-compound, from which the mono-derivative may be separated by repeated solution in, and crystallisation from, about 90 per cent. alcohol. It forms colourless needles melting at  $101$ — $102^{\circ}$ .

Analysis gave 32·65 per cent. bromine; the formula  $C_{13}H_9Br$  requires 32·54 per cent.

This substance is exceedingly soluble in cold chloroform.

Both the mono- and di-bromofluorenes yield on oxidation a substituted diphenylene ketone. The product appears to be the same whether chromic acid in glacial acetic or permanganate is used.

*Dibromodiphenylene ketone,  $C_{13}H_7Br_2O$ .*

This is best obtained by oxidising the ( $165^{\circ}$ )- $\alpha$ -dibromofluorene with chromic acid in acetic acid solution. It forms bright yellow microscopic crystals from acetic acid, melting at  $198^{\circ}$ .

Analysis gave 47·34 per cent. bromine; the formula requires 47·39.

The monobromofluorene, when carefully oxidised with the theoretical amount of chromic anhydride, yields bromdiphenylene ketone,  $C_{13}H_7BrO$ , in dark yellow needles melting at  $104^{\circ}$ .

The production of diphenylene ketone alone, by oxidation of the fluorene, and the formation of the dibromo-compound melting at  $165^{\circ}$ , was sufficiently conclusive that the hydrocarbon we are dealing with had the constitution assumed as that of ortho- or  $\alpha$ -methylene-diphenylene.

The sulphonic acid,  $C_{13}H_9SO_3H$ , was therefore made by dissolving the hydrocarbon in chloroform and adding the theoretical quantity of sulphuric chlorohydrine,  $SO_3HCl$ , to form the monosulphonate.

The action is a very violent one, and requires to be moderated by careful cooling during the operation.

The free acid is a gummy substance very soluble in water. It was neutralised by potassium carbonate, and the salt  $C_{13}H_9SO_3K$  was crystallised from warm water, in which it is somewhat less soluble than in cold. It forms microscopic cubic crystals, which are difficult to obtain colourless.

The barium salt is also very soluble in water, from which it separates in very small crystals, containing two molecules of water.

*Analysis. Barium Salt.*

0.974 air dried at  $130^\circ$  gave 0.053  $OH_2$ .  
0.921 " " " 0.343  $BaSO_4$ .

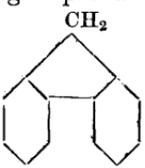
	Theory		Found.
	$(C_{13}H_9SO_3)_2Ba + (OH_2)_2$		
$OH_2$ . . . . .	5.43		5.43
$Ba$ . . . . .	20.66		20.70

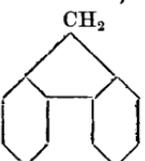
The cadmium salt 0.5 gram gave on drying at  $130^\circ$  0.0764.

" " 1.0 " 0.2012 gram  $CdS = 0.1565$  I.

	Theory		Found.
	$(C_{13}H_9SO_3)_2Cd + 6OH_2$		
$OH_2$ . . . . .	15.28	$OH_2$ . . . . .	15.28 per cent.
$Cd$ . . . . .	15.77	$Cd$ . . . . .	15.65 "

It was at first thought probable that the sulphonic group would

occupy the position  to the methylene group in the fluorene molecule, and that on fusion with potassium hydroxide a

fluorol,  might be obtained.

A considerable quantity of the potassium sulphonate was therefore

\* There are as yet no particular grounds on which to base the assumption of the position of the  $SO_3$ .

fused at first with slightly aqueous potash, but after a few trials as to the conditions of the reaction, it was fused with dry potash at a temperature a little above  $400^{\circ}C$ . The operation requires great care, as the reaction takes place within very narrow limits of temperature, below which there is no result, and above which the substance is completely decomposed.

The fused mass, after treating with water and acidification, was repeatedly shaken out with ether and chloroform, which extracted a sparingly soluble substance crystallising, on evaporation of the solvents, in almost colourless needles. The crystals dissolved in aqueous potassium carbonate, and were reprecipitated unchanged by acids.

This substance is almost insoluble in cold water, but readily in hot, and more so in alcohol. From hot aqueous solutions it separates in very brilliant small rhombic prisms, melting at  $205^{\circ}$ , which become glassy after fusion, and decompose when heated to between  $220$ — $230^{\circ}$ . Its solution in water gives no coloration with ferric chloride. It forms crystalline nitro- and oxidation-products, which, however, have not yet been analysed.

The yield from the potash fusion, even under the most favourable conditions, is very small, and considerable loss is experienced in separating it from a tarry body formed at the same time, which protects it from the action of the water or potassium carbonate solution employed for extraction. It was afterwards found better to distil the acidified product of the fusion with steam.

The first portions of the steam-distillate came over charged with a white crystalline substance which, on the first crystallisation from hot water, showed itself to be a mixture of crystals of the same form as those obtained by extraction of the fused product with ether-chloroform, with others of much smaller size, and differing from the former in shape and in their solubility in water.

This second body is easily separated from the one previously named, melting at  $205^{\circ}$ , by its extreme solubility in hot water, and by not separating from this solution until cooled to between  $10^{\circ}$  and  $15^{\circ}$ , whereas the body first mentioned is completely deposited, even while the temperature is so high as  $30$ — $35^{\circ}$ . It forms very small colourless acicular crystals, which melt at about  $180^{\circ}$ .

The aqueous solution gives no colour-reaction with ferric chloride.

#### *Analysis.*

Substance 0.0492 gram gave 0.0234 gram  $OH_2$  and 0.1288 gram  $CO_2$ .

		Theory $C_{12}H_{10}O_3$ .
C. . . . .	71.37	C. . . . . 71.28
H . . . .	5.28	H . . . . 4.25

The quantity of the two trihydroxydiphenyls at our disposal hitherto is not very large, and in consequence we have not been able to try the action of zinc-dust on a scale large enough to give definite results.

*Analysis of the Body melting at 204—205°.*

I....	0·0775	substance =	0·2025	CO <sub>2</sub> and	0·0387	OH <sub>2</sub> .
II....	0·0640	„	=	0·1670	„	0·0290 „

	I.	II.		Theory for C <sub>12</sub> H <sub>10</sub> O <sub>3</sub> .
C....	71·27	71·17	C <sub>12</sub> ....	71·28
H ..	5·54	5·00	H <sub>10</sub> ....	4·95
			O <sub>3</sub>	

*Other Analyses, Material not quite Pure.*

	III.	IV.
Substance ..	0·0492	0·0448
CO <sub>2</sub> .....	0·1282	0·1167
OH <sub>2</sub> .....	0·0237	0·0215
C.....	71·06	71·05 (p. c.)
H .....	5·35	5·29 „

This was a very extraordinary result, and could scarcely be explained as arising from the reaction of potash with a monosulphate only. The formula C<sub>12</sub>H<sub>10</sub>O<sub>3</sub> indicates a trihydroxydiphenyl, and such a body could result only from the splitting off of the methylene-group in fluorene, and its replacement by two hydroxyl-groups.

No exactly analogous case of the action of potash occurred to us, but it did not seem very unlikely that the five-carbon ring or group might not be sufficiently stable to be able to resist the action of the fused potash. The hydrocarbon was therefore dropped into potash in a state of fusion (at a pretty high temperature, about 400° C.) in a silver dish. A small quantity volatilised unchanged, the greater part, however, forming a combination of a red colour with the potash, was apparently non-volatile, and floated as a distinct red layer on the excess of fused potash. On cooling and treatment with water, it was at once apparent that several products had been formed, a red substance insoluble in the alkaline solution, together with a little unchanged hydrocarbon, and another body, also of a yellow or red colour, remaining in solution in the alkali. This latter body was precipitated, for the most part, on acidifying the potash solution, as a yellowish flocculent substance, soluble in boiling water, and slowly separating therefrom on cooling in a crystalline form. It was crystallised several times from water, becoming each time less strongly coloured but we have not yet

been able to obtain it quite colourless, which it probably would be if quite pure. We have not yet examined the other products of the fusion.

The substance crystallised from water gives a decided colour reaction with ferric chloride. It melts at  $98^\circ$ , without any decomposition.

*Analysis I.*

0.1163 gram substance gave 0.3290  $CO_2$   
and 0.0535  $OH_2 = C$  77.15  
H 5.11

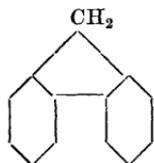
*Analysis II.*

0.1070 gram substance gave 0.3028  $CO_2$   
and 0.0526  $OH_2 = C$  77.17  
H 5.46

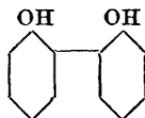
These figures indicate a composition—

$C_{12}H_{10}O_2$ . Theory C 77.41  
H 5.37

or a dihydroxydiphenyl presumably formed by the splitting off of the methylene-group.



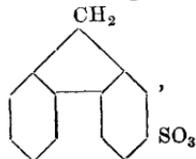
in fluorene, and the introduction of two hydroxyl groups



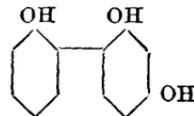
That the fluorene has been reduced to a diphenyl derivative there is little doubt, for this substance when heated with zinc-dust was very easily reduced to diphenyl, distinctly recognised by its melting point and odour. We have not yet sufficient for analysis.

That the reaction takes place during the fusion of the potassium monosulphonate, the sulphonic group and the methylene being simultaneously replaced by hydroxyl, seems quite evident; but we are not yet in a position to account for the formation of two trihydroxydiphenyls.

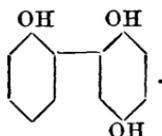
Assuming that the monosulphonate has the  $SO_3$  in the position



the trihydroxy body derived from it would have the constitution



which is probably that of the body melting at  $180^\circ$ , whilst the body of higher melting point ( $205^\circ$ ) would possibly have the structure



The former, however, is produced in decidedly larger

quantity than the latter. It is, however, possible that two mono-sulphonic acids are produced by the action of  $\text{SO}_3\text{HCl}$ . These we are trying to isolate.

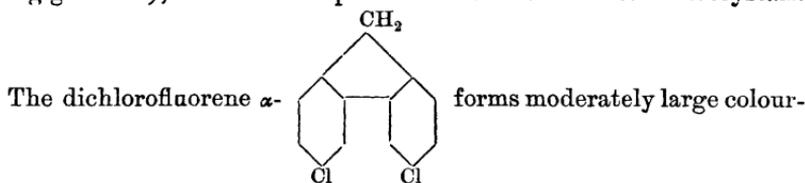
The trioxydiphenyl melting at  $180^\circ$  gives on heating with acetic anhydride an acetate melting at  $100^\circ$ .

As the hydrocarbon itself was so readily acted upon by fused potash, it was thought that the halogen-compounds might likewise be acted upon under the same circumstances, and that in this way some idea of the mechanism of the reaction would be obtained.

It was attempted in the first place to obtain a more highly brominated body than the dibromofluorene, but this we have not succeeded in doing. The dibromo-compound is acted upon very violently by fused potash, and it has not been found possible to separate the products. It is also acted upon by alcoholic potash, as we shall show later, although the contrary is stated by Barbier (*loc. cit.*).

The chlorine derivatives are much more convenient (we can find no account of their being previously prepared) for this purpose.

Fluorene is moderately soluble in cold chloroform, and if chlorine (dry) be passed into this solution, it is rapidly absorbed, with slight elevation of temperature, up to a point at which nearly the whole of the hydrocarbon has formed a dichloro-derivative (hydrogen chloride being given off), which then separates out of the chloroform in crystals.



less plates, melting at  $128^\circ$ , and subliming unchanged.

On oxidation with chromic acid, a dichlorodiphenylene ketone corresponding with the bromo-compound is produced. Its tint of yellow is lighter than that of the dibromo-ketone. It melts at  $158^\circ$ , and distils without decomposing.

By acting on the dichlorofluorene dissolved in boiling chloroform, or better in carbon tetrachloride, with chlorine, more highly chlorinated products have been obtained. The highest product obtained in this way, by the aid of a trace of iodine to the  $\text{CCl}_4$  solution, appears to be a pentachlorodichloride.

Analysis of the perchlorinated compound once crystallised from alcohol, and melting at  $104^\circ$  :—

0·0759 gram substance, heated with lime (Iceland spar) took  
 27 c.c. Ag solution. 1 c.c. = 0·00168 Cl = 59·8 per cent. Cl.  
 0·0902 gram substance = 32·5 c.c. Ag solution.

Found.

$C_{13}H_3Cl_7$  = Cl 60·6    I.. 59·8    II.. 60·5

The substance is still not quite pure, the long needle-shaped crystals of the permanently perchlorinated body being accompanied by small cubic crystals of apparently the same solubility in alcohol.

This perchlorinated substance is readily oxidised by chromic acid, giving a yellow ketone (?) melting at 103—104°.

A totally different chlorine-derivative is produced when the gas is passed into boiling fluorene (both quite dry). Hydrogen chloride is then given off, and the boiling point rises from about 300° to over 360°; no decomposition, however, appears to take place, and the resulting chlorinated substance remains liquid or semi-liquid, even at 0°. It is not oxidised by chromic acid. The results of further study of this body will be given later.

Fused potash acts very energetically on the chloro-derivatives, much more so than in the case of the dibromofluorene.

With the body termed provisionally the perchlorinated substance, reaction takes place with almost explosive violence, and compound containing chlorine being volatilised by the heat of the reaction.

Alcoholic potash acts upon the substance ( $C_{13}H_5Cl_7$ ), producing a beautiful red or pink coloration, due to the formation of a body containing less chlorine. This substance is insoluble in alcohol, but dissolves in chloroform, petroleum, and acetic acid, from which solutions it crystallises on slow evaporation. It melts to a deep red liquid at about 110°, and crystallises on cooling. Nitric and chromic acids are without effect upon it. It is a most difficult substance to analyse, as it almost refuses to burn. These analyses are therefore only very approximate.

*Red Body containing Chlorine.*

- I. 0·1328 substance = 40·5 c.c. Ag sol. 1 c.c. = 0·00168 Cl,  
 51·2 per cent. Cl.  
 II. 0·0893 substance = 27·25 c.c. Ag sol., 51·2 per cent. Cl.  
 0·1035 gram substance = 0·1657  $CO_2$  and 0·0193  $OH_2$  =  
 C 43·7, H 2·06.  
 0·0123 gram took 27·3 c.c. Ag sol. = Cl 51·2 per cent.

Found.

$C_{13}$ .....	46·0	43·7
$H_5$ .....	1·5	2·06
$Cl_6$ ....	52·5	51·2

We find that a mixture of potassic hydrate and carbonate acts much less energetically than the potash alone, and we hope to be able soon to obtain the haloid dihydroxydiphenyls by this means.

The  $\alpha$ -dibromo-fluorene forms a sulphonic acid which is obtained by the action of sulphuric chlorhydrin in theoretical proportion, on the dibromo-derivative in chloroform solution. On evaporation of the solvent, beautiful colourless crystals of the free acid are obtained. It melts at  $142^\circ$ , and decomposes at a few degrees higher. The barium salt forms colourless crystals.

*Analysis.*

I. . . . 0.0765 gram water lost  $0.010$  at  $120^\circ$ .

II. . . . 0.2029 gram lost  $0.0260$  and gave  $0.0431$   $\text{BaSO}_4$ .  
=  $0.02534$  Ba.

	Found.	I.	II.
$(\text{C}_{13}\text{H}_7\text{Br}_2\text{SO}_3)_2\text{Ba}$ + $8\text{OH}_2$ .			
OH <sub>2</sub> . . . .	13.28	13.08	12.88
Ba . . . .	14.52	—	14.32

We are continuing the investigation of these derivatives.

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